

Natural Orbitals in the Quantum Theory of Two-Electron Systems*

PER-OLOV LÖWDIN, *Quantum Chemistry Group, Uppsala University, Kemikum, Uppsala, Sweden*

AND

HARRISON SHULL,† *Department of Chemistry and Institute for Atomic Research, Iowa State College, Ames, Iowa*

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The wave functions for the singlet and triplet states of a two-electron system in a given nuclear framework are investigated as superpositions of configurations and are shown to be transformationally equivalent to quadratic forms having certain ranks and signatures. By introducing the "natural orbitals" diagonalizing the generalized first-order density matrix, the total wave functions may also be brought to principal form. If the basis contains M one-electron functions, the singlet and triplet wave functions contain respectively $M(M+1)/2$ and $M(M-1)/2$ configurations, but the transformation to natural orbitals reduces the number of terms to M and $[M/2]$, respectively. The natural expansion having the

best convergence is also characterized by another important extremum property. The approximate wave function of rank r having the smallest quadratic deviation from the exact eigenfunction is obtained by interrupting the natural expansion of the eigenfunction after r terms and renormalizing the result. For the singlet state, the wave function of rank two and signature zero has a special importance as giving a simple extension of the visual one-electron picture to include a large part of the correlation effects. The theory is illustrated by some results on helium obtained by using radial configuration interaction.

TWO-ELECTRON systems occur commonly in nature and are of great importance. The series of helium-like ions: H^- , He, Li^+ , Be^{+2} , $\dots O^{+6}$, etc., is of considerable interest in physics and astrophysics and has been studied by several authors. The homopolar chemical bond is another example of a two-electron system of fundamental meaning for chemistry, and the electronic structure of the hydrogen molecule as well as the π electrons of ethylene, etc., have been investigated in great detail.

In the quantum theory of the electronic structure of matter, the two-electron systems provide a valuable bridge between the comparatively simple one-electron systems and the systems containing many electrons. The structure of an electronic system within a given nuclear framework depends not only on the balance between the kinetic energy of the electrons and their attraction to the nuclei, but also on the mutual electronic repulsion. The last effect causes considerable difficulties in the theory, since it may not be treated within the conventional "one-electron approximation." The accurate solution of the many-electron Schrödinger equation therefore demands other methods, and the results for two-electron systems are then also of guiding importance in treating systems containing many electrons. Two types of solutions of the two-electron Schrödinger equation have been discussed, namely an eigenfunction in the form of a "superposition of configurations" and a form containing the interelectronic distance as a variable. Both types were first investigated by Hylleraas in his pioneer works on the helium problem.¹ Hylleraas found that the series of configurations converged rather slowly and that a much quicker

convergence could be obtained by introducing r_{12} explicitly in the solution. Wave functions containing r_{12} have later been treated for the H_2 molecule by James and Coolidge,² for the H^- ion by Henrich,³ and for the He series by Eriksson,⁴ by Baber and Hassé,⁵ and by Chandrasekhar and Herzberg.⁶ The wave functions containing r_{12} have the disadvantage that it seems impossible to give them an interpretation of simple physical visuality, and it is further difficult to generalize the approach to many-electron systems.⁷

The success of the r_{12} method was so large that, for a rather long time, it was almost generally believed in the literature⁸ that "electronic correlation" could be taken into account only by introducing the interelectronic distances r_{ij} explicitly into the wave function. However, it was already known in the early days of quantum mechanics that the wave function for a many-electron system could be expressed as a superposition of configurations built up from one-electron functions, provided that the one-electron set was complete.⁹ The first eigenfunction of this type was derived for helium by Hylleraas,¹ but it seems as if less attention to this paper has been paid in the literature than to his r_{12} work. It

² H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933); see also A. A. Frost and J. S. Braunstein, *J. Chem. Phys.* **19**, 1133 (1951).

³ L. R. Henrich, *Astrophys. J.* **99**, 59 (1944); see also S. Chandrasekhar, *Astrophys. J.* **100**, 176 (1944).

⁴ H. A. S. Eriksson, *Z. Physik* **109**, 762 (1938); *Nova Acta Regiae Soc. Sci. Upsalensis* **IV**, **11**, No. 9 (1940); *Arkiv Mat. Astron. Fysik* **B30**, No. 6 (1944); *Nature* **161**, 393 (1948).

⁵ T. D. H. Baber and H. R. Hassé, *Proc. Cambridge Phil. Soc.* **33**, 253 (1937).

⁶ S. Chandrasekhar and G. Herzberg, *Phys. Rev.* **98**, 1050 (1955).

⁷ Compare E. Wigner, *Phys. Rev.* **46**, 1002 (1934); *Trans. Faraday Soc.* **34**, 678 (1938).

⁸ See, e.g., C. A. Coulson, *Proc. Cambridge Phil. Soc.* **34**, 204 (1938).

