In conclusion, we would like to consider some equations of the perturbation theory concept of the method. For this purpose, consider Eq. (163), which we want to apply to the system of three hydrogen atoms. So from Eq. (163a)

$$\Delta' = -5{,}978 \text{ a.u.}$$
$$\Delta_{aa} = \Delta_{HH} = -1{,}9037 \text{ a.u.} . \qquad (186)$$

The function $P(R)$ of Eq. (148) was determined from analytical potential curves. As stated above, the q values were taken into consideration in approximation form.

One always finds at about $R = 1.9$ a.u. an energy minimum of -0.165 ± 0.05 a.u. for the H_3 system, which corresponds to an increase in energy of about 3–9 kcal/mol over the H_2 molecule (a good result in view of the applied approximation in the q functions).

It is worth remarking that disregarding the q functions in Eq. (160), which led to representation (154), still did not give a reasonable minimum in the potential curve of the H_3 complex if the separation of neighboring H atoms were set equal in the linear system and varied. Likewise omitting the association $[ac|b]$ results in an unsatisfying course of the curve, if the arrangement of the three atoms is a–b–c.

The examples show that the equations of the atomic association method in the frame of a variation treatment or in the perturbation theory representation reproduce, in their simplest form, interactions between atoms that are essentially correct.

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Structure of Fermion Density Matrices

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1. INTRODUCTION

CAN the wave function be eliminated from quantum mechanics and its role be taken over, in the discussion of physical systems, by reduced density matrices? The author has believed in the affirmative answer to this question for over ten years. In the present paper, he attempts to muster the main current evidence in support of this belief. Prior to the Hylleraas Symposium, the available evidence, probably, would not have convinced the average physicist. However, the discovery, during the Symposium of Theorem 9.3, and subsequently of Theorem 9.4, gives real substance to the hope that it will soon be possible to calculate the energy of the ground state of an N-fermion system using density matrices as the main mathematical tool.

In his summary[1] of the Boulder Conference on Molecular Quantum Mechanics, June 1959, C. A. Coulson remarking on the striking resurgence of interest in the density matrix approach to the N-body problem stated, "It has frequently been pointed out that a conventional many-electron wave function tells us more than we need to know. . . . There is an instinctive feeling that matters such as electron correlation should show up in the two-particle density matrix . . . but we still do not know the conditions that must be satisfied by the density matrix. Until these conditions have been elucidated, it is going to be very difficult to make much progress along these lines."

Conditions on the *wave function* are known. It must (i) satisfy Schrödinger's equation, and (ii) be symmetric or antisymmetric with respect to the interchange of similar bosons or fermions, respectively. Condition (i) is easily translated into a variational condition on the two-particle density matrix. However, when Professor Coulson spoke there was no convenient formulation of the conditions on a reduced density matrix implied by the symmetry or antisymmetry of the wave function of the system. This is the important lacuna to which Coulson drew attention,

[1] C. A. Coulson, Rev. Mod. Phys. **32**, 175 (1960).

and with which the present paper is concerned. We refer to the problem as the *N-representability problem*—how can we recognize that an alleged two-particle density matrix is, in fact, the reduced density matrix of a system of N-indistinguishable particles. Apart from occasional side remarks, we restrict our attention to the case of fermions.

In Part I, we focus on the problem of approximating an antisymmetric function of N particles by means of sums of products of a lesser number of particles. We begin by proving a famous theorem of Erhardt Schmidt which reveals the significance of Löwdin's natural spin orbitals as functions peculiarly suitable for a least-squares approximation to N-particle functions, independently of any symmetry considerations. The reduced density matrix appears in this context as the kernel of an integral equation which determines the natural spin orbitals. The duality between the pth order and $(N - p)$th order reduced density matrices, noted by Carlson and Keller,[2] is an immediate consequence of Schmidt's theorem. We obtain new results when, to the situation considered by Schmidt, we add the requirement of antisymmetry. As a *necessary* condition that an alleged pth order reduced density matrix be N representable we obtain upper bounds on its eigenvalues. We also show that the 1-particle natural spin orbitals form a complete set for the expansion of the wave function and all its reduced density matrices. Finally, we show that N representability is invariant with respect to unitary transformations of a basis of one-particle functions and, hence, that the N representability of a *one*-particle matrix must be expressible as a condition on its eigenvalues.

In Part II, we use an argument of Fukashi Sasaki, to obtain the *best-possible* upper bounds for the eigenvalues of the *two*-particle reduced density matrix. This enables us to correct an error of Bopp[3] and to obtain a lower bound for the energy level of the ground state of a system of N fermions. By an argument also used by Bopp, we relate the energy of a many particle system to the energy of helium-like systems.

Part III solves the N representability problem for the *one*-particle reduced density matrix of an ensemble and takes an important step towards its solution for the *two*-particle matrix. Other important new results pertinent to pure states are: (i) an explicit necessary and sufficient condition for the N representability of a one-particle reduced density matrix of rank $N + 2$, and (ii) a rather complicated algorithm by which the N representability of a one-particle matrix of rank r is made to depend on the $(N - 1)$ representability of a matrix of smaller rank *and* the N representability of another matrix of smaller rank.

The work reported in this paper was begun in 1951 at the Summer Research Institute of the Canadian Mathematical Congress which was supported by the National Research Council of Canada. At that time, the solution of the case $p = 1$, $N = 2$ of Theorem 4.1 was obtained. The main ideas of the paper, except for those of Sec. 9, were presented to the Physics Colloquium of the University of Toronto in 1958, announced[4] without proof in 1961, and treated[5] in a report of the Quantum Chemistry Group of Uppsala University. Theorem 9.3 was discovered during the Hylleraas Symposium in the course of vivid discussions with L. H. Thomas and L. Witten to whom the author expresses his lively appreciation. The possibility that the N representability of the two-particle matrix is not expressible by means of its eigenvalues alone was first suggested to the author in 1957 by his graduate student, C. A. J. Pegis.

PART I—NATURAL EXPANSIONS

2. The Central Problem

Fortunately, the existence of the two excellent review articles by McWeeny[6] and ter Haar[7] makes unnecessary any extended discussion of the manifold applications or the considerable literature of density matrices. We recall the salient facts. As shown by von Neumann[8] the *statistical operator* D or, as ter Haar[9] proposes to call it, the *density matrix*, is a more satisfactory mathematical object than the wave function for describing a quantum mechanical system, since it is equally applicable to pure states and to statistical ensembles. In general, $D = \sum w^i D_i$ where D_i are projectors onto pure states of the Hilbert space of N particle functions and w^i are positive real numbers with sum 1, so that D corresponds to a sum of pure states D_i with weight w^i. The wave-function language applies strictly only to pure states which seldom—some physicists would say, *never*—occur in nature. Furthermore, the two-particle *reduced* density matrix σ contains all the information needed to discuss two-particle interactions. In particular, the en-

[2] B. C. Carlson and J. M. Keller, Phys. Rev. **121**, 659 (1961).
[3] F. Bopp, Z. Physik **56**, 348 (1959).
[4] A. J. Coleman, Can. Math. Bull. **4**, 209 (1961).
[5] A. J. Coleman, Quantum Chemistry Group, Uppsala University, Report No. 80, 1962 (unpublished).
[6] R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).
[7] D. ter Haar, Rept. Progr. Phys. **24**, 304 (1961).
[8] J. von Neumann, *Mathematische Grundlagen der Quantenmechanik* (Springer–Verlag, Berlin, 1932), Chap. IV.
[9] D. ter Haar, Physica **26**, 1041 (1960).

ergy of a system of N electrons can be expressed exactly in terms of σ. As shown by Dirac, in the case that Ψ is a single Slater determinant the energy is determined even by the *one*-particle density matrix. The hope that σ might prove a mathematically more tractable object than Ψ has caused much of the recent attention to density matrices and is the inspiration of the present paper.

Unfortunately, the terminology and notation of our subject is still in some confusion. For example, there are, in the literature, three different normalizations according to which the trace of the pth order reduced density matrix is (i) 1, (ii) $\binom{N}{p}$, (iii) $p!\binom{N}{p}$. The present author follows ter Haar in preferring (i) which corresponds to the statistical interpretation of the density matrices. The normalization (ii) was natural to adopt when it was conjectured by many people including the author that the reciprocal of $\binom{N}{p}$ is the least upperbound for the eigenvalues of an N-representable pth-order fermion density matrix. However, we show in Part II that the conjecture, and Bopp's alleged proof of it, is false so that normalization (ii) loses all cogency. The normalization (iii) used by McWeeny and by Yang is the natural one to adopt if one employs the notation of second quantization, however, the usefulness of that notation seems restricted to the case $p = 1$. It can be argued that for $p = 1$, the normalizations (ii) and (iii) allow the single configuration case to be characterized by the idempotency of the one-particle density matrix. However, the characterization $N\mu^2 = \mu$ is just as convenient and, in any case, it appears that the path of progress requires that we pass beyond the single configuration approximation.

All workers on problems concerned with N particles in quantum mechanics are plagued with the difficulty that the essence of the matter is frequently hidden by a host of variables, subscripts, and superscripts which create an impression of a "big, buzzing confusion." For some problems, the notation of second quantization has definite advantages, particularly, if one is interested in one-particle expansions, that is, in terms of *orbitals*. However, for expansions in terms of *geminals*, that is, two-particle functions, the current formulation of second quantization appears to be quite inadequate. This may explain why so much of the discussion of interaction problems in quantum field theory appears to be indiscriminate beating of the air.

Probably, ter Haar[9] has given the most serious thought to the problems of terminology in our subject. However, ter Haar's proposals fail to meet the desideratum that good terminology attaches *short* terms to the most important and most frequently recurring ideas. These are (i) the pth-order reduced density matrix of a N-particle system; (ii) the eigenfunctions of the pth-order reduced density matrix; and (iii) the corresponding eigenvalues.

Since for molecular and atomic problems the number of electrons does not change during the discussion, N may be specified implicitly and we may speak of the *p matrix* of a system without ambiguity. Thus, our *p matrix* is ter Haar's pth-order reduced density matrix; our *N matrix* is his density matrix and von Neumann's statistical operator; our 1 *matrix* is ter Haar's first-order reduced density matrix and Tolman's, or Dirac's, density matrix. By a *natural p state* of a system we shall mean an eigenfunction of the p matrix of the system. We use the term *orbital* for any *one-particle function* (with or without spin according as is most convenient) and *geminal*[10] for any *two-particle* function so that a natural 1 state will more often be called a *natural orbital* and a natural 2 state, a *natural geminal*. When he feels particularly daring the author uses the contractions "norb" and "nag" for natural orbital and natural geminal, respectively! We shall call the eigenvalues of a p matrix, pth-*order eigenvalues*.

We frequently have occasion to partition the N indistinguishable particles of our physical system into two sets of p and q particles with $p + q = N$ ($0 \leq p$, $q \leq N$). The symbols p and q as superscripts will also indicate that an operator or function pertains to the space of functions of the particular p or q particles into which the N particles were partitioned. Denoting the spatial (and spin) coordinates of the ith particle by x_i, the p *particles will always have coordinates* $x_1, x_2, \cdots, x_p$ and *the* q *particles,* $x_{p+1}, x_{p+2}, \cdots, x_N$.

The p matrix of a system will be denoted by D^p. For a system of N particles in a state with wave function Ψ, D^p may be regarded as an integral operator with kernel

$$D^p(x_1,x_2\cdots x_p;x_1',x_2'\cdots x_p') = \int \Psi(x_1\cdots x_N) \times \bar{\Psi}(x_1'x_2'\cdots x_p'x_{p+1}\cdots x_N)d\mu_q\,, \tag{2.1}$$

where the integration is with respect to the Lebesgue–Stieltjes measure μ_q on the q particles. The kernel may also be denoted by

$$D^p(1,2\cdots p;1',2'\cdots p') = D^p(s;s')\,. \tag{2.2}$$

We reserve the variables s and t for generic points in the p and q particle spaces, respectively, in order to be able to denote $\Psi(1,2\cdots N)$ by $\Psi(s,t)$ and, thus,

[10] The term *geminal*, with the same root as the latin Gemini —the Twins—is due to Harrison Shull.

bring out its analogy with the Hilbert-Schmidt-Fredholm kernel $K(s,t)$ of all textbooks[11] on non-symmetric integral equations. Similarly, the q matrix, D^q, has kernel

$$D^q(p+1,\cdots N;(p+1)'\cdots N') = D^q(t;t') = \int \Psi(s,t)\bar{\Psi}(s,t')d\mu_p\,, \tag{2.3}$$

where the integration is over the generic point s in p-particle space. For an *ensemble* which may be analyzed as a sum of pure states Ψ_i with weights w^i, the p matrix

$$D^p = \sum_i w^i D_i^p\,, \tag{2.4}$$

where D_i^p is the p matrix of Ψ_i.

As was remarked by von Neumann[8] the set of all D^N is identical with the set $\mathcal{P}^N$ of positive Hermitian operators of unit trace on the Hilbert space of antisymmetric N-particle functions. The set $\mathcal{P}^N$ is *convex*, that is, if A and B belong to $\mathcal{P}^N$ then so does $\alpha A + \beta B$ where α and β are non-negative real numbers such that $\alpha + \beta = 1$. We recall that C is an *extreme* point of a convex set if $C = \alpha A + \beta B$ implies that A and B are multiples of C. The extreme elements of $\mathcal{P}^N$ are the pure states. Equation (2.4) is, thus, a particular case of the Krein–Milman theorem which asserts that a compact convex set is determined by its extreme points.