⁹ An antisymmetric wave function may be expressed as a sum of Slater determinants over all "ordered" configurations; for a simple proof, see, e.g., P.-O. Löwdin, *Phys. Rev.* **97**, 1474 (1955), p. 1477.

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† This work was performed under a fellowship grant from the John Simon Guggenheim Foundation. Present address: Chemistry Department, Indiana University, Bloomington, Indiana.

¹ E. A. Hylleraas, *Z. Physik* **48**, 469 (1928); *Z. Physik* **54**, 347 (1929).

has now also been shown by Green *et al.*¹⁰ how the r_{12} forms may be transformed into "superpositions of configurations."

The method of "configuration interaction" has the great advantage that it may be directly generalized to many-electron systems. However, since the basic one-electron set ψ_k may be chosen quite arbitrarily, the coefficients in the series of configurations cannot have any simple physical importance, and it is therefore difficult to give usable interpretations of the original wave functions presented in this way. In order to try to tackle this problem, it was shown in a previous paper⁹ that, for each wave function, there exists a certain set of one-electron functions having such characteristic properties that it naturally seems to belong to the system and state under consideration. These *natural spin orbitals* χ_k are defined as forming the set which diagonalizes the generalized first-order density matrix

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = N \int \Psi^*(\mathbf{x}_1' \mathbf{x}_2 \cdots \mathbf{x}_N) \times \Psi(\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_N) dx_2 dx_3 \cdots dx_N, \quad (1)$$

where Ψ is the antisymmetric wave function, $\mathbf{x}_i = (\mathbf{r}_i, s_i)$ is the space-spin coordinate of electron i , and N the number of electrons. It was shown that, if the wave function Ψ is expressed in terms of configurations built up from the natural spin orbitals, this *natural expansion* of Ψ is distinguished as the superposition of configurations of most rapid convergence.¹¹ The use of the natural spin orbitals gives a nice interpretation of the generalized first-order density matrix, and it also simplifies greatly the treatment of the higher order density matrices. In order to start a more detailed investigation of the "natural expansion" of a wave function of a many-electron system, we will study in this paper the particular properties of two-electron systems. The results are of importance for all the fundamental two-electron systems occurring in nature, and it is also hoped that they may give some guidance concerning the more complicated many-electron case. From the very beginning, we will therefore assume that the exact solution of the two-electron Schrödinger equation really exists¹² and that it is given as an infinite sum of configurations of a complete one-electron set.

1. TREATMENT OF THE SINGLET STATE

In a two-electron system, the spins of the electrons may combine to form either a singlet or a triplet state.

¹⁰ Green, Mulder, Milner, Lewis, Woll, Kolchin, and Mace. *Phys. Rev.* **96**, 319 (1954).

¹¹ See also P.-O. Löwdin, *Advances in Phys.* **5**, 1 (1956), particularly p. 150.

¹² Bartlett, Gibbons, and Dunn, *Phys. Rev.* **47**, 679 (1935); A. S. Coolidge and H. M. James, *Phys. Rev.* **51**, 855 (1937); T. Kato, *Trans. Am. Math. Soc.* **70**, 212 (1951); J. H. Bartlett, *Phys. Rev.* **88**, 525 (1952); **98**, 1067 (1955); V. Fock, *Izvest. Akad. Nauk. S. S. S. R.* **18**, (2), 161 (1954); E. A. Hylleraas, *Svensk Kem. Tidskr.* **67**, 372 (1955).

The simplifications of the general theory obtainable in this case are of an instructive nature. Let us assume that the functions $\psi_k(\mathbf{r})$ form a *complete* set of orbitals depending only on the one-electron space coordinate \mathbf{r} and that $\alpha(s)$ and $\beta(s)$ are the two spin functions. The most general antisymmetric two-electron wave functions which may be constructed by superposition of configurations of the spin orbitals $\psi_{k\alpha}$ and $\psi_{k\beta}$ have then the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}} \sum_{kl} A_{kl} \det\{\psi_{k\alpha}; \psi_{l\beta}\}. \quad (2)$$

This function has $S_z = 0$ and is the sum of a singlet component and a triplet component. The two triplets having $S_z = +1$ and $S_z = -1$ are built up similarly from the pairs $\psi_{k\alpha}, \psi_{l\alpha}$ and $\psi_{k\beta}, \psi_{l\beta}$, respectively.

(a) Singlet Wave Function

In order to select the singlet component of (2), we apply the projection operator¹³ ${}^1O = 1 - \frac{1}{2}S^2 = \frac{1}{2}(1 - P_{12}^\sigma)$ and obtain

$${}^1\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}} \sum_{kl} C_{kl} \det\{\psi_{k\alpha}; \psi_{l\beta}\}, \quad (3)$$

where $C_{kl} = \frac{1}{2}(A_{kl} + A_{lk})$. The singlet is hence characterized by the symmetry property $C_{kl} = C_{lk}$. The Slater determinants in (3) with the factor $2^{-\frac{1}{2}}$ form an orthonormal set, and the singlet wave function (3) is hence normalized if

$$\sum_{kl} |C_{kl}|^2 = 1.$$

This relation may be condensed in the form $\text{Tr}(\mathbf{C}\mathbf{C}^\dagger) = 1$, where Tr (= trace) means formation of the diagonal sum. By expanding the determinants, the wave function (3) may also be written in the form

$${}^1\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{\alpha_1\beta_2 - \alpha_2\beta_1}{\sqrt{2}} \Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (4)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{kl} C_{kl} (\psi_k, \psi_l), \quad (5)$$

where (ψ_k, ψ_l) is an abbreviation for the "symmetrized product":

$$(\psi_k, \psi_l) = \frac{1}{2} [\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2) + \psi_l(\mathbf{r}_1)\psi_k(\mathbf{r}_2)]. \quad (6)$$

The singlet wave function may therefore be factorized into a pure spin part and a pure space function. This result, which is strictly limited to $N \leq 2$, greatly simplifies the treatment of the two-electron problem and has been of essential importance for the development of the whole theory. In using (6), it should be observed that this quantity is normalized for $k=l$ but that the normalization integral has the value $\frac{1}{2}$ for $k \neq l$.

The coefficients C_{kl} in the symmetric space function (5) may be found by the variational principle corresponding to the Schrödinger equation, which leads to a certain secular equation.¹⁴ The numerical solution is

¹³ P.-O. Löwdin, *Phys. Rev.* **97**, 1509 (1955).

¹⁴ For a short description of this procedure, see, e.g., reference 9 p. 1482.

then often presented in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k \bar{C}_{kk} \psi_k(1) \psi_k(2) + \sum_{k < l} \bar{C}_{kl} [\psi_k(1) \psi_l(2) + \psi_l(1) \psi_k(2)] / \sqrt{2}, \quad (7)$$

with the normalization condition

$$\sum_k |\bar{C}_{kk}|^2 + \sum_{k < l} |\bar{C}_{kl}|^2 = 1. \quad (8)$$

A comparison between (5), (6), and (7) then gives the connection formulas

$$C_{kk} = \bar{C}_{kk}, \quad C_{kl} = C_{lk} = 2^{-\frac{1}{2}} \bar{C}_{kl}, \quad (9)$$

for the formation of the fundamental matrix \mathbf{C} .

(b) Natural Spin Orbitals

The generalized first-order density matrix $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$ is defined by (1), and, by using (4) and (5), we obtain

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = (\alpha_1' \alpha_1 + \beta_1' \beta_1) \sum_{kl} \psi_k^*(\mathbf{r}_1') \psi_l(\mathbf{r}_1) \gamma_{lk}, \quad (10)$$

where

$$\gamma_{lk} = \sum_m C_{lm} C_{km}^*, \quad \gamma = \mathbf{C} \mathbf{C}^\dagger. \quad (11)$$

The matrix γ is therefore a Hermitean matrix, which may be brought to diagonal form \mathbf{n} by the unitary transformation \mathbf{U} :

$$\mathbf{U}^\dagger \gamma \mathbf{U} = \mathbf{n}. \quad (12)$$

The *natural orbitals* $\chi(\mathbf{r})$ are then defined⁸ by the matrix relation $\chi = \psi \mathbf{U}$ or

$$\chi_k(\mathbf{r}) = \sum_m \psi_m(\mathbf{r}) U_{mk}, \quad (13)$$

and the natural spin orbitals are represented by the functions $\chi_{k\alpha}$ and $\chi_{k\beta}$. Introducing the relations $\psi = \chi \mathbf{U}^\dagger$ and $\psi^* = \mathbf{U} \chi^*$ into (10), we obtain

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = (\alpha_1' \alpha_1 + \beta_1' \beta_1) \sum_k n_k \chi_k^*(\mathbf{r}_1') \chi_k(\mathbf{r}_1), \quad (14)$$

where the coefficients n_k , i.e., the eigenvalues of the matrix γ , may be interpreted as the *occupation numbers* of the natural orbitals χ_k . They satisfy here the relation

$$\sum_k n_k = \text{Tr}(\gamma) = \text{Tr}(\mathbf{C} \mathbf{C}^\dagger) = 1, \quad (15)$$

which corresponds to the condition $\int \gamma(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1 = 2$. In the general theory^{9,11} it was shown that the introduction of the natural spin orbitals into the total wave function would lead to a "natural expansion" of this function, which was characterized by having the most rapid convergence of all superpositions of configurations representing the same solution. In the two-electron case, this natural expansion has particularly simple properties, as we now will show.