For fermions, the set $\mathcal{P}^p$ consists of all positive Hermitian operators of unit trace on the space of antisymmetric p-particle functions. Whereas the set of all D^N coincides with $\mathcal{P}^N$, the set of D^p is a proper subset of $\mathcal{P}^p$ which we denote by $\mathcal{P}_N^p$. It consists of those positive operators of unit trace on the Hilbert space of antisymmetric p-particle functions which are p matrices derived from ensembles of N-particle systems. It is easily seen that $\mathcal{P}_N^p$ is a convex subset of $\mathcal{P}^p$ and that its extreme elements are the p matrices of extreme elements (i.e,. the pure state operators) in $\mathcal{P}^N$. However, the p matrix of a pure state in $\mathcal{P}^N$ is not necessarily extreme in $\mathcal{P}_N^p$ as we shall see in Part III.

We are now able to state precisely the *problem of N representability* to which Professor Coulson drew attention.

Give an intrinsic characterization of $\mathcal{P}_N^p$ as a subset of $\mathcal{P}^p$. In other words, give criteria by which to recognize when a positive Hermitian operator on the Hilbert space of p-particle functions admits a representation in the form (2.4) *where the D_i^p is representable in the form* (2.1) *by means of an N-particle wave function Ψ_i.*

Stated in this manner, the problem is pertinent to bosons and fermions and may be specialized to one or the other by requiring that Ψ_i be symmetric or antisymmetric. (The problem may be generalized by requiring other symmetry types such as those occurring in the purely spin or orbital factors of a wave function.) Our concern in this paper is directed to the case of fermions unless an explicit statement to the contrary is made.

By the Krein–Milman theorem $\mathcal{P}_N^p$ is characterized by its extreme points. It is, therefore, *sufficient to solve the N-representability problem for pure states.* Whereas for a given pure state with wave function Ψ Eq. (2.1) defines the kernel of the integral operator D^p, we must solve the converse problem: *Given an integral operator D^p, decide whether or not there exists an antisymmetric function Ψ of N particles such that the kernel of D^p is representable in the form (2.1).*

It seems that we have here a new mathematical problem of considerable difficulty. The case $p = 1$ will be treated in Part III, but at present we do not have a complete solution of the case of greatest physical interest, $p = 2$.

3. The Natural Expansion of a Function of Several Variables

Löwdin and Shull[12] and Davidson[13] have given striking numerical examples of the advantage of employing natural orbitals in a configuration expansion for He and H_2. We turn now to the proof of a theorem which probably reveals the full scope of this property of natural p states of a given wave function. The theorem and its proof are due, in essence, to Schmidt[14]; however, we reproduce it in a modified form appropriate to our present purpose, for the convenience of the reader.

If f^p and g^p are complex-valued functions of p particles we define a *scalar product* in the usual manner as

$$\langle f^p|g^p\rangle = \int f^p\bar{g}^p d\mu_p \tag{3.1}$$

and the norm $||f^p||$ by $||f^p||^2 = \langle f^p|f^p\rangle$. Similarly,

$$||\Psi||^2 = \int |\Psi(s,t)|^2 d\mu_p d\mu_q\,.$$

We employ $\Psi(s,t)$ as the kernel of two different integral operators denoted by Ψ_q^p and Ψ_p^q. If f^p and f^q are functions on p and q space, respectively, then $\Psi_p^q f^p$

[11] For example, cf. F. Smithies, *Integral Equations* (Cambridge University Press, Cambridge, 1958), Chap. VIII.

[12] Per Olov Löwdin and Harrison Shull, Phys. Rev. **101**, 1730 (1956).

[13] E. R. Davidson, J. Chem. Phys. **37**, 577, 2966 (1962).

[14] Erhardt Schmidt, Math. Ann. **63**, 433 (1907).

and $\Psi_q^p f^q$ are functions on q and p space defined by

$$\Psi_p^q f^p(t) = \int f^p(s)\Psi(s,t)d\mu_p\,, \tag{3.2}$$

$$\Psi_q^p f^q(s) = \int \Psi(s,t)f^q(t)d\mu_q\,. \tag{3.3}$$

Thus, (2.3) and (2.4) may be expressed as follows:

$$D^p = \Psi_q^p\bar{\Psi}_p^q\,, \tag{3.4}$$

$$D^q = \Psi_p^q\bar{\Psi}_q^p\,. \tag{3.5}$$

Suppose that α^p is a normalized eigenfunction of D^p with eigenvalue λ so that

$$D^p\alpha^p = \lambda\alpha^p\,, \tag{3.6}$$

and

$$\lambda||\alpha^p||^2 = \langle D^p\alpha^p|\alpha^p\rangle = \langle\bar{\Psi}_p^q\alpha^p|\bar{\Psi}_p^q\alpha^p\rangle \geq 0\,.$$

Thus, λ is a non-negative real so that D^p, and similarly D^q, are positive Hermitian operators, with finite traces equal to $||\Psi||^2$.

We may associate eigenfunctions of D^p with those of D^q. Let c be a complex number such that $|c|^2 = \lambda$ and define β^q by

$$c\beta^q = \Psi_p^q\bar{\alpha}^p\,. \tag{3.7}$$

Then

$$cD^q\beta^q = \Psi_p^q\bar{\Psi}_q^p\Psi_p^q\bar{\alpha}^p = \Psi_p^q\overline{D}^p\bar{\alpha}^p = \lambda\Psi_p^q\bar{\alpha}^p$$
$$\therefore D^q\beta^q = \lambda\beta^q\,,$$

so that β^q is an eigenfunction of D^q with the *same* eigenvalue λ. Further,

$$\bar{c}\Psi_q^p\bar{\beta}^q = \Psi_q^p\bar{\Psi}_p^q\alpha^p = D^p\alpha^p = \lambda\alpha^p$$
$$\therefore \Psi_q^p\bar{\beta}^q = c\alpha^p\,. \tag{3.8}$$

The norm of β^q is 1, for

$$\lambda\langle\beta^q|\beta^q\rangle = \langle c\beta^q|c\beta^q\rangle = \langle\Psi_p^q\bar{\alpha}^p|\Psi_p^q\bar{\alpha}^p\rangle = \langle\bar{\alpha}^p|\overline{D}^p\bar{\alpha}^p\rangle = \lambda$$

since α^p is normalized.

$$\therefore \langle\beta^q|\beta^q\rangle = 1\,.$$

Thus, Eqs. (3.7) and (3.8) effect a 1:1 correspondence between normalized eigenfunctions of D^p and D^q with the same eigenvalue. The correspondence is unique except for the phase of β^q. We assume henceforth that the *p*th-*order eigenvalues*, λ_i^p, are numbered so that they form a *monotonely nondecreasing* sequence; so that $\lambda_1^p = \max\{\lambda_i^p\}$. The theory of integral operators allows us to conclude that if λ_i^p corresponds to the *natural p state* α_i^p then

$$D^p(s;s') = \sum_i \lambda_i^p\alpha_i^p(s)\bar{\alpha}_i^p(s')\,, \tag{3.9}$$

$$D^q(t;t') = \sum_i \lambda_i^q\alpha_i^q(t)\bar{\alpha}_i^q(t')\,, \tag{3.10}$$

where

$$\Psi_p^q\bar{\alpha}_i^p = c_i^q\alpha_i^q\,, \quad \Psi_q^p\bar{\alpha}_i^q = c_i^p\alpha_i^p \tag{3.11}$$

$$c_i^p = c_i^q\,, \quad |c_i^p|^2 = \lambda_i^p = \lambda_i^q \tag{3.12}$$

$$||\Psi||^2 = \sum_i \lambda_i^p\,. \tag{3.13}$$

Equation (3.12) expresses the duality between the p matrix *and the q matrix* which was noticed by Carlson and Keller[2] but was probably first discovered by Schmidt.[14] We *henceforth assume* that the natural p states and the natural q states are related by (3.11).

We now turn to the proof of a theorem which reveals the role of natural states in the approximation of functions of many particles.

Theorem 3.1. (Schmidt) Given a square integrable function $\Psi(s,t)$ where s belongs to p space and t to q space, suppose that for $u \leq v$, $f_i(s)$ with $1 \leq i \leq u$ and $g_j(t)$ with $1 \leq j \leq v$ are linearly independent square integrable functions *then the minimum*, $||\Psi||^2 - \sum_1^u \lambda_i^p$, of

$$\Delta = ||\Psi(s,t) - \sum_{i,j} a_{ij}f_i(s)g_j(t)||^2\,, \tag{3.14}$$

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 $f_i(s) = \alpha_i^p(s)\,, \quad g_i(t) = \alpha_i^q(t)\,.$

In other words, the best least-squares approximation to Ψ as a sum of uv products of the form $f_i(s)g_j(t)$ is

$$\sum_1^u c_i\alpha_i^p(s)\alpha_i^q(t)\,. \tag{3.15}$$

Proof. There is no loss of generality in replacing $\{f_i(s)\}$ by $\{\alpha_i(s)\}$, where α_i is an orthonormal set of u functions equivalent to $\{f_i(s)\}$. Assume that this has been done. Defining $c_i\beta_i = \sum_j a_{ij}g_j$, where c_i is a complex number chosen so that $||\beta_i|| = 1$, we have $\sum a_{ij}f_i(s)g_i(t) = \sum c_i\alpha_i(s)\beta_i(t)$. We expand Δ and follow the classical procedure of completing the square.

$$\begin{aligned}\Delta &= ||\Psi - \textstyle\sum_i c_i\alpha_i\beta_i||^2\,,\\ &= ||\Psi||^2 - \textstyle\sum \bar{c}_i\langle\Psi_p^q\bar{\alpha}_i|\beta_i\rangle - \sum c_i\langle\beta_i|\Psi_p^q\bar{\alpha}_i\rangle\\ &\qquad + \textstyle\sum c_i\bar{c}_i\,,\\ &= ||\Psi||^2 + \textstyle\sum ||c_i\beta_i - \Psi_p^q\bar{\alpha}_i||^2 - \sum\langle\Psi_p^q\bar{\alpha}_i|\Psi_p^q\bar{\alpha}_i\rangle\,.\end{aligned}$$

For arbitrary α_i, the best choice of β_i is to make the second term zero, that is, we must set

$$c_i\beta_i = \Psi_p^q\bar{\alpha}_i\,. \tag{3.16}$$

The minimum of Δ is then attained for α_i chosen to maximize $\sum \langle \Psi_p^q \overline{\alpha}_i | \Psi_p^q \overline{\alpha}_i \rangle = \sum \langle \overline{D}^p \overline{\alpha}_i | \overline{\alpha}_i \rangle$ which, as is well known, is achieved by choosing as α_i the first u natural p states, α_i^p. It then follows from (3.16) that $\beta_i = \alpha_i^q$, and all the assertions of the theorem follow immediately.

Note that Theorem 3.1 makes no use of the symmetry of Ψ, but assumes merely that some definite partition of the N particles into groups of p and q particles has been effected. If Ψ is either symmetric or antisymmetric, it is easily seen that D^p does not depend on the choice of the p particles to which we ascribe the coordinates $x_1, x_2, \cdots, x_p$. *Thus, for bosons and fermions, there is a unique p matrix associated with a given system.* Such is not the case if Ψ belongs to a symmetry type corresponding to a Young tableau other than $[N]$ or $[1^N]$. In particular, the natural orbitals of a boson or fermion system are unique. The following result is, therefore, not surprising.

Theorem 3.2. If Ψ is symmetric or antisymmetric in N particles *then* for $1 \leq p \leq N$, each α_j^p may be expanded in terms of natural orbitals α_i^1.

Proof. From (3.13) and Theorem 3.1 it follows that, except possibly on a set of measure zero,

$$\Psi(s,t) = \sum_i c_i \alpha_i^p(s) \alpha_i^q(t) . \tag{3.17}$$

Thus, setting $p = 1$, $q = N - 1$,

$$\Psi(s,t) = \sum_i c_i \alpha_i^1(s) \alpha_i^q(t) , \tag{3.18}$$

and, hence,

$$c_j \alpha_j^q(t) = \int \overline{\alpha}_j^1(s) \Psi(s,t) d\mu_p . \tag{3.19}$$

Hence, α_j^q is symmetric or antisymmetric according as Ψ is. Now suppose that $\beta(s)$ is an orbital orthogonal to all the Ψ-natural orbitals α_i^1. Thus, by (3.17),

$$0 = \int \overline{\beta}(1) \Psi(1,2,3 \cdots N) d\mu(1) = - \int \overline{\beta}(1) \Psi \times (2,1,3 \cdots N) d\mu(1) ,$$

and, hence, by (3.19),

$$\int \overline{\beta}(1) \alpha_j^q(1,3, \cdots N) d\mu(1) = 0 .$$

Thus, any function orthogonal to the α_i^1 is orthogonal to α_j^{N-1}. and, for $x_3, x_4, \cdots x_N$ fixed, $\alpha_j^{N-1}(2,3 \cdots N)$ can be expanded in terms of $\alpha_i^1(2)$. By induction we see that

$$\Psi(1,2 \cdots N) = \sum c^{i_1 i_2 \cdots i_N} \alpha_{i_1}^1(1) \alpha_{i_2}^1(2) \cdots \alpha_{i_N}^1(N) . \tag{3.20}$$

Since for any p, α_j^p are obtained from Ψ by integration, the required result follows immediately.

Theorem 3.2 underlines the importance of the natural orbitals as the most suitable set of one-particle functions to use in discussing a quantum system and heightens our interest in finding a practicable method of obtaining the natural p states of a system without prior knowledge of Ψ. The following theorem valid only for *fermions* will be very useful in the sequel for the case $p = 1$.

Theorem 3.3. If Ψ is antisymmetric and p is odd with $2p \leq N$ *then*

$$\int \overline{\alpha}_j^p(p+1, \cdots, 2p) \alpha_j^q(p+1, \cdots N) \times d\mu(p+1, \cdots, 2p) = 0 .$$

Proof. By the analog of (3.19) for general p,

$$c_j \int \overline{\alpha}_j^p(p+1, \cdots 2p (\alpha_j^q(p+1, \cdots N) d\mu(p+1, \cdots 2p) = \int \overline{\alpha}_j^p(1, \cdots p) \overline{\alpha}_j^p(p+1 \cdots 2p) \Psi(1 \cdots N) \times d\mu(1, \cdots 2p) . \tag{3.21}$$

In the last integrand the product of the first two factors is symmetric with respect to the permutation $(1,p+1)(2,p+2) \cdots (p,2p)$, whereas Ψ is antisymmetric. Whence by renumbering the variables of integration we see the integral vanishes. Since $c_j \neq 0$, the required result follows.

Since the integral in (3.21) depends on $N - 2p$ free variables we shall express Theorem 3.3 by saying that for odd p,α_j^p is *strongly orthogonal* to α_j^q.

4. Antisymmetric Expansion

It is clear from their definition that the natural p states of a fermion system are antisymmetric, however, it is not immediately apparent that the right-hand side of (3.17) is antisymmetric. We shall expect the antisymmetry requirement to lead to interrelations among the $\{\alpha_i^p\}$ and $\{\alpha_i^q\}$ and to impose conditions on the values allowed for c_i^p. Our next theorem makes explicit a condition of this latter type. Perhaps, it is of interest to record that the following result, obtained only in 1962, contains the particular case $p = 1$ which was the first interesting result in the subject obtained by the present author in 1951!

Theorem 4.1. If $N = 2p$ and p is odd, then the pth-order eigenvalues of a fermion system in a pure state Ψ are evenly degenerate.

Proof. Since $p = q$, $D^p = D^q$, and p odd implies $\Psi_q^p = -\Psi_p^q$.

Suppose α^p is a p state corresponding to eigenvalue

λ. Then by (3.11), $\Psi_p^q\bar{\alpha}^p = c\alpha^q$ is also a p state with eigenvalue λ. But α^q is orthogonal to α^p by Theorem 3.3. Thus, λ is at least doubly degenerate.

Suppose f^p is a further p state with eigenvalue λ and that f^p is orthogonal to both α^p and α^q. Then, by (3.11), $\Psi_p^q\bar{f}^p$ is also a p state with eigenvalue λ. Further

$$\langle\Psi_p^q\bar{f}^p|\alpha^q\rangle = \langle f^p|\bar{\Psi}_q^p\alpha^q\rangle = \bar{c}\langle\bar{f}^p|\bar{\alpha}^p\rangle = \bar{c}\langle\alpha^p|f^p\rangle = 0\,.$$

Using $\Psi_q^p = -\Psi_q^p$, we may show similarly that $\Psi_p^q\bar{f}^p$ is orthogonal to α^p. It is orthogonal to f^p by Theorem 3.3. Thus, if the multiplicity of λ is greater than 2, it is at least 4. Proceeding by induction we show that the multiplicity of λ is even or infinite. It is not infinite since D^p has finite trace.

Our next result which follows easily from Theorem 3.1 will be needed in the proof of Theorem 4.4 but is of intrinsic interest since it involves a new property of natural p states.

Theorem 4.2. If Ψ is a given antisymmetric N-particle function, and f^p and f^q are, respectively, functions of the p and q particles arbitrary except that their norms are unity, *then* the maximum of $|\langle\Psi|f^pf^q\rangle|^2$ equals λ_1^p and occurs when $f^p = \alpha_1^p$ and $f^q = \alpha_1^q$.

Proof. The minimum of $||\varphi||$, if $\varphi = \Psi - cf^pf^q$ (see Fig. 1) occurs for c chosen so that $\varphi \perp f^pf^q$ or when

$$\langle\Psi|f^pf^q\rangle = c\,,$$

and the minimum equals $||\Psi||^2 - |c|^2$. But by Theorem 3.1 this equals $||\Psi||^2 - \lambda_1^p$, and the minimum occurs when f^p and f^q are natural states.

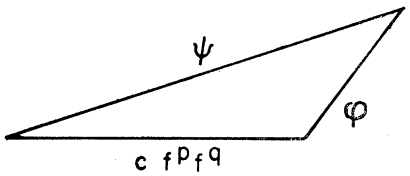

FIG. 1.

Thus, the maximum of $|c|^2$ is λ_1^p, occuring when $f^p = \alpha^p$, $f^q = \alpha_2^q$.

It is well known that a *projector* P, that is an idempotent Hermitian operator ($P^2 = P, P^\dagger = P$), never increases the length of a vector on which it acts. This follows easily from Schwarz's inequality.

$$\langle Px|Px\rangle = \langle x|P^2x\rangle = \langle x|Px\rangle$$
$$\therefore |\langle Px|Px\rangle|^2 \leq \langle x|x\rangle\langle Px|Px\rangle\,.$$
$$\therefore \text{if} \quad ||Px|| \neq 0 \quad ||Px|| \leq ||x||\,.$$

The equality sign obtains if and only if $x = Px$.

We shall apply the above property to the antisymmetrizers A_N and A_{q+1} which are idempotents operating on functions of the variables $1,2,\cdots,N$ and $p,p+1,\cdots,N$, respectively. Thus,

$$A_N = (N!)^{-1}\sum \epsilon(\pi)\pi\,,$$

where the sum is over the $N!$ elements, π, of the group of permutations of the N particles. By f^pf^q we mean a function of the N particles, which at the point $x_1x_2,\cdots x_N$ of N-particle space assumes the value $f^p(1,2\cdots p)f^q(p+1,\cdots N)$. The reader will now interpret $(p,p+1)f^pf^q$ as the function which assigns to $x_1,\cdots x_N$ the value $f^p(1,2,\cdots p-1,p+1) \times f^q(p,p+2\cdots N)$. It may be easily verified that for $q < N$

$$A_N^2 = A_N = A_N^\dagger\,, \tag{4.1}$$

$$A_NA_{q+1} = A_{q+1}A_N = A_N\,. \tag{4.2}$$

The numbers

$$a_i^p = \langle(p,p+1)\alpha_i^p\alpha_i^q|\alpha_i^p\alpha_i^q\rangle \tag{4.3}$$

are apparently of considerable significance in analyzing interrelations among the natural states. Together with analogous numbers obtained by replacing $(p,p+1)$ by $(p-1,p+2)(p,p+1)$, and so on, they play a decisive role in Part II. If (4.3) is written as an integral by means of (3.1) then we see that Theorem 3.3 implies that

$$\text{if} \quad p = 1\,, \qquad a_i^1 = 0\,. \tag{4.4}$$

For any p we may prove that

$$a_i^p \geq 0\,. \tag{4.5}$$

These preliminaries enable us to state and prove an important theorem.

Theorem 4.3. If Ψ is normalized and antisymmetric, then

$$\lambda_i^p = \lambda_i^q \leq \langle\alpha_i^p\alpha_i^q|A_N\alpha_i^p\alpha_i^q\rangle\,, \tag{4.6}$$

with equality if, and only if, $\Psi = cA_N\alpha_i^p\alpha_i^q$ where c is some constant. Further

$$\langle\alpha_i^p\alpha_i^q|A_N\alpha_i^p\alpha_i^q\rangle \leq \frac{1}{q+1}[1 - qa_i^p]\,. \tag{4.7}$$

When $p = 1$

$$\langle\alpha_i^p\alpha_i^q|A_N\alpha_i^p\alpha_i^q\rangle = 1/N\,. \tag{4.8}$$

When $p = q = 2$ *and* α_i^p *is proportional to* α_i^q,

$$\langle\alpha_i^2\alpha_i^2|A_4\alpha_i^2\alpha_i^2\rangle = \tfrac{1}{3}[1 - 2a_i^2]\,. \tag{4.9}$$

Proof. From (3.12) and (3.15) it follows that

$$\lambda_i^p = \lambda_i^q = |\langle\Psi|\alpha_i^p\alpha_i^q\rangle|^2\,,$$

$$= |\langle A_N\Psi|\alpha_i^p\alpha_i^q\rangle|^2 ,$$
$$= |\langle\Psi|A_N\alpha_i^p\alpha_i^q\rangle|^2 ,$$
$$\leq \langle\Psi|\Psi\rangle\langle A_N\alpha_i^p\alpha_i^q|A_N\alpha_i^p\alpha_i^q\rangle$$

with equality if, and only if, $A_N\alpha_i^p\alpha_i^q$ and Ψ are proportional. By (4.1) the result (4.6) follows.

To prove (4.7) we use (4.1) and (4.2).

$$\langle\alpha_i^p\alpha_i^q|A_N\alpha_i^p\alpha_i^q\rangle = \langle A_N\alpha_i^p\alpha_i^q|A_N\alpha_i^p\alpha_i^q\rangle ,$$
$$= \langle A_NA_{q+1}\alpha_i^p\alpha_i^q|A_NA_{q+1}\alpha_i^p\alpha_i^q\rangle ,$$
$$\leq \langle A_{q+1}\alpha_i^p\alpha_i^q|A_{q+1}\alpha_i^p\alpha_i^q\rangle .$$

The last inequality follows because A_N is a projector. The equality obtains if and only if $A_N\alpha_i^p\alpha_i^q = A_{q+1}\alpha_i^p\alpha_i^q$, which is obviously the case if (i) $p = 1$, $N = q + 1$, but may also occur if (ii) $p = q = 2$ and α_i^p is proportional to α_i^q.

Making use of the antisymmetry of α_i^q we see that

$$A_{q+1}\alpha_i^p\alpha_i^q = \frac{1}{q+1}[1 - (p,p+1) - (p,p+2)\cdots - (pN)]\alpha_i^p\alpha_i^q .$$

By explicit use of (3.1), we see that for $u > p$

$$\langle\alpha_i^p\alpha_i^q|(pu)\alpha_i^p\alpha_i^q\rangle = a_i^p .$$

Thus,

$$\langle A_{q+1}\alpha_i^p\alpha_i^q|A_{q+1}\alpha_i^p\alpha_i^q\rangle = \langle\alpha_i^p\alpha_i^q|A_{q+1}\alpha_i^p\alpha_i^q\rangle = \frac{1}{q+1}[1 - qa_i^p] .$$

Noting (4.4), the results (4.7), (4.8), and (4.9) follow immediately.

Theorem 4.3 immediately provides us with important necessary conditions for N representability.

Corollary 4.3A. The first-order eigenvalues are bounded above by $1/N$. The bound is reached if, and only if, Ψ is proportional to $A_N\alpha^1\alpha^{N-1}$.

The fact that

$$\lambda_i^1 \leq 1/N \tag{4.10}$$

is well known.[15] However, our corollary goes beyond the mere inequality (4.10) to a necessary and sufficient condition for the attainment of the bound. In the Hartree–Fock (HF) approximation for Ψ by means of a single Slater determinant there are only N natural orbitals, but since $\sum\lambda_i^1 = 1$, (4.10) implies that $\lambda_i^1 = N^{-1}$. Indeed, this last equality completely characterizes the Hartree–Fock approximation. If N of the $\lambda_i^1 = N^{-1}$, we are in the HF approximation; if only $\lambda_1^1 = N^{-1}$ the corollary restates our problem with the help of an $(N-1)$-particle function. Cases intermediate between these two extremes will be considered in Part III.

By combining (4.6) and (4.7) we have a further corollary.

Corollary 4.3B. The eigenvalues of an antisymmetric normalized Ψ satisfy

$$\lambda_i^p = \lambda_i^q < \frac{1}{q+1}[1 - qa_i^p] ,$$

if $2 < p \leq q$.

Since the sum of λ_i^p is unity, it follows that Ψ has at least $q + 2$ natural p states. We also see that for $p > 2$

$$\lambda_i^p < 1/(q+1) . \tag{4.11}$$

This does not seem to be a very good upper bound since there are, apparently, cogent physical reasons for believing that λ_i^2 is bounded by the reciprocal of $\frac{1}{2}N(N-1)$. This belief was held rather widely (even by the present author for some months), however we show in Part II that for $p = 2$, (4.11) gives the best possible upper bound!

Combining (4.6) and (4.9) and taking note of the exceptional cases we obtain

Corollary 4.3C. For $p = q = 2$ with $\Psi = cA_4[\alpha_1^2(12) \times \alpha_1^2(34)]$,

$$\lambda_1^2 = \tfrac{1}{3}[1 - 2a_1^2] . \tag{4.12}$$

This corollary will guide our search in Part II for an example to test the sharpness of (4.11).