Let us consider the fundamental case when the basic Hamiltonian is not only Hermitean but also *real* so that $H_{\text{op}} = H_{\text{op}}^\dagger = H_{\text{op}}^*$. The energy eigenfunctions may then also be represented in real form and this implies that, if the basic set ψ_k is chosen real, the coefficients C_{kl} will also turn out to be real. In this important case, the matrix \mathbf{C} is Hermitean and may be brought to diagonal

form \mathbf{c} by the unitary transformation \mathbf{V} , so that $\mathbf{V}^\dagger \mathbf{C} \mathbf{V} = \mathbf{c}$. By using (11), we then obtain

$$\mathbf{V}^\dagger \gamma \mathbf{V} = \mathbf{V}^\dagger \mathbf{C}^2 \mathbf{V} = \mathbf{c}^2 = \text{diagonal matrix}. \quad (16)$$

This means that, unless the matrix γ is degenerate and two or more occupation numbers are equal, the transformation \mathbf{V} must be identical with the transformation \mathbf{U} . The eigenvalues c_k of \mathbf{c} are apparently the square roots of the occupation numbers:

$$c_k = \pm n_k^{\frac{1}{2}}, \quad (17)$$

and the signs are uniquely determined by the coefficients C_{kl} of the original wave function; the physical meaning of these signs will be discussed later. In the nondegenerate and real case, the introduction of the natural orbitals χ into the total wave function (4) by the substitution $\psi = \chi \mathbf{U}^\dagger = \mathbf{U} \chi$ will lead to a natural expansion of the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}} (\alpha_1 \beta_2 - \alpha_2 \beta_1) \sum_k c_k \chi_k(\mathbf{r}_1) \chi_k(\mathbf{r}_2). \quad (18)$$

We observe here¹¹ that the series $\sum_k c_k^2$ is term-by-term more rapidly convergent than the series $\sum_k (\sum_l C_{kl})^2$ for any other superposition of configurations.

The simplification rendered by the natural expansion is perhaps still more striking for the approximate wave functions. If the basic set ψ_k contains only M orbitals ($k=1, 2, \dots, M$), the wave function (7) contains $M(M+1)/2$ different terms, but, by the introduction of the corresponding approximate natural orbitals, this expansion is reduced to only M terms. It should be emphasized that, in the many-electron case, we cannot expect such a drastic simplification of the total wave function which, in the two-electron case, seems to depend on particular properties of the wave function itself.

(c) Equivalence of the Total Wave Function and a Quadratic Form. Rank and Signature of the Wave Function

The natural expansion (18) does not contain any cross products ($\chi_k \chi_l$) for $k \neq l$, and this result depends essentially on the fact that, in the two-electron case, the total singlet wave function is equivalent to a *real quadratic form*. In order to prove this we observe that the "symmetrized product" (6) is symmetric in k and l and that, under a linear transformation $\psi_k = \sum_m \psi_m' a_{mk}$, it transforms like an ordinary product:

$$(\psi_k \psi_l) = \sum_{mn} (\psi_m' \psi_n') a_{mk} a_{nl}. \quad (19)$$

Hence we obtain

$$\sum_{kl} C_{kl} (\psi_k \psi_l) = \sum_{mn} C_{mn}' (\psi_m' \psi_n'), \quad (20)$$

where $C_{mn}' = \sum_{kl} C_{kl} a_{mk} a_{nl}$. This relation implies that the space function transforms just like a real quadratic form.

Let us for a moment consider an approximate wave function, which is built up of configurations of a basic

set ψ_k of finite order M , such that when $M \rightarrow \infty$ the approximate solution tends to the exact eigenfunction.¹² A quadratic form of finite order is now characterized by two integers, its *rank* and its *signature*, which are invariant against nonsingular linear transformations.¹⁵ The rank of the quadratic form is defined as the rank r of the determinant of its coefficients, $\det\{C_{kl}\}$, and, according to an elementary theorem, the quadratic form is then reducible by a nonsingular linear transformation to a sum of "squares," which contains just r terms. If the linear transformation is kept real, the coefficients of the squares may be positive or negative. The number p of positive terms minus the number q of negative terms is called the *signature* s of the quadratic form, and the quantities

$$r = p + q, \quad s = p - q,$$

are then the fundamental invariants of the form. The equivalence theorem then implies that each approximate wave function of finite order has a definite rank and signature and that it may be reduced to a sum of "squares"; this gives the explanation of the simple form (18).

The equivalence theorem is a valuable tool for discussing the properties of the wave function. Let us, for instance, investigate in which cases the space function (5) is reducible to a single symmetrized product

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (u, v), \quad (21)$$

which means a state where one electron is occupying the orbital $u(\mathbf{r})$ and the other the orbital $v(\mathbf{r})$. Since

$$uv = \frac{1}{4}(u+v)^2 - \frac{1}{4}(u-v)^2, \quad (22)$$

the right-hand member of (21) has for $u \neq v$ the rank $r=2$ and the signature $s=0$. This implies that only wave functions (5) of this rank and signature may be reduced to the (u, v) -form. We note further that every function (5) having $r=2$ and $s=0$ may be expressed in the form (21), for, after reducing it to a sum of "squares," we obtain

$$c_1(\chi_1, \chi_1) - c_2(\chi_2, \chi_2) = (c_1^{\frac{1}{2}}\chi_1 + c_2^{\frac{1}{2}}\chi_2, c_1^{\frac{1}{2}}\chi_1 - c_2^{\frac{1}{2}}\chi_2), \quad (23)$$

where $c_1 > 0$ and $c_2 > 0$. A special case of this theorem was first found by Coulson and Fischer¹⁶ who pointed out that, in the hydrogen molecule, the molecular-orbital method using semilocalized orbitals leads to a wave function which was equivalent to a superposition of two configurations consisting of doubly occupied orbitals. The best (u, v) form for the H_2 molecule has further been studied by Kotani.¹⁷