It is well known that the Hartree–Fock approximation to an antisymmetric function is considerably more accurate than the Hartree approximation. This is a consequence of the fact that the former reproduces the antisymmetry. The HF function corresponding to the Hartree function $f^N(1,2\cdots N) = \varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)$ is simply A_Nf^N. If we denote the cofactor of $\varphi_1(1)$ in $A_Nf^N(1,2\cdots N)$ by $f^{N-1}(2,3\cdots N)$ it is apparent that, apart from a constant factor, $A_Nf^N(1,2\cdots N)$ and $A_N[\varphi_1(1) \times f^{N-1}(2,3,\cdots N)]$ are equal. This latter expression has the same form as the N particle function which appeared in Corollary 4.3A, except that here, as a factor in a HF function, f^{N-1} is expressible as a Slater determinant, whereas the α^{N-1} of Corollary 4.3A was an arbitrary antisymmetric function of $N-1$ particles. Since the latter is more general, we anticipate that functions of the type of Corollary 4.3A would lead to better approximations than are possible by means of a HF function, that is, a single Slater determinant.

We are, thus, led to the following problem. If f^p and f^q are arbitrary normalized antisymmetric func-

[15] For example, Eq. (75) of P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

tions, of p and q particles, respectively, and

$$\delta = ||\Psi - cA_N f^p f^q|| , \tag{4.13}$$

what choice of c, f^p and f^q minimizes δ? We shall not solve this problem. Indeed, some evidence suggests that no minimum is attained in the general case if $p > 1$. However, the following interesting result is easily proved.

Theorem 4.4. If f^p and f^q are corresponding p and q natural states, c may be chosen so that

$$\delta^2 \leq ||\Psi||^2 - (q+1)\lambda_1^p , \tag{4.14}$$

with equality if and only if $p = 1$.

Proof. As in the proof of Theorem 4.2, we see that for the best choice of c

$$\langle \Psi | A_N f^p f^q \rangle = c \langle A_N f^p f^q | A_N f^p f^q \rangle$$

and that

$$\begin{aligned} \delta^2 &= ||\Psi||^2 - ||cA_N f^p f^q||^2 \\ &= ||\Psi||^2 - \frac{|\langle \Psi | f^p f^q \rangle|^2}{\langle f^p f^q | A_N f^p f^q \rangle} . \end{aligned} \tag{4.15}$$

The proof of (4.7) depended only on the fact that α_i^p and α_i^q were antisymmetric and normalized, and not that they were natural states of Ψ. Thus,

$$\langle f^p f^q | A_N f^p f^q \rangle \leq 1/(q+1)$$

with equality if, and only if, $p = 1$. Thus,

$$\delta^2 \leq ||\Psi||^2 - (q+1)|\langle \Psi | f^p f^q \rangle|^2 \tag{4.16}$$

with equality if, and only if, $p = 1$. By choosing $f^p = \alpha_1^p$ and $f^q = \alpha_1^q$ we have the required result.

In the case $p = 1$, equality obtains throughout the above argument so that we have the following more explicit result.

Corollary 4.4A. For $p = 1$ the minimum value, $\delta_{\min}$, of δ in (4.13) is given by

$$\delta_{\min}^2 = ||\Psi||^2 - N\lambda_1^1 . \tag{4.17}$$

Since $\delta_{\min}^2 \geq 0$, we have a new proof that $N\lambda_1^1 \leq 1$ when $||\Psi|| = 1$.

A comparison of Theorem 4.2 with Theorem 4.4 and Corollary 4.4A again illustrates the great advantage to be gained in approximating functions by means of functions of the appropriate symmetry. The extension of this technique to general types of symmetry is the main idea underlying the *projection operator technique* exploited so strikingly in recent years by Löwdin and his associates.

5. N Representability is a Unitary Invariant

We return to a consideration of the central problem, which we discuss in terms of the physically important cases of the 1 matrix and the 2 matrix. Since these will recur again and again, it is convenient to have a notation for them which does not involve indices. We suggest

$$D^1 = \mu , \qquad D^2 = \sigma , \tag{5.1}$$

so that

$$\mu(1;1') = \bar{\mu}(1';1) , \tag{5.2}$$

$$\sigma(12;1'2') = -\sigma(21;1'2') = \bar{\sigma}(1'2';12) . \tag{5.3}$$

We have agreed that σ is N representable if there is an antisymmetric function Ψ of N particles such that

$$\sigma = \Psi_{N-2}^2 \bar{\Psi}_2^{N-2} . \tag{5.4}$$

The crux of our problem can then be stated as follows:

Given a function σ satisfying conditions (5.3). Find explicit criteria by which to recognize whether or not σ is N representable.

Stated in this form the problem seems to involve integration and, therefore, to be a problem in analysis. However, it may also be given an algebraic formulation, which is encouraging since, on the whole, algebra is easier than analysis!

Suppose $\{g_i(1)\}$ is a complete set of orthonormal functions in terms of which it is possible to expand Ψ and σ. Let

$$\Psi = c^{i_1 i_2 i_3 \cdots i_N} g_{i_1}(1) g_{i_2}(2) \cdots g_{i_N}(N) \tag{5.5}$$

and

$$\sigma = s^{j_1 j_2 j_3 j_4} g_{j_1}(1) g_{j_2}(2) \bar{g}_{j_3}(1') \bar{g}_{j_4}(2') . \tag{5.6}$$

A necessary and sufficient condition that Ψ be antisymmetric is that $c^{i_1 i_2 \cdots i_N}$ be antisymmetric in its indices. The conditions (5.3) are equivalent to

$$s^{j_1 j_2 j_3 j_4} = -s^{j_2 j_1 j_3 j_4} = \bar{s}^{j_3 j_4 j_1 j_2} , \tag{5.7}$$

and condition (2.1) is equivalent to

$$s^{j_1 j_2 j_3 j_4} = \sum_{i_3 \cdots i_N} c^{j_1 j_2 i_3 \cdots i_N} \bar{c}^{j_3 j_4 i_3 \cdots i_N} . \tag{5.8}$$

In this notation, the central problem may be formulated as follows:

Determine criteria which will enable us to recognize whether or not a tensor $s^{i_1 i_2 i_3 i_4}$, satisfying (5.7), may be expressed as in (5.8) by means of a tensor $c^{i_1 i_2 \cdots i_N}$, antisymmetric in N indices.

The only parameter which enters either formulation of the central problem is N, the number of particles in the system; thus, the criteria we are seeking must be expressible in terms of N. The difficulty and novelty of the problem consists in the necessity

of imposing a symmetry condition by means of the nonlinear expression on the right-hand side of Eq. (5.8).

We referred to symbols occurring in (5.7) and (5.8) as *tensors*, though in fact, so far, they are merely symbols whose indices enjoy prescribed symmetry properties and no allusion to changes of reference frame has been made. If we replace $g_i(1)$ by any other orthonormal system

$$g_{i'}(1) = a_{i'}^{i} g_i(1) , \tag{5.9}$$

where $a_{i'}^{i}$ is a constant unitary transformation such that

$$\sum_{i,j} \delta_{ij} a_{i'}^{i} a_{j'}^{j} = \delta_{i'j'} ,$$

our conditions on Ψ and σ would take the same form (5.7) and (5.8) with $s^{i_1 i_2 j_3 j_4}$ and $c^{i_1 i_2 \cdots i_N}$ replaced by their transforms as contravariant tensors by means of $a_{i'}^{i}$ and its inverse $a_{i}^{i'}$. We are using Schouten's notation for tensors.[16] It follows that *the N representability of* $s^{i_1 i_2 j_3 j_4}$ *is invariant with respect to unitary transformations.* Thus, *the criteria* we are seeking, in addition to being expressible in terms of N, should *involve only unitary invariants of* $s^{i_1 i_2 j_3 j_4}$.

The above arguments apply equally well to density matrices of any order. In particular, since the λ_i^1 together with their multiplicities, constitute a complete set of unitary invariants of the Hermitian form $\mu(1;1')$, it follows that *the conditions for the N representability of a one-particle density matrix may be expressed in terms of* λ_i^1 *and the parameter N.*

Alternatively, since the sums of the principal minors of a Hermitian matrix also constitute a complete set of unitary invariants, if

$$\mu(1;1') = m^{i_1 i_2} g_{i_1}(1) \bar{g}_{i_2}(1') , \tag{5.10}$$

where

$$m^{i_1 i_2} = \textstyle\sum_j s^{i_1 j i_2 j} , \tag{5.11}$$

then the N representability of μ should be *expressible in terms of* t_u, where t_u is the sum of the principal minors of m^{ij} of order u, that is,

$$t_u = \sum_{i,j} \delta_{i_1 i_2 \cdots i_u}^{j_1 j_2 \cdots j_u} m^{i_1 j_1} m^{i_2 j_2} \cdots m^{i_u j_u} .$$

The t_u have the advantage of being rational expressions in m^{ij}.

For $\mu(1;1')$, $\{\lambda_i^1\}$ or $\{t_u\}$ constitute a complete and nonredundant set of unitary invariants. Löwdin[15] has interpreted the λ_i^1 as occupation factors for the natural spin orbitals. (Löwdin's n_i equals $N\lambda_i^1$.) It would be very interesting to obtain a complete, nonredundant, set of unitary invariants of σ and to give them a physical interpretation. For example, λ_i^2 is easily recognized as an *occupation factor for the natural geminal,* α_i^2. Doubtless there are other invariants of σ which could be interpreted as *bonding* or *correlation* factors between natural geminals or between natural orbitals and natural geminals. If μ has finite rank, r, then the number of essential unitary invariants of σ is $\frac{1}{8} r(r^2 - 1)(r - 2)$ as was pointed out by E. R. Davidson in discussion.

In the particular case that all 1 eigenvalues are simple, the α_i^1 constitute an intrinsically determined orthonormal set. If, expanding with respect to this set, we have

$$\sigma(12;1'2') = s^{j_1 j_2 j_3 j_4} \alpha_{j_1}^1(1) \alpha_{j_2}^1(2) \bar{\alpha}_{j_3}^1(1') \bar{\alpha}_{j_4}^1(2') ,$$

then $\{s^{i_1 i_2 j_3 j_4}\}$ is a complete set of unitary invariants of σ, in general, redundant. Presumably, s^{1212} provides a measure of the occupation of the geminal $(1/\sqrt{2}) \times [\alpha_1^1(1)\alpha_2^1(2) - \alpha_1^1(2)\alpha_2^1(1)]$; whereas s^{1234} would measure the correlation between that geminal and $(1/\sqrt{2})[\alpha_3^1(1)\alpha_4^1(2) - \alpha_3^1(2)\alpha_4^1(1)]$. It would appear that the coefficients $s^{i_1 j_2 j_3 j_4}$, which are unitary invariants associated with σ, are the most obvious building material from which to construct a satisfactory theory of bonding. Work along this line was reported by Shull at the Sanibel Conferences in 1962 and 1963.

However, the numerical success of Hylleraas' approach to helium suggests that satisfactory accuracy will not be obtainable by methods using geminals of the simple form above but will only be achieved when we can work directly with the natural geminals, α_j^2.

PART II—BOUNDS ON λ_i^p AND ENERGY

Our main interest in this Part is to obtain bounds on the eigenvalues of the 2-matrix and to use these to give a lower bound for the energy of the ground state of any system of fermions. This latter bound is expressed in terms of energy levels of helium-like atoms, a topic to the understanding of which Professor Hylleraas has made the fundamental contributions. In the course of the discussion, we are led to consider wave functions which we describe as of *extreme type* and which also appear in the BCS–Bogoljubov theory of superconductivity.

6. Sasaki's Formula

In this section we prove a formula[17] due to Sasaki which should be extremely useful whenever a system

[16] J. A. Schouten, *Tensor Analysis for Physicists*, (Oxford University Press, Oxford, 1951).

[17] Fukashi Sasaki, Quantum Chemistry Group, Uppsala, Report No. 77, 1962 (unpublished).

of N particles is partitioned into two subsystems. The proof we give is more pedestrian than Sasaki's original unpublished argument which makes subtle use of diagrams representing the action of any permutation on the partitioned system.

Recall that A_N, A_p, and A_q are antisymmetrizing projectors which operate on functions of the N, p, and q particles, respectively.

Theorem 6.1. Interpreting t_0 as the identity permutation and setting $t_j = (1,p+1)(2,p+2)\cdots(j,p+j)$ for $1 \leq j \leq p$, we have *Sasaki's formula*

$$\binom{N}{p} A_N = A_p A_q \Big[\sum_{j=0}^{p} (-1)^j \binom{p}{j}\binom{q}{j} t_j \Big] A_p A_q \,. \tag{6.1}$$

Proof. Denote the symmetric group of all permutations of the N, p, and q particles by S_N, S_p, and S_q, respectively. The direct product $H = S_p \times S_q$ is a subgroup of S_N of order $p!q!$. We say an element of S_N is of j type if it interchanges j of the p particles with j of the q particles.

How many elements of j type are there? There are $\binom{p}{j}\binom{q}{j}$ distinct *ordered pairs* of sets such that the first contains j p particles and the second set contains j q particles. If s is of j type, it must interchange the two sets of one such ordered pair. Suppose a fixed s_0 of j type interchanges the same two sets, then $s_0^{-1}s = h \in H$. Thus, $s = s_0 h$. Conversely for all $h \in H$, $s_0 h$ is of j type and is associated with the *same* ordered pair of sets. Hence, there are $\binom{p}{j}\binom{q}{j} p!q!$ elements in S_N of j type. A check on this result is provided by the observation that $\sum_{j=0}^{p} \binom{p}{j}\binom{q}{j}$ is the coefficient of x^p in $(1+x)^p(1+x)^q$ and, hence, that

$$p!q! \sum_{j=0}^{p} \binom{p}{j}\binom{q}{j} = N! \,.$$

The representative of j type, s_0, can always be taken in the form kt_jk^{-1}, where $k \in H$. Hence, any j type $s = s_0 h = kt_jk^{-1}h$ where $k,h \in H$ and, therefore, every j type element is contained in the double coset Ht_jH. Since, counting repetitions, the latter contains $(p!q!)^2$ elements, each j type permutation occurs in Ht_jH with frequency

$$f_j = j!(p-j)!j!(q-j)! \,.$$

Let $T_N = N!A_N = \sum \epsilon(s)s$, where the summation is over all $s \in S_N$ and where $\epsilon(s)$ is the parity of s. Similarly, for T_p and T_q. Setting $T_N^j = \sum' \epsilon(s)s$ where the summation is over all s of j type, we have $T_N = \sum_{j=0}^{p} T_N^j$. Using the fact that the parity is a character we see that

$$(-1)^j T_p T_q t_j T_p T_q = f_j T_N^j \,. \tag{6.2}$$

Thus,

$$p!q!T_N = T_p T_q [\sum (-1)^j \binom{p}{j}\binom{q}{j} t_j] T_p T_q$$

and dividing by $(p!q!)^2$ we obtain Sasaki's formula.

Replacing $\epsilon(s)$ by 1 throughout the above argument we obtain

Corollary 6.1A. If A_N, A_p, and A_q are symmetrizing projectors, then

$$\binom{N}{p} A_N = A_p A_q \Big[\sum_{j=0}^{p} \binom{p}{j}\binom{q}{j} t_j \Big] A_p A_q \,. \tag{6.3}$$

Using (6.1) we now prove a formula, also due to Sasaki, for the value of $\langle f^p f^q | A_N f^p f^q \rangle$. Since we shall discuss p matrices derived from a variety of functions, we introduce the notation $D^p(\Psi)$ for the p operator of which the kernel is given by (2.1).

Theorem 6.2. For antisymmetric functions f^p and f^q,

$$\binom{N}{p}\langle f^p f^q | A_N f^p f^q \rangle = \sum_{j=0}^{p} (-1)^j \binom{p}{j}\binom{q}{j} \operatorname{tr}[D^j(f^p) D^j(f^q)] \,, \tag{6.4}$$

where tr stands for the trace of an operator.

Proof. Since $A_p f^p = f^p$, $A_q f^q = f^q$, and A_p and A_q are Hermitian, it follows that

$$\langle f^p f^q | A_p A_q t_j A_p A_q f^p f^q \rangle = \langle f^p f^q | t_j f^p f^q \rangle \,.$$

Therefore, by (6.1),

$$\binom{N}{p}\langle f^p f^q | A_N f^p f^q \rangle = \sum_{j=0}^{p} (-1)^j \binom{p}{j}\binom{q}{j} \langle f^p f^q | t_j f^p f^q \rangle \,. \tag{6.5}$$

For $j = 1$, the scalar product on the right-hand side is

$$\begin{aligned} \langle f^p f^q | (1,p+1) f^p f^q \rangle &= \int f^p(1\cdots p) f^q(p+1,\cdots N) \\ &\qquad \overline{f}^p(p+1,2\cdots p)\overline{f}^q(1,p+2\cdots N) d\mu_N \\ &= \int D^1(f^p|1;p+1) D^1(f^q|p+1;1) d\mu(1,p+1) \\ &= [\operatorname{tr} D^1(f^p) D^1(f^q)] \,. \end{aligned} \tag{6.6}$$

The other terms in the right-hand side of (6.5) may be discussed similarly giving (6.4).

It is important for the sequel to estimate the value of

$$\operatorname{tr}[D^j(f^p) D^j(f^q)] \,. \tag{6.7}$$

Since both operators in (6.7) are positive Hermitian, (6.7) is non-negative. Any Hermitian operator, A, of finite trace may be expressed as $A = \sum_0^\infty \alpha^i P_i$, where $\{P_i\}$ is a resolution of the identity. That is, $AP_i = P_i A$, $P_i = P_i^\dagger$, $P_i P_j = \delta_{ij} P_i$. P_i is a projector onto an eigenvector with eigenvalue α^i. If $\alpha^0 = 0$, and $\alpha^i \neq 0$ for $i \neq 0$ we may take all P_i, except P_0, to have unit trace, and $\sum P_i = I$, the identity operator. Suppose that $\{Q_i\}$ is a similar resolution of the identity corresponding to a second Hermitian operator $B = \sum \beta^i Q_i$, then

$$\operatorname{tr}(AB) = \sum_{i,j} \alpha^i \beta^j \operatorname{tr}(P_i Q_j) \,. \tag{6.8}$$

Now

$$\begin{aligned}\text{tr } (P_iQ_j) &= \text{tr } (P_i^2Q_j^2) = \text{tr } (P_iQ_j^2P_i)\\ &= \text{tr } [(P_iQ_j)(P_iQ_j)^\dagger] \geq 0 .\end{aligned}$$

Suppose A and B are positive and that α^i and β^i are ordered monotonically decreasing, then

$$\begin{aligned}\text{tr } (AB) &\leq \alpha^1 \sum_{i,j} \beta^j \text{ tr } (P_iQ_j) \leq \alpha^1 \sum \text{tr } (\beta^jQ_j)\\ &\leq \alpha^1 \text{ tr } (B) .\end{aligned}$$

Whence, if tr (A) = tr (B) = 1, tr $(AB) \leq$ min of $[\alpha^1,\beta^1]$, where α^1 and β^1 are, respectively, the largest eigenvalues of the positive operators A and B. In particular,

$$\text{tr } [D^j(f^p)D^j(f^q)] \leq \min [\lambda_1^j(f^p),\lambda_1^j(f^q)] . \quad (6.9)$$

Following the general lines of Sasaki's report[17] we are now able to prove his result on the bound for λ_i^p which settles a conjecture of Yang.[18] Independently, Professor Yang has obtained an alternative proof of his conjecture by a quite different and very interesting method.

We first define

$$\Lambda^p(N) = \binom{N}{p} \sup (\lambda_1^p) , \quad (6.10)$$

where the supremum is taken over all normalized antisymmetric N functions Ψ and λ_1^p is the largest p eigenvalue of Ψ. It then follows from (6.9) that

$$\binom{q}{j} \text{ tr } [D^j(\alpha_i^p)D^j(\alpha_i^q)] \leq \Lambda^j(q) \quad (6.11)$$

for all i. Thus, if we drop the negative terms in (6.4) and note (4.6) we obtain

Corollary 6.2A:

$$\Lambda^p(p+q) \leq 1 + \sum \binom{p}{2s}\Lambda^{2s}(q) , \quad (6.12)$$

where the summation is on integral s such that $2 \leq 2s \leq p$, that is, on even values of j in (6.4). Instead of (6.12), consider the *equality*

$$g(p,N) = 1 + \sum \binom{p}{2s} g(2s,N-p) . \quad (6.13)$$

This difference equation determines $g(p,N)$ for $N \geq p$ if we know it for $p \leq N < 2p$. From the structure of (6.13) we see that a solution $g(p,N)$ which dominates $\Lambda^p(N)$ for $p \leq N < 2p$ will dominate $\Lambda^p(N)$ for all values of p and N. For *even* p, (6.13) becomes

$$\begin{aligned}g(p,N) - g(p,N-p) = 1 &+ \binom{p}{2} g(2,n-p) + \cdots\\ &+ \binom{p}{p-2} g(p-2,N-p)\end{aligned} \quad (6.14)$$

and, in particular,

$$\Delta_2 g(2,N) = 1 , \quad (6.15)$$

$$\Delta_4 g(4,N) = 1 + 6g(2,N-4) , \quad (6.16)$$

$$\Delta_6 g(6,N) = 1 + 15g(2,N-6) + 15g(4,N-6) , \quad (6.17)$$

where we use Δ_p for the backward p difference of N. Similarly, for *odd* p, (6.13) becomes

$$\begin{aligned}g(p,N) = 1 &+ \binom{p}{2} g(2,N-p) \cdots\\ &+ \binom{p}{p-1} g(p-1,N-p)\end{aligned} \quad (6.18)$$

and, in particular,

$$g(1,N) = 1 , \quad (6.19)$$

$$g(3,N) = 1 + 3g(2,N-3) , \quad (6.20)$$

$$g(5,N) = 1 + 10g(2,N-5) + 5g(4,N-5) . \quad (6.21)$$

The general solution of Eq. (6.13) has not been obtained. However, the solution may be obtained by recursion up to reasonable values of p fairly easily. To fix the initial values we note that $\Lambda^p(p) = 1$ and also, by the Keller duality, $\Lambda^p(p+q) = \Lambda^q(p+q)$. For $p = 1$, (6.19) gives $\Lambda^1(N) \leq 1$, which is a best possible result since, in fact, Corollary 4.3A implies that $\Lambda^1(N) = 1$. For $p = 2$, (6.15) gives

$$g(2,N) = [N/2] + c ,$$

where c may depend on whether N is even or odd and where the symbol $[x]$ represents the greatest integer less than or equal to the real number x. Since $\Lambda^2(2) = 1$ and $\Lambda^2(3) = \Lambda^1(3) = 1$, we see that

$$g(2,N) = [N/2] \quad (6.22)$$

dominates $\Lambda^2(N)$ and is, therefore, an upper bound for $\binom{N}{2}\lambda_i^2$. In other words, for all i,

$$\lambda_i^2 \leq \begin{cases}(N-1)^{-1} , & \text{if } N \text{ is even}\\ N^{-1} , & \text{if } N \text{ is odd} .\end{cases} \quad (6.23)$$

For even N, (4.11) gave the same bound, however, the present result is sharper for N odd.

For $p = 3$, (6.20) and (6.22) lead to $g(3,N) = 1 + 3[(N-3)/2]$ and hence

$$\Lambda^3(N) \leq 1 + 3[(N-3)/2] . \quad (6.24)$$

For $p = 4$, we note that $\Lambda^4(4) = 1$, $\Lambda^4(5) = \Lambda^1(5) = 1$, $\Lambda^4(6) = \Lambda^2(6) \leq 3$ by (6.22), and $\Lambda^4(7) = \Lambda^3(7) \leq 7$ by (6.24). When Eq. (6.16) is solved, we find

$$\Lambda_4(N) \leq \tfrac{1}{8} N[3N - 13 + 3(-1)^N] + \gamma_N , \quad (6.25)$$

where γ_N equals 0, 13/8, -3, 21/8 according as N is

[18] C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962)—the first conjecture, on p. 696.

congruent to 0, 1, 2, or 3 modulo 4.

It is clear that we could continue in this way to solve (6.13) for increasing values of p. However, the precise solution is probably not worth obtaining since the most we can hope from it is a *rough* upper bound on $\Lambda^p(N)$. Already, $\Lambda^3(5) = \Lambda^2(5) \leq 2$ by (6.22), whereas the bound given by (6.24) is 4 which is in excess by 100%!

However, without obtaining the exact solution, Yang's conjecture,[18] that for even p, $g(p,N)$ is of order $N^{p/2}$, follows immediately from (6.14) by induction starting from (6.22). From (6.18) it then follows that $g(p,N)$ is of order $N^{(p-1)/2}$ if p is odd. This was noted by Sasaki in his Uppsala report.[17]

We can go further and determine the coefficient, δ_p, of the leading term in $g(p,N)$. Suppose that $g(p,N) \backsim \delta_p N^{p/2} + \cdots$, then for p *even* (6.14) implies that

$$\delta_p[N^{p/2} - (N-p)^{p/2}] \sim \binom{p}{2}\delta_{p-2}N^{(p-2)/2},$$

whence

$$\delta_p = [(p-1)/p]\delta_{p-2}\,. \tag{6.26}$$

From (6.18) we see that for p *odd*,

$$\delta_p = p\delta_{p-1}\,. \tag{6.27}$$

Setting $\delta_0 = 1$, we have $\delta_1 = 1$, $\delta_2 = \frac{1}{2}$, $\delta_3 = \frac{3}{2}$, $\delta_4 = \frac{3}{8}$ in agreement with (6.22), (6.24), and (6.25). We draw the most important of the above results together in another theorem.

Theorem 6.3. The p eigenvalues, λ_i^p, of a system of N fermions are bounded by $\binom{N}{p}^{-1}Q_p(N)$, where $Q_p(N)$ is a polynomial in N of degree $[p/2]$ with leading coefficient δ_p given by

$$\delta_p = \tfrac{1}{2}\cdot\tfrac{3}{4}\cdot\tfrac{5}{6}\cdots\frac{p-1}{p} \tag{6.28}$$

for *even* p, and by

$$\delta_p = p\delta_{p-1} \tag{6.29}$$

for *odd* p.

Because of different normalization for D^p, Yang's β_p is related to our δ_p by

$$\beta_p = p!\delta_p\,. \tag{6.30}$$

In the preprint alluded to above, Yang has conjectured that the maximum of λ_i^p is attained for pure states of the extreme type defined in the next section and on this basis has proposed a value for the best possible $p!\Lambda^p(N)$. In any case, $p!\Lambda^p(N)$ cannot be less than the value proposed by Yang nor greater than the solution $p!g(p,N)$ of (6.13).