Other special results for functions of rank $r=2$ were derived by Mulliken¹⁸ in connection with the Shelter

Island Conference in 1951. The form (u, v) of the wave function corresponds to the conventional "closed-shell" structure of the two-electron system. This function, which has rank $r=1$ and signature $s=1$, may be considered as a degenerate form of (21) for $u=v$. Mulliken characterized the (u, v) function (21) for $u \neq v$ as an "open-shell" form and pointed out that this function would contain an improved electronic correlation by letting the two electrons move in considerably different orbitals, thus increasing their mean distance. Remarkably good results for helium had previously been obtained by Hylleraas¹ and by Eckart¹⁹ by using the simple form (21). It seems to us as if the (u, v) form is of great value for describing the structure of a two-electron system in a simple way to a rather high degree of accuracy, and further investigations are in progress here.

(d) Extremum Properties of the Natural Expansion Taken Term by Term

The "natural expansion" (18) is characterized by the general property of having the most rapid convergence of all superpositions of configurations describing the same wave function. We will now show that, for a two-electron system, the natural expansion has an additional extremum property. Let Ψ be the *exact* eigenfunction and let Ψ_r be an arbitrary wave function of rank r . In order to determine the "best" approximation of Ψ of rank r , we will then try to minimize the total quadratic deviation

$$\int |\Psi - \Psi_r|^2 dx_1 dx_2 = 2 \left(1 - \int \Psi \Psi_r dx_1 dx_2 \right), \quad (24)$$

i.e., to maximize the overlap integral

$$S = \int \Psi \Psi_r dx_1 dx_2. \quad (25)$$

The "best" function Ψ_r of rank r is then obtained simply by interrupting the natural expansion (18) after the first r terms and renormalizing the finite series to unity.

In order to prove this theorem, we observe that an arbitrary space function of rank r may be written in the form

$$\Psi_r(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=1}^r \epsilon_k (u_k, u_k). \quad (26)$$

If the functions u_1, u_2, \dots, u_k are assumed to form an arbitrary linearly independent but not necessarily orthonormal set, the coefficients ϵ_k may be restricted to have fixed values, e.g., $\epsilon_k = \pm 1$. Each function u_k is expandable in the complete orthonormal set χ_k of natural orbitals:

$$u_k = \sum_{m=1}^{\infty} \chi_m a_{mk}, \quad (27)$$

¹² See, for instance, G. Kowalewski, *Determinantentheorie* (Walter de Gruyter and Company, Berlin and Leipzig, 1925), second edition, pp. 172-200.

¹⁶ C. A. Coulson and I. Fischer, *Phil. Mag.* **40**, 386 (1949).

¹⁷ M. Kotani, Proceedings of the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, 1951 (unpublished), p. 139.

¹⁸ R. S. Mulliken, *Proc. Natl. Acad. Sci. U. S.* **38**, 160 (1952).

¹⁹ C. Eckart, *Phys. Rev.* **36**, 878 (1930).

and the coefficients a_{mk} may here be varied completely arbitrarily. Substituting (27) into (26), we obtain

$$\Psi_r(\mathbf{r}_1, \mathbf{r}_2) = \sum_{m,n=1}^{\infty} A_{mn}(\chi_m, \chi_n), \quad (28)$$

where the coefficients

$$A_{mn} = \sum_{k=1}^r \epsilon_k a_{mk} a_{nk} \quad (29)$$

form a symmetric matrix of rank r . The normalization condition gives

$$\sum_{m,n=1}^{\infty} A_{mn}^2 = \text{Tr}(\mathbf{A}^2) = 1. \quad (30)$$

Introducing (18) and (28) into the overlap integral (25), we obtain further

$$S = \sum_{m=1}^{\infty} c_m A_{mm} = \text{Tr}(\mathbf{cA}), \quad (31)$$

where \mathbf{c} is the diagonal matrix formed by the elements c_m .