7. Best Possible Bounds for the Second-Order Eigenvalues

In this section we define wave functions of *extreme type* and use them to show that (6.23) gives the best possible upper bound for λ_1^2. This result is important and surprising. The example of $\Lambda^3(5)$ showed that, in general, $g(p,N)$ of Sec. 6 is not the best possible bound for $\Lambda^p(N)$ and it is, therefore, of interest that an argument, which involved neglecting the negative terms in (6.4), yet gives the best possible bound in the case $p = 2$. Furthermore, seemingly cogent arguments guided by physical intuition based on a one-particle picture can be advanced to suggest that the upper bound for λ_1^2 is the reciprocal of $\binom{N}{2}$. Indeed, this was a widespread conjecture for which Bopp[3] published an alleged proof. However, near the end of his argument Bopp assumes, incorrectly, that his basis set is orthonormal. The correct result for $N = 4$ was known to the author in 1958, but, as far as he is aware, the general case for arbitrary N was first decided by Sasaki.[17] The case of N even was treated independently by Yang.[18]

Since the energy of a classical quantum mechanical system involving two-particle interaction can be expressed exactly in terms of the 2 matrix, *any* information about the 2 matrix will, almost certainly, be important. In fact, as we show in the next section, (6.23) leads directly to a lower bound on the energy of the ground state of a fermion system. Further, the wave functions of the BCS theory are of the type defined in (7.1).

In order to avoid useless proliferation of indices we adopt the following notation *throughout this section:* g denotes a *normalized geminal* which at point (x_1,x_2) assumes the value $g(12)$; gg and $(23)gg$ denote functions of four particles which at (x_1,x_2,x_3,x_4) assume, respectively, the values $g(12)g(34)$ and $g(13)g(24)$; f is a *normalized orbital* strongly orthogonal to g, that is, $\int \bar{f}(1)g(12)d\mu(1) = 0$ for all x_2; for *even* N, g^N is a normalized function of N particles proportional to the antisymmetrized product of $N/2$ equal factors g; for *odd* N, f^N is a normalized function of N particles proportional to the antisymmetrized product of f and $(N-1)/2$ equal factors g. Thus, for N *even*

$$g^N(1,2\cdots N) = c_N A_N[g(12)g(34)\cdots g(N-1,N)]\,, \tag{7.1}$$

where c_N is a normalization factor which, without loss of generality, we assume to be real and positive.

Further, for N *odd*

$$f^N(1,2\cdots N) = d_N A_N[f(1)g(23)\cdots g(N-1,N)]\,, \tag{7.2}$$

where again we assume the normalization factor d_N is real and positive.

The functions g^N and f^N are of *extreme type* if the 1 eigenvalues of g are equal and if f is strongly orthogonal to g. The latter condition implies that g, and g^N, have finite rank, r, equal to the reciprocal of a 1 eigenvalue of g, and that the rank of f^N is $r+1$. Note that, for N even, $r \geqslant N$, otherwise g^N would be identically zero.

Our next theorem generalizes Corollary 4.3C.

Theorem 7.1. If N is *even*,

$$A_N[g(12)g^{N-2}(3,4\cdots N)] = A_{N-1}[g(12)g^{N-2}(3\cdots N)]\,, \tag{7.3}$$

where A_{N-1} is the antisymmetrizing projector on $2,3\cdots N$. Further,

$$\langle gg^{N-2}|A_N gg^{N-2}\rangle = \frac{1}{N-1}[1-(N-2)a_N]\,, \tag{7.4}$$

where

$$a_N = \mathrm{tr}\,[D^1(g)D^1(g^{N-2})]\,. \tag{7.5}$$

Proof. By (7.1)

$$\begin{aligned} A_N[g(12)g^{N-2}(3\cdots N)] &= c_{N-2}A_N[g(12)A_{N-2}g(34)\cdots \\ &\quad \times g(N-1,N)] \\ &= c_{N-2}A_N[g(12)g(34)\cdots \\ &\quad \times g(N-1,N)] \end{aligned} \tag{7.6}$$

by (4.2). If $N = 2m$, the expression $g(12)\cdots g(N-1,N)$ is left unchanged, except for sign, by $2^m m!$ elements of S_N. Thus, in the expansion of the right-hand side of (7.6) there are $(2m)!2^{-m}(m!)^{-1} = 1.3.5\cdots(2m-1)$ distinct terms. On the other hand, any term in $A_{N-1}[g(12)\cdots g(N-1,N)]$ occurs in (7.6), and this also contains $(2m-1)!2^{-(m-1)} \times ((m-1)!)^{-1} = 1.3.5\cdots(2m-1)$ terms since S_{N-1} contains a subgroup of order $2^{m-1}(m-1)!$ which leaves each term unchanged apart from sign. Checking the coefficient of the leading term we see that

$$\begin{aligned} A_N[g(12)\cdots g(N-1,N)] &= A_{N-1}[g(12)\cdots \\ &\quad \times g(N-1,N)] \end{aligned} \tag{7.7}$$

$$\begin{aligned} \therefore A_N[gg^{N-2}] &= c_{N-2}A_{N-1}[g(12)g(34)\cdots g(N-1,N)], \\ &= c_{N-2}A_{N-1}\{g(12)A_{N-2}[g(34)\cdots \\ &\quad \times g(N-1,N)]\}\,, \\ &= A_{N-1}[gg^{N-2}]\,. \end{aligned}$$

Thus, (7.3) is proved and (7.4) follows immediately by the same argument as Corollary 4.3C.

Corollary 7.1A. For *even* N and Ψ, a normalized function of the form $cA_N[gg^{N-2}] = g^N$

$$\frac{1}{N-1}[1-(n-2)a_N] \leq \lambda_1^2 < \frac{1}{N-1}\,. \tag{7.8}$$

Proof. The second inequality is an immediate consequence of (4.6), (4.7) and the observation that a_N cannot be zero since g^{N-2} may be expanded in terms of the natural orbitals of g.

From the proof of Theorems 3.1 and 4.3, we have

$$\lambda_1^2 = \max |\langle\Psi|\alpha^2\alpha^{N-2}\rangle|^2\,,$$

where α^2 and α^{N-2} are arbitrary normalized functions. Therefore,

$$\begin{aligned} \lambda_1^2 &\geq |\langle\Psi|gg^{N-2}\rangle|^2\,, \\ &\geq |c|^2|\langle A_N gg^{N-2}|gg^{N-2}\rangle|^2\,, \\ &\geq \langle A_N gg^{N-2}|gg^{N-2}\rangle\,, \end{aligned}$$

since c is a normalization constant. The first inequality in (7.8) follows from (7.4).

Corollary 7.1B. If N is even $(N-1)^{-1}$ is the best possible upper bound for λ_1^2.

Proof. From (6.9) and (7.5) it follows that

$$a_N \leq \min\,(\alpha^1,\beta^1)\,,$$

where α^1 and β^1 are the greatest eigenvalues of $D^1(g)$ and $D^1(g^{N-2})$, respectively. Thus, if we take for g a function of rank r with equal 1 eigenvalues, r^{-1}, we have $a_N \leq r^{-1}$ and

$$1-(N-2)a_N \geq (r-N+2)/r\,.$$

For sufficiently large r, (7.8) implies that λ_1^2 is arbitrarily close to $(N-1)^{-1}$.

It can be shown that for even N, the natural orbitals of g^N are the same as those of g, and that the 1 eigenvalues of g^N are a function of the corresponding 1 eigenvalue of g. The proof of these and related results will be published elsewhere. It may also be shown that a_N is a minimum for g of extreme type (among g of the same rank) and that in this case the first inequality of (7.8) becomes an equality so that $\lambda_1^2 = (N-1)^{-1}(r-N+2)r^{-1}$, as was proved by Yang.

We turn now to the case of *odd* N. Using Theorem 6.1 with $p=1$, $q=N-1$

$$\begin{aligned} \langle fg\cdots g|A_N fg\cdots g\rangle &= \frac{1}{N}\langle fg\cdots g|A_{N-1}[1-(N-1) \\ &\quad \times (12)]A_{N-1}fg\cdots g\rangle\,, \\ &= \frac{1}{N}\langle fg\cdots g|A_{N-1}fg\cdots g\rangle\,, \end{aligned}$$

since f is strongly orthogonal to g. Using (7.1), (7.2), and the idempotency of A_N and A_{N-1} we have

$$1 = \frac{1}{N} d_N^2 \langle fg\cdots g | f A_{N-1} g\cdots g\rangle ,$$

$$= \frac{1}{N} d_N^2 \langle A_{N-1} g\cdots g | A_{N-1} g\cdots g\rangle = \frac{1}{N}\frac{d_N^2}{c_{N-1}^2} ,$$

$$\therefore d_N^2 = N c_{N-1}^2 . \tag{7.9}$$

Furthermore,

$$\langle A_N g f^{N-2} | g f^{N-2}\rangle = d_{N-2}^2 \langle A_N f g\cdots g | A_N f g\cdots g\rangle ,$$

$$= \frac{d_{N-2}^2}{N}\frac{1}{c_{N-1}^2} = \frac{N-2}{N}\frac{c_{N-3}^2}{c_{N-1}^2} \tag{7.10}$$

by (7.9). However, by (7.4) for *even* N,

$$\frac{1}{N-1}[1 - (N-2)a_N] = c_{N-2}^2 \langle A_N g\cdots g | A_N g\cdots g\rangle$$

$$= \frac{c_{N-2}^2}{c_N^2} . \tag{7.11}$$

Thus, for *odd* N, (7.10) and (7.11) imply

$$\langle A_N g f^{N-2} | g f^{N-2}\rangle = (1/N)[1 - (N-3)a_{N-1}] . \tag{7.12}$$

By the same argument as for Corollary 7.1A and 7.1B we may prove a

Corollary 7.1*C*. For *odd* $N > 1$ if Ψ is of type f^N of (7.2), then

$$(1/N)[1 - (N-3)a_{N-1}] \leq \lambda_1^2 \leq (1/N) \tag{7.13}$$

and, hence, N^{-1} is the best possible upper bound for λ_1^2.

For Ψ of extreme type with g of rank r, $a_{N-1} = r^{-1}$ and the lower bound for λ_1^2 in (7.13) becomes

$$\frac{1}{N}\frac{r-N+3}{r} . \tag{7.14}$$

8. Ground-State Energy

Though we have criticized Bopp's article,[3] in fact, it is both important and ingenious. The gist of Bopp's argument is reproduced in ter Haar's review[7] and we shall be guided by it to obtain a lower bound for the ground state of any system of fermions.

When the Hamiltonian of a system of N indistinguishable fermions involves only one- and two-particle interactions so that

$$H = \sum_i H_1(i) + \sum_{i<j} H_2(ij) , \tag{8.1}$$

it is possible to greatly simplify the calculation of the energy of the system for the pure state Ψ. By the well-known simple calculation, the energy E may be expressed as

$$E = (N/2)\ \mathrm{tr}\,[K\sigma] , \tag{8.2}$$

where $\sigma = D^2$ and

$$K = H_1(1) + H_1(2) + (N-1)H_2(12) . \tag{8.3}$$

In particular, for N electrons in an atom of nuclear charge Z,

$$K = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{N-1}{r_{12}} \tag{8.4}$$

for a common approximation which neglects spin.

The advantage of (8.2) is that it does not involve the N-particle wave function but only the 2 matrix $\sigma(12;1'2')$, it is exact, and unlike approximations to the energy in terms of the 1 matrix, it is *linear* in the density matrix and occupation numbers. One could, therefore, hope to obtain the ground-state energy of an N-particle system merely by choosing σ to minimize (8.2). It was while he enjoyed the hospitality of the Summer Research Institute of the Canadian Mathematical Congress in 1951 that this possibility first occurred to the present author. He proceeded to calculate the energy of the ground state of Li and was somewhat surprised to obtain a value about 30% *too low!* This shook his naive and unexamined faith in Ritz and Rayleigh but aroused his interest. In that first attempt σ had been varied over too large a class of functions. The restriction to N-representable σ had not been imposed. If the N-representability problem can be solved for the 2 matrix, the way will be open for the direct application of (8.2). In the next section a restricted class of N-representable σ will be described with the help of which, together with (8.2), it should be possible to obtain moderately good upper bounds for the ground state of N-fermion systems.

However, it is possible to use (8.2) to obtain a lower bound, without having solved the N representability problem completely, by merely employing the bound (6.23) on λ_1^2. Let $\varphi_i(12)$ be an eigenfunction of K with eigenvalue ϵ_i so that $K\varphi_i = \epsilon_i\varphi_i$, and suppose that $\{\varphi_i\}$ form a complete orthonormal set of two-particle functions, so that we may find complex numbers $s_{ij} = \bar{s}_{ji}$ such that

$$\sigma(12;1'2') = \sum_{i,j} s_{ij}\varphi_i(12)\bar{\varphi}_j(1'2') . \tag{8.5}$$

Substituting this in (8.2) gives *Bopp's formula*

$$E = (N/2)\sum s_{ii}\epsilon_i \tag{8.6}$$

Since σ is a positive operator of unit trace

$$s_{ii} = \langle\varphi_i|\sigma\varphi_i\rangle \geq 0 ,$$

and $\sum s_{ii} = 1$.

From the extremal properties of the natural geminals

$$s_{ii} \leq \lambda_1^2 . \tag{8.7}$$

It follows that for N *even*, $s_{ii} \leq (N-1)^{-1}$; for N *odd*, $s_{ii} \leq N^{-1}$. We may, therefore, conclude that for the ground state ($E < 0$) if N is *even*

$$E > \frac{N}{2} \frac{1}{N-1} \sum_1^{N-1} \epsilon_i , \tag{8.8}$$

and for N *odd*

$$E > \frac{N}{2} \frac{1}{N} \sum_1^{N} \epsilon_i = \frac{1}{2} \sum_1^{N} \epsilon_i , \tag{8.9}$$

where the summations are over the lowest eigenvalues of K. The bound (8.8) was announced in 1958 to the Physics Colloquium of the University of Toronto and is similar to the result obtained independently by Bopp except for the factor and range of summation. However, Bopp goes a step farther and notices that by a change of the unit of length (8.4) may be transformed into the Hamiltonian for a two-electron atom with charge $Z/(N-1)$. Thus, for Be^+, $Z/(N-1) = 2$ and ϵ_i can be obtained from the spectrum of He. In this particular case of $N = 3$. his factor $N(N-1)/2$ and our factor N coincide so the bounds given by Bopp and (8.9) are identical, Because of the inaccuracy involved in substituting $1/3$ for s_{11}, s_{22}, and s_{33} and neglecting all higher terms, one would expect a very poor approximation. It is astonishing that for Be^+, the bound is within 1% of the actual value, and almost incredible that for O^{5+} with $Z = 8$, $N = 3$ the bound is low by less than 3 parts in 14,107. These results suggest that it would be of considerable interest to expand the known wave functions of Be^+ in terms of natural geminals to decide how close they are to functions of extreme type.

Bopp's method of evaluating (8.8) and (8.9) has the advantage that it uses atoms as calculating machines, but it is restricted in application to cases for which $Z/(N-1)$ happens to be an integer. It is possible to eliminate this restriction by dividing K of (8.4) by Z^2 and replacing Zr_1 by r_1, etc., so that

$$E = (NZ^2/2) \text{ tr } (\tilde{K}\sigma) , \tag{8.10}$$

where

$$\tilde{K} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\gamma}{r_{12}}, \tag{8.11}$$

with

$$\gamma = (N-1)/Z .$$

Calculations by Hylleraas and Mitdal and by Sharma and Coulson for the lowest energies of two-electron systems as functions of Z may be used to obtain the lowest eigenvalue of $\tilde{K}$ as functions of γ. For a neutral atom with large N, γ is less than but close to 1, so that $\tilde{K}$ approximates the Hamiltonian of H^- which apparently has only one bound state. On the other hand a theorem[19] of Zhislin asserts that for $\gamma < 1$, $\tilde{K}$ has an infinite number of bound states with energies below the dissociation energy. Thus, for N large there is apparently a *gap* between the one lowest eigenvalue of (8.11) and the eigenvalues of an infinity of bound states close to the dissociation energy. Zhislin's theorem shows that there is a similar "gap" associated with the K appropriate to a neutral lattice, so that it is an obvious temptation to relate this energy gap to the famous energy gap in the theory of superconductors.

PART III—N REPRESENTABILITY

In Part III we make a direct attack on the problem of N representability of the one- or two-particle density matrix which may be viewed in two aspects, according to whether the matrix is derivable from a pure N state or from a statistical ensemble of pure N states. Since the latter matrices form a convex set (cf., Sec. 2) we search for its extreme elements. In Theorem 9.1 and 9.3 we provide a complete and simple characterization of 1 matrices representable by ensembles of N particle states. Theorem 9.3 provides the proof of a conjecture made by L. H. Thomas at the Hylleraas Symposium. Theorem 9.4, which was discovered since the Symposium, states that, for N *even*, wave functions of the extreme type defined in Sec. 7 give rise to 2 matrices which are extreme points of the convex set $\mathcal{P}_N^2$. Theorem 9.4 seems to bring us close to the solution of the N-representability problem for the 2 matrix and provides us with a large class of suitable σ which, when used in Eq. (8.2), should lead to extremely good upper bounds for the energy of the ground state of a fermion system.

9. Ensemble Matrices

We recall that, in Sec. 2, $\mathcal{P}^p$ was defined as the set of all *positive Hermitian* operators of *unit trace* on the Hilbert space of p-particle functions, and $\mathcal{P}_N^p$ as the subset of elements of $\mathcal{P}^p$ which are ensemble N representable.

Theorem 9.1. An extreme element, μ, of the convex set $\mathcal{P}_N^1$ is representable by a single Slater determinant which is uniquely determined by μ except for phase.

Proof. The 1 matrix of a single Slater determinant is of rank N and, as follows from Corollary 4.3A, has eigenvalues all equal to N^{-1}. Suppose that

$$\mu(1;1') = (1/N)[\varphi_1(1)\bar{\varphi}_1(1') + \cdots + \varphi_N(1)\bar{\varphi}_N(1')] . \tag{9.1}$$

[19] G. M. Zhislin, Tr. Mosk. Mat. Obšč. 9, 81 (1960), Theorem III, p. 84.

A direct calculation shows that μ is Ψ representable with

$$\Psi = (N!)^{-\frac{1}{2}}[\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)] , \qquad (9.2)$$

where $[\varphi_1(1)\cdots\varphi_N(N)]$ is the Slater determinant formed from the orthonormal set $\varphi_i(1)$. The expression in square brackets in (9.1) is the Dirac density matrix $\rho(1;1')$ which is idempotent, Hermitian, and of tr N. Regarded as an operator, ρ is the projector in the 1-particle Hilbert space onto the N-dimensional subspace spanned by $\{\varphi_i\}$. By Theorem 3.2, if μ is Ψ representable, then Ψ may be expanded in terms of the eigenfunctions φ_i of μ. Apart from phase, there is only one normalized antisymmetric function of N variables which can be expressed in terms of the N functions φ_i. Equation (9.2) defines such a function.

We next note that the dimension of the range of the sum of two positive Hermitian operators A and B which act on a finite dimensional space is equal to the dimension of the *union* of their ranges. For we may choose eigenvectors f_i and g_j of A and B, respectively, which span their ranges such that $Af_i = \alpha_i f_i$, $Bg_j = \beta_j g_j$ with $\alpha_i > 0$, $\beta_j > 0$, $1 \leq i \leq r_1$, $1 \leq j \leq r_2$. Suppose f is any linear combination of the f_i and g_j, then $(A + B)f = 0$ implies that $Af = -Bf$ and, therefore, that $\langle f|Af\rangle = -\langle f|Bf\rangle$ which is possible only if $Af = 0$ and $Bf = 0$ since A and B are positive. Thus, the dimension of the range of $A + B$ is equal to the dimension of the set spanned by such f, namely, the dimension of the linear space spanned by all the f_i and g_j.

We may now easily see that *any μ of the form* (9.1) *is extreme in* $\mathcal{P}_N^1$. If not then

$$\mu = \alpha\mu_1 + \beta\mu_2 , \qquad (9.3)$$

where $\alpha > 0$, $\beta > 0$, $\alpha + \beta = 1$ and μ_1 and μ_2 are N representable. By Corollary 4.3A the rank of each of μ_1 and μ_2 is at least N, therefore, the rank of the right-hand side of (9.3) is greater than N unless the natural orbitals of μ_1 span the same space, of dimension N, as the natural orbitals of μ_2. In the latter case $\mu_1 = \mu_2 = \mu$, by the first paragraph above.

To prove the theorem we must show that every extreme element of $\mathcal{P}_N^1$ is of the form (9.1). This we do by proving that any $\mu \in \mathcal{P}_N^1$ is a weighted mean of μ of the form (9.1).

Suppose μ is Ψ representable where Ψ is a pure N state. By Theorem 3.2,

$$\Psi = \sum c_K[K] , \qquad (9.4)$$

where $[K]$ is a normalized Slater determinant, and K runs through some appropriate set of indices. We form $D^1(\Psi)$ according to (2.1). Since the $[K]$ were expressed in terms of natural orbitals of Ψ, all cross terms disappear in (2.1) and we find

$$\mu(1;1') = \sum_i [\sum_K |c_K|^2]\alpha_i^1(1)\bar{\alpha}_i^1(1') \qquad (9.5)$$

where for each i the inner summation on K is on those K such that φ_i occurs in $[K]$. It is apparent that

$$\mu = \sum_K |c_K|^2 \rho_K , \qquad (9.6)$$

where

$$\rho_K = ND^1([K]) .$$

The proof of Theorem 9.1 is thus complete and we may deduce

Corollary 9.1A. The set of ensemble N-representable 1 matrices is the convex set containing all 1 matrices of Dirac type (9.1).

The $\rho = N\mu$ in (9.1) is completely determined by the N-dimensional space spanned by $\varphi_1, \varphi_2, \cdots\varphi_N$. Thus, if we work in a space $\mathfrak{G}$ spanned by a basis set of dimension M, there is an extreme 1 matrix associated with *each* N-dimensional *subspace* of $\mathfrak{G}$. The set of such subspaces may be put into 1:1 correspondence with the points of a so-called Grassman variety[20] in a space of dimension $\binom{M}{N}$. We, thus, have

Corollary 9.1B. The extreme elements of $\mathcal{P}_N^1$ may be indexed by the points of a Grassman variety.

We next prove a conjecture of L. H. Thomas which will lead to a more practical characterization of $\mathcal{P}_N^1$ than that given by Theorem 9.1. Let $\mathfrak{L}$ consist of all vectors $v = (v_1, v_2, v_3, \cdots)$ in a space of arbitrary but fixed dimension with $1 \geq v_i \geq 0$ and $\sum v_1 = N$. The v_i are real numbers.

Theorem 9.2. The set $\mathfrak{L}$ is convex and its extreme points are the vectors with N components equal to 1 and all others equal to zero.

Proof. The proof that $\mathfrak{L}$ is convex is obvious.

By the condition on the vectors in $\mathfrak{L}$, each has at least N positive components. Thus, a mean of any two has more than N components unless the nonzero components of the original vectors were the same and equal to 1. Thus, the vectors with N components equal to 1, are extreme.

No other vector in $\mathfrak{L}$ is extreme. Suppose $\mathbf{v} \in \mathfrak{L}$ and that $\mathbf{v}$ is not of the above type and, therefore, has at least $N + 1$ positive components which, without loss of generality, we assume to include $v_1, v_2, \cdots v_{N+1}$ with $v_1 \geq v_2 \geq \cdots \geq v_{N+1}$. Let $\mathbf{u} = (1,1\cdots1,0,0\cdots)$ have its first N components equal to 1, the others must be zero.

Since $v_{N+1} < 1$ it is possible to choose $\epsilon > 0$ so that

[20] W. E. Jenner, *Rudiments of Algebraic Geometry* (Oxford University Press, Oxford, 1963), Chap. VI.

$v_{N+1} < 1 - \epsilon$ and also so that $0 < \epsilon < v_N$. With any such ϵ we define $\mathbf{w}$ by means of the equation

$$\mathbf{v} = \epsilon\mathbf{u} + (1 - \epsilon)\mathbf{w} . \tag{9.7}$$

For $1 \leq i \leq N$, $w_i = (v_i - \epsilon)/(1 - \epsilon)$. Clearly $0 \leq w_i \leq 1$. For $N < i$, $w_i = v_i/(1 - \epsilon) < 1$. We easily verify that $\sum w_i = N$. Thus, $\mathbf{w} \in \mathfrak{L}$ and by means of (9.7) $\mathbf{v}$ is expressed as a mean of $\mathbf{u}$ and $\mathbf{w} \in \mathfrak{L}$. Hence, $\mathbf{v}$ is not extreme.

By the *Thomas space*, we designate the set, $\mathfrak{I}_N$, of elements of $\mathcal{P}^1$ with eigenvalues less than or equal to N^{-1}. Thus, for $\mu \in \mathfrak{I}_N$, $\mu = \sum \alpha^i P_i$ where $0 \leq N\alpha^i \leq 1$. Hence, $\mu - N\mu^2 = \sum \alpha^i(1 - N\alpha^i)P_i$ and, therefore, $\mu - N\mu^2$ is a positive operator. An immediate consequence of Theorems 9.1 and 9.2 is

Theorem 9.3. $\mathcal{P}^1_N = \mathfrak{I}_N$ and, therefore, $\mathcal{P}^1_N$ consists of those operators $\mu \in \mathcal{P}^1$ such that $\mu - N\mu^2$ is positive.

The importance of this theorem is difficult to exaggerate. It means that the conditions on the 1 matrix, sometimes referred to as the Pauli conditions, are not only necessary, but also sufficient for a given 1 matrix to be N representable by a pure state or a mixture of pure states. It justifies many past procedures in the statistical mechanics of fermion systems and helps explain their success. Theorem 9.3 is the answer to a question first posed to the author by Löwdin at the Sanibel Conference in 1962.

As was remarked in Sec. 2, the preimages in $\mathcal{P}^N$ of the extreme elements of $\mathcal{P}^1_N$ are pure states. Theorem 9.1 shows that it is *not* true, conversely, that the images in $\mathcal{P}^1_N$ of pure states are extreme. An interesting unsolved problem which we discuss briefly in the next section is to characterize those matrices in $\mathcal{P}^1_N$ which derive from pure states.