In order to maximize the overlap integral S by putting $\delta S = 0$, we cannot vary the elements A_{mn} in (30) and (31) *independently* since they are subject to the condition of forming a matrix \mathbf{A} of definite rank r . However, since the coefficients a_{mk} in (27) may be varied arbitrarily, we obtain from (31) and (30)

$$\delta S = 2 \sum_{m=1}^{\infty} \sum_{k=1}^r c_m \epsilon_k a_{mk} \delta a_{mk} = 0, \quad (32)$$

$$4 \sum_{m,n=1}^{\infty} \sum_{k=1}^r A_{mn} \epsilon_k a_{nk} \delta a_{mk} = 0.$$

Introducing a Lagrangian multiplier λ on the first relation formally changed to a double sum, we get further

$$\sum_{m,n=1}^{\infty} \sum_{k=1}^r (A_{mn} - \lambda c_m \delta_{mn}) \epsilon_k a_{nk} \delta a_{mk} = 0, \quad (33)$$

and

$$\sum_{n=1}^{\infty} (A_{mn} - \lambda c_m \delta_{mn}) \epsilon_k a_{nk} = 0. \quad (34)$$

In order to solve this system of equations, we will multiply (34) by a_{pk} and sum over k from 1 to r , which leads to

$$\sum_{n=1}^{\infty} (A_{mn} - \lambda c_m \delta_{mn}) A_{np} = 0, \quad (35)$$

or the matrix relation

$$(\mathbf{A} - \lambda \mathbf{c})\mathbf{A} = 0. \quad (36)$$

By forming the trace of (36) and using (30) and (31), we obtain easily the value of the multiplier λ :

$$1 = \text{Tr}(\mathbf{A}^2) = \lambda \text{Tr}(\mathbf{cA}) = \lambda S; \quad \lambda = S^{-1}. \quad (37)$$

Since \mathbf{A} is a symmetric matrix, the same is true for \mathbf{A}^2 and, according to (36), this leads to $(\mathbf{cA})_{mn} = (\mathbf{cA})_{nm} = \lambda^{-1}(\mathbf{A}^2)_{mn}$ and

$$(c_m - c_n)A_{mn} = 0. \quad (38)$$

This implies that, if $c_m \neq c_n$, all the nondiagonal elements A_{mn} vanish. In the nondegenerate case, the matrix \mathbf{A} of rank r consists therefore of just r diagonal elements, A_{kk} , which fulfill the relation $A_{kk}^2 - \lambda c_k A_{kk} = 0$, or

$$A_{kk} = \lambda c_k. \quad (39)$$

According to (28), the optimum wave functions of rank r may then be written

$$\Psi_r(\mathbf{r}_1, \mathbf{r}_2) = \lambda \sum_k^{(r)} c_k (\chi_k, \chi_k), \quad (40)$$

where the symbol (r) indicates that k is to be summed over r selected indices. Substitution of (39) into (31) leads to the formula

$$\lambda^{-1} = S = \left\{ \sum_k^{(r)} c_k^2 \right\}^{\frac{1}{2}} = \left\{ \sum_k^{(r)} n_k \right\}^{\frac{1}{2}}, \quad (41)$$

and, since the function (40) hence turns out to be normalized, the solution of the variation problem is consistent. In order to obtain a maximum overlap, we have now only to select the r largest occupation numbers n_k . If the natural orbitals χ_k are numbered in order of decreasing occupation numbers, the "best" wave function of rank r has consequently the form

$$\Psi_r(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=1}^r c_k (\chi_k, \chi_k) / \left(\sum_{k=1}^r n_k \right)^{\frac{1}{2}}. \quad (42)$$

This proves our theorem.

We have treated here the expansion of the exact solution, but we observe that the same theorem holds also for the expansions of approximate wave functions of rank higher than r . The approximations of low rank are of particular interest and will be considered somewhat more in detail.

Rank one.—A total wave function of rank $r=1$ may be written in the form $\Psi(\mathbf{r}_1, \mathbf{r}_2) = (u, u)$, and this "closed-shell" form therefore corresponds physically to a state containing a doubly occupied orbital $u(\mathbf{r})$. According to (42), the function of rank one which has maximum overlap with the exact eigenfunction is simply

$$\Psi_{r=1} = (\chi_1, \chi_1), \quad (43)$$

where χ_1 is the first natural orbital associated with the exact solution and having the largest occupation number n_1 . By using (41), we obtain for the overlap integral that $S = n_1^{\frac{1}{2}}$.

Let us now consider the relation between the form (43) and the Hartree-Fock form. For a two-electron system, the Hartree-Fock solution $(u_{\text{HF}}, u_{\text{HF}})$ is defined as the function of rank one having the best value of the total energy. This extreme value condition leads to a nonlinear process of the first order for the orbital u_{HF} ,

whereas the first natural orbital χ_1 is defined by a linear process of infinite order. The two functions χ_1 and u_{HF} are therefore not identical, but the examples investigated so far have indicated that they are extremely closely related; see also Table IV for $r=1$. Of practical importance is that the *linear process* leading to the first and higher natural orbitals seems to be considerably simpler than the nonlinear "self-consistent-field" method.