In the Hartree–Fock case for which Ψ is a single Slater determinant, μ is of the form (9.1) and

$$\sigma(12;1'2') = \beta[\mu(1;1')\mu(2;2') - \mu(1;2')\mu(2;1')] , \tag{9.8}$$

where $\beta = N(N - 1)^{-1}$. In the general case, it would seem to be worth attempting to approximate σ by (9.8) subjecting μ only to the condition that it lies in Thomas space and choosing β so that the trace of σ is unity. A more elaborate suggestion along these lines will be found in the author's Uppsala report,[5] (Theorem 12).

Will arguments similar to those above throw light on the N representability of the 2 matrices? We easily see that $D^2(\Psi)$ for Ψ a single Slater determinant $[1,2\cdots N]$ has the form

$$\sigma = \frac{2}{N(N-1)} \sum_{i<j} [ij][\bar{i}\bar{j}] , \tag{9.9}$$

where $[ij]$ is a normalized two-particle Slater determinant. Since this gives rise to a 1 matrix of form (9.1) which has a unique preimage in $\mathcal{P}^N$, we easily see that (9.9) is extreme in $\mathcal{P}^2_N$. However, there must be other extreme elements, because weighted means of operators of the type (9.9) could never have eigenvalues greater than $2/N(N - 1)$ which do occur for $N > 3$ according to Corollaries 7.1B and 7.1C.

Since the set $\mathcal{R}_N$ of elements of $\mathcal{P}^2$ with eigenvalues less than N^{-1} is convex, it is natural to conjecture that $\mathcal{R}_N$ coincides with $\mathcal{P}^2_N$ for N odd and also with $\mathcal{P}^2_{N+1}$. While the discussion of Sec. 5 showed that it would be possible to characterize $\mathcal{P}^1_N$ merely by conditions on the eigenvalues of its elements, this is rather too much to expect for $\mathcal{P}^2_N$. Indeed, the following counterexample disposes of the above conjecture.

Let P_{ij} denote the projector on the space spanned by the single Slater determinant $[ij]$, then $(N + 1)^{-1} \times [P_{12} + P_{13} + \cdots + P_{1N} + P_{23} + P_{24}]$ belongs to $\mathcal{R}_N$, but it has an image in $\mathcal{P}^1$ whose largest eigenvalue is $(N - 1)/(N + 1)$ which is impossible, by Corollary 4.3A, if $N > 2$.

However, combining the results of Sec. 7 with the second paragraph in the proof of Theorem 9.1, we can prove

Theorem 9.4. The $D^2(\Psi)$ obtained from Ψ of extreme type are extreme elements of the convex set $\mathcal{P}^2_N$.

Proof. Recall that Ψ of extreme type were defined by (7.1) and (7.2) with g such that $D^1(g)$ has finite rank, r, and equal eigenvalues $\lambda^1_i = r^{-1}$. The corresponding 2-matrix $D^2(\Psi)$ has an eigenvalue λ^2_1 equal to the maximum possible for any Ψ of rank r. $D^2(\Psi)$ must be extreme. For if not, it is a weighted mean of N representable 2 matrices of lesser or equal rank. The maximum eigenvalue of a 2 matrix of lesser rank is strictly less that λ^2_1 by Sec. 7, and, therefore, weighted means of such matrices could not have eigenvalue λ^2_1. On the other hand, any matrix of the same rank spanned by the same set of orbitals as $D^2(\Psi)$ which is to contribute towards the eigenfunction g with eigenvalue λ^2_1, must have the same function g with the same eigenvalue and must, therefore, result from the extreme Ψ of (7.1) in the case N *even* or from (7.2) in case N is *odd*. This proves the theorem.

Setting $r = N$ for N *even* in (7.8), or $r = N - 1$ for N *odd* in (7.14), gives the eigenvalue $2/N(N - 1)$ and we obtain another proof that σ of (9.9) is extreme.

Theorem 9.4 provides us with a very large class of extreme elements of $\mathcal{P}^2_N$. Any weighted mean of these extreme elements would, when substituted for σ in (8.2), give an upper bound on the ground-state energy. For a fixed basis set of r linearly independent

φ_i we may choose g of extreme type in a continuous infinity of ways. Since r is arbitrary we have an innumerable number of classes each containing a continuous infinity of extreme elements of $\mathcal{P}_N^2$. This seems almost enough! If we have found all the extreme elements then (certainly if we restrict ourselves to D^2 of finite rank) $\mathcal{P}_N^2$ could be characterized as the convex set containing the extreme elements described in Theorem 9.4. It is an open conjecture that Theorem 9.4 does indeed describe *all* the extreme elements of $\mathcal{P}_N^2$.

10. Representability by Pure States

A pure state is on the frontier of the space $\mathcal{P}^N$. Because of the linear nature of the transition (2.1) from D^N to D^p; the images of pure states will be on the frontier of $\mathcal{P}_N^p$. Can they be characterized in a more precise manner? In this section we state a few of the more important results obtained in this connection for the 1 matrix. For proofs, the interested reader is referred to Secs. 6 and 8 of our Uppsala Report.[5]

Throughout this section, N *representability* refers to representability by means of a pure state and μ is an arbitrary member of $\mathcal{P}^1$.

Theorem 10.1. μ is N representable if each of its eigenvalues has multiplicity divisible by N.

Theorem 10.2. μ is 2 representable if, and only if, all its eigenvalues have even multiplicity.

Theorem 10.3. If μ is N representable, its rank $r \neq N + 1$.

Theorem 10.4. If the rank of μ is $N + 2$ it is N representable if, and only if, (i) *for N odd,* $\lambda_1^1 = N^{-1}$ and the remaining eigenvalues are evenly degenerate and less than N^{-1}; (ii) *for N even,* its eigenvalues have even multiplicity and are less than N^{-1}.

Theorem 10.5. If μ is N representable and its first m eigenvalues equal N^{-1}, then there is an orthonormal set $\varphi_1, \varphi_2, \cdots \varphi_m$ such that $\mu(1;1') = N^{-1} \sum_1^m \varphi_i(1)\bar{\varphi}_i(1') + \mu_1(1;1')$, where μ_1 is $(n - m)$ representable by means of a function which is strongly orthogonal to all φ_i.

Theorem 10.6. μ is N representable by Ψ if, and only if, it may be expressed in the form

$$\mu = \lambda_1^1 \alpha^1 \bar{\alpha}^1 + (N - 1)\lambda_1^1 \mu_1 + (1 - N\lambda_1^1)\mu_2 ,$$

where α^1 is a natural orbital of Ψ, μ_1 is $(N - 1)$ representable by α^{N-1} the corresponding $(N - 1)$ natural state of Ψ, and μ_2 is N representable by a function which is strongly orthogonal to α^1 and α^{N-1}.

This theorem settles the question of N representability of 1 matrices, *in principle,* by a double induction on N and the rank. The proof given in the Uppsala Report can be greatly simplified by using the notation of second quantization. If, in that notation, the a_i refer to natural orbitals, Theorem 10.6 is a consequence of the obvious fact that Ψ may be expressed as

$$\Psi = a_1^\dagger a_1 \Psi + \varphi$$

where $a_1\varphi = 0$. The $(N - 1)$ function $a_1\Psi$ plays the role of α^{N-1} above.

The final two theorems are rather tantalizing, suggesting as they do, that the theory of graphs might play a decisive role in characterizing N-representability. We shall say that two natural orbitals α_i^1 and α_j^1 are *connected* if they occur in the same Slater determinant in the expansion of Ψ in terms of natural orbitals. This condition, in the notation of second quantization is $a_i a_j \Psi \neq 0$.

Theorem 10.7.

$$\sum (\lambda_i^1)^{\frac{1}{2}} \geq (N - 1)(\lambda_j^1)^{\frac{1}{2}} ,$$

where the summation is on all i connected with j, and where equality obtains if, and only if, α_j^1 belongs to an isolated set of N mutually connected natural orbitals (all are elements of one Slater determinant and occur in no other).

Theorem 10.8. If $\lambda_i^1 + \lambda_j^1 > N^{-1}$ then α_i^1 and α_j^1 are connected.

11. Concluding Remarks

Have we succeeded in eliminating the wave function from quantum mechanics? Not quite! However, Sec. 9 has almost made it unnecessary for the calculation of the energy of the ground state of fermion systems. The final step towards this desirable goal will probably be taken when the conjecture at the end of Sec. 9 has been decided. Even if the conjecjecture is incorrect there is a good chance that it cannot be settled without providing us sufficient insight to obtain all the extreme elements of $\mathcal{P}_N^2$.

Since wave functions of type g^N play a crucial role in the BCS theory of superconductors it would seem that a necessary development in solid-state physics is for us to develop facility in thinking in terms of geminals rather than orbitals as in the past. The exactness of Eq. (8.2) might further suggest, as a fundamental tool in analyzing the states of solids, the graph of λ_i^2 against ϵ_i since λ_i^2 can be interpreted as the occupancy number of the corresponding geminal.

It is clear that we have raised many new problems for chemists, physicists, and mathematicians. There is the problem of developing proper numerical techniques for the effective use of Sec. 9 in the formula (8.2). It would be of interest to analyze known wave

functions in terms of natural orbitals and natural geminals. Can the unitary invariants of σ be used to develop a rational theory of bonding? of off-diagonal long range orders? Algebraic geometry may throw some light on the set of extreme points of $\mathcal{P}_N^p$, as may graph theory. A deeper understanding of $\mathcal{P}_N^p$ for $p > 2$ will be of value for any physical situation which requires more than two-body interactions for its analysis.

Note added in proof. (a) H. W. Kuhn in his paper "Linear Inequalities and the Pauli Principle," *Proceedings of Symposia in Applied Mathematics* (American Mathematical Society, Providence, Rhode Island, 1960) Vol. X, Combinatorial Analysis, pp. 141–147, proved Theorem 9.2 by a considerably more elegant method. (b) T. Ando, in a private communication [see also following paper, p. 690], has pointed out that in the statement of Theorem 10.4 (ii) the phrase "are less than" should read "are less than or equal to." (c) Dr. Kummer of the Institute for Physical Chemistry, Zurich remarked in private conversation that the conjecture at the end of Sec. 9 is false for $N = 2$. The author subsequently proved that $D^2(\mathrm{A}_3(fg))$ are extreme in $\mathcal{P}_N^2$ for all g strongly orthogonal to f. However, it appears from (7.14) that $N = 3$ is somewhat peculiar, and he still maintains the conjecture for N greater than 3. (d) In view of the role of g^N in the relatively successful BCS theory, and of Yang's proof[18] that large λ_1^2 implies magnetic flux quantization, it would appear that the first inequality of (7.8) gives us a criterion for the onset of the correlated superconducting state.

Discussion on "Structure of Fermion Density Matrices" by A. J. Coleman

LÖWDIN: In connection with Professor Coleman's talk, I would like to repeat a comment which I made to him at the winter institute one year ago. Irrespective of the normalization, the expectation value of the Hamiltonian $H = H_0 + \sum_i H_i + \sum_{i<j} H_{ij}$ can be written in the form [Cf. P. O. Löwdin, Phys. Rev. **97**, 1474 (1955), particularly p. 1477; *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 207; particularly p. 319]

$$\langle H_{\mathrm{op}} \rangle_{\mathrm{av}} = \frac{\int \left\{ H_0 + NH_1 + \binom{N}{2} H_{12} \right\} \Gamma(x_1 x_1 | x_1' x_2') dx_1 dx_2}{\int \Gamma(x_1 x_2 | x_1 x_2) dx_1 dx_2},$$

i.e., it can be defined in terms of the second-order density matrix. Here it is convenient to characterize every function $\Gamma(x_1 x_2 \cdots x_p | x_1' x_2' \cdots x_p')$ which is Hermitian, positive definite and of finite trace as a Fermion "density matrix."

Some of the first calculations using a variation of the density matrix were carried out by Mayer [Cf. J. E. Mayer, Phys. Rev. **100**, 1579 (1955)], but his restrictions on Γ have been considered too weak [Cf. R. H. Tredgold, Phys. Rev. **105**, 1421 (1957)].

Professor Coleman has focused the attention on the conditions such a matrix has to fulfill to be derivable from a wave function $\Psi = \Psi(x_1, x_2, \cdots x_N)$ for N particles, i.e., to be N-representable. Here I would like to emphasize the existence of a theorem (1956) saying that, if $\Gamma(x_1 x_2 | x_1' x_2')$ is derivable from an Nth-order density matrix $\Gamma(x_1 x_2 \cdots x_N | x_1' x_2' \cdots x_N)$, then

$$\langle H \rangle_\Gamma \geq E_0 ,$$

where E_0 is the lowest eigenvalue of H; the equality sign holds only if the Nth-order density matrix corresponds to the exact eigenfunction Ψ_0.

The proof is simple, provided one can use the fact that the solutions Ψ_k to the eigenvalue problem $H\Psi_k = E_k \Psi_k$ form a complete set. In the general case, Γ_N represents a mixture of states and may be expanded in the form

$$\Gamma(X|X') = \sum_{kl} \Psi_k(X) C_{kl} \Psi_l^*(X') ,$$

where $X = (x_1, x_2, \cdots x_N)$. Introducing the normalization $\mathrm{Tr}\ (\Gamma_N) = 1$, and the convention that H operates only on the unprimed coordinates, one obtains