Rank two.—The total wave function of rank $r=2$ has either signature $s=0$ or $s=2$. According to (42), the function of rank two which has the smallest total quadratic deviation from the exact eigenfunction has a space function of the form

$$\Psi_{r=2} = [c_1(\chi_1, \chi_1) + c_2(\chi_2, \chi_2)] / (n_1 + n_2)^{\frac{1}{2}} \quad (44)$$

In the case when $s=0$, this function may be written in (u, v) -form with the orbitals

$$\begin{aligned} u &= (n_1^{\frac{1}{2}}\chi_1 + n_2^{\frac{1}{2}}\chi_2) / (n_1 + n_2)^{\frac{1}{2}}, \\ v &= (n_1^{\frac{1}{2}}\chi_1 - n_2^{\frac{1}{2}}\chi_2) / (n_1 + n_2)^{\frac{1}{2}}. \end{aligned} \quad (45)$$

The increase of the rank of the wave function gives rise here to a "correlation splitting" of the closed-shell form (43) into an open-shell form, where at least part of the effect of the inter-electronic repulsion is taken into account.

In the case when in (44) the coefficients c_1 and c_2 are both found to be positive ($s=2$), the orbitals u and v turn out to be complex and such that $u^* = v$. This implies that both particles have the same orbital distribution $|u|^2 = |v|^2$ in ordinary space but different probability distributions in momentum space. It seems likely, therefore, that this case will occur only when one has reason to expect that a "correlation splitting" in momentum space will be energetically more favorable than an orbital splitting in ordinary space. So far, no example of $r=2$ and $s=2$ has been found in the simple two-electron systems.

Recently the Hartree-Fock scheme has been generalized to include at least part of the electronic correlation by introducing different orbitals for different spins.¹³ For two-electron systems this implies that, instead of the (u, u) -form, one is interested in the (u, v) -form having the best energy. Since the extended Hartree-Fock equations have a nonlinear character and are comparatively hard to solve, it is of practical importance to observe that the functions (45), formed from the first two natural orbitals and χ_1 and χ_2 found by a *linear process*, seem to give an approximate solution of excellent accuracy of the energy problem, too. Further calculations on this point are in progress.

(e) Example: Some Results for the Ground State of Helium

The method of "superposition of configurations" has already been successfully applied to the problem of the ground state of helium by Hylleraas in his first paper.¹

Recently Taylor and Parr²⁰ re-examined the same problem and, using configurations built up from hydrogen-like orbitals, they obtained the discouraging result that the series of radial configurations led to an extremely poor convergence for the energy towards the limit to be expected. A closer investigation shows, however, that this failure of the method depends essentially on the fact that Taylor and Parr neglected the contribution from the continuum.²¹

We have now repeated and extended Hylleraas' first calculation on helium by using the complete orthogonal set

$$(2\eta)^{\frac{3}{2}} \{ (n+l+1)! \}^{-\frac{1}{2}} \{ (n-l-1)! \}^{\frac{1}{2}} \times (2\eta r)^l L_{n+l+1}^{2l+2} (2\eta r) e^{-\eta r} Y_{lm}(\vartheta, \varphi), \quad (46)$$

where L are the Laguerre polynomials, η is an adjustable effective charge, and Y_{lm} are the ordinary spherical harmonics. Since this set is entirely discrete, one can thus avoid the treatment of the otherwise rather annoying continuum wave functions. We will here discuss the results of the *radial* configurational interaction in order to exemplify the use of natural orbitals and to show the convergence properties of a natural expansion.²²

The calculations were based on a finite set of (ns) -orbitals of order M of the form

$$\psi_{ns} = \frac{1}{(4\pi)^{\frac{1}{2}} (n+1)! [n(n+1)]^{\frac{1}{2}}} (2\eta)^{\frac{3}{2}} L_{n+1}^2 (2\eta r) e^{-\eta r}.$$

In the general theory,⁹ a "measure of convergence" ϑ was defined with the property that the natural expansion had the smallest ϑ value possible of all superpositions of configurations of one and the same wave function. Eliminating the spin, the quantity ϑ is here defined by

$$\vartheta = 1 - \sum_{k=1}^M \gamma_{kk}^2, \quad (47)$$

where γ_{kk} may be evaluated according to (11). The quantities ϑ for the original superposition of configurations and for the natural expansion are given in Table I. These quantities should be compared with the total

TABLE I. Ground state of helium. Comparison between the original superposition of configurations and the natural expansion in order to show the reduction of the number of essential terms.

$M =$	Number of terms				Measure of convergence $= \vartheta$			
	1	2	3	4	1	2	3	4
Original form	1	3	6	10	0	0.032907	0.070987	0.073251
Natural expansion	1	2	3	4	0	0.004976	0.008643	0.008729

²⁰ G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. 38, 154 (1952). This paper was also presented at the Shelter Island Conference (reference 17) in 1951.

²¹ H. Shull and P. O. Löwdin, J. Chem. Phys. 23, 1362 (1955).

²² A preliminary report was given by H. Shull and P.-O. Löwdin, J. Chem. Phys. 23, 1565 (1955).

TABLE II. Occupation numbers n_k for the natural orbitals χ_k for different values of M .

$M =$	1	2	3	4
$k=1$	1.000000	0.9975561	0.9956599	0.9956166
$k=2$		0.0024439	0.0042652	0.0043114
$k=3$			0.0000748	0.0000655
$k=4$				0.0000065

numbers of terms in Ψ , which has decreased from $M(M+1)/2$ in the original form to M in the natural expansion. It should perhaps be emphasized that the quantity ϑ cannot be used for estimating the energy accuracy of *different* wave functions. For each wave function, only the lowest value ϑ_{nat} is uniquely defined, and ϑ_{nat} increases with M towards a certain limit from its lowest value $\vartheta_{\text{nat}}=0$ for the Hartree-Fock approximation ($M=1$), at the same time as the energy accuracy is also increasing. Other "measures of convergence" are also easily constructed.

In Tables II and III, the occupation numbers n_k and the natural orbitals χ_k for $M=1, 2, 3, 4$ are listed, and it is remarkable how rapidly these quantities converge towards a definite limit when M increases. The total wave functions may then be found by using formulas (17) and (42), where it should be observed that, for the ground state of helium, we have hitherto found only the first coefficient c_1 to be positive, whereas all the others have turned out to be negative. The signature of a wave function of rank r is therefore $s=2-r$, and the wave function may be presented in the form

$$\Psi_r(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_1^{\frac{1}{2}}(\chi_1, \chi_1) - n_2^{\frac{1}{2}}(\chi_2, \chi_2) - \dots - n_r^{\frac{1}{2}}(\chi_r, \chi_r)}{\left(\sum_{k=1}^r n_k\right)^{\frac{1}{2}}}. \quad (48)$$

In Table IV, the energy values of the wave functions (48) are given in the modified atomic unit $e^2/a_{0, \text{He}} (=2hc \text{ Ry}_{\text{He}})$; only radial configurations are here taken into account. We observe how quickly the energy converges towards the radial limit to be expected. The original wave function for $M=4$ contains *ten* terms and is rather clumsy to handle, but, after the transformation to natural spin-orbitals, it is reduced to only *four* terms; in both cases the energy is -2.87860 . The last term is here relatively unimportant, and, if it is omitted, the

renormalized function of rank $r=3$ containing only *three* terms has the energy -2.87850 . The natural spin orbitals seem therefore to provide a useful tool for simplifying the total wave functions.

The series of energy values for a fixed rank r are of interest since, for $M \rightarrow \infty$, they converge towards a limit which is closely related to (but not identical with) the best energy value which is obtainable for functions of rank r by an extension of the Hartree-Fock method. In fact, our function $(\chi_1)^2$ has for $M=3$ and $M=4$ the energy values -2.861335 and -2.861415 , respectively, whereas the self-consistent field (SCF) energy reported by Wilson²³ is -2.8615 ; it should also be noted that the function $\chi_{1, M}$ does not differ from Wilson's numerical SCF function in any part of space by more than ± 0.0056 for $M=3$ and ± 0.0061 for $M=4$. Recently Green *et al.*²⁴ have reported a somewhat better SCF energy, -2.86167 , for an analytic SCF function; the value of the overlap integral between $\chi_{1, M}$ and this function is 0.9999724 for $M=3$ and 0.9999754 for $M=4$, showing a slight improvement in the convergence of $\chi_{1, M}$ with increasing M .

For the rank $r=2$, no SCF results seem to exist so far, but it would probably be comparatively easy to solve the extended Hartree-Fock equations¹³ in this case by starting from the first two natural orbitals, χ_1 and χ_2 , obtained. However, the optimum energy will probably not be much better than our value -2.87769 for $M=4$ and $r=2$. The result already obtained is remarkable, for, if the radial limit is estimated to be about -2.879 or -2.880 , it implies that between 84% and 89% of the radial correlation energy is actually taken into account in the simple (u, v) -form, which may be constructed from χ_1 and χ_2 by using (45).

2. TREATMENT OF THE TRIPLET STATE

In order to select the triplet component of the total wave function (2), we will apply the projection operator¹³ ${}^3O = \frac{1}{2}S^2 = \frac{1}{2}(1 + P_{12}^o)$ and obtain

$${}^3\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}} \sum_{kl} \frac{1}{2} (A_{kl} - A_{lk}) \det\{\psi_{k\alpha}; \psi_{l\beta}\}. \quad (49)$$

The triplet is hence characterized by the antisymmetry property of the matrix of the coefficients $\frac{1}{2}(A_{kl} - A_{lk})$ and is normalized to unity, if $\sum_{kl} \frac{1}{4} (A_{kl} - A_{lk})^2 = 1$. The triplet wave function (49) may also be factorized in

TABLE III. Approximate natural orbitals χ_k for the ground state of helium for different values of M ; $\eta=2$.

$M =$	1	2	χ_1	3	4	2	χ_2	3	4	3	χ_3	4	χ_4
1s	1.000000	+0.992794	+0.983545	+0.982955	+0.119833	+0.178369	+0.179264	+0.028690	+0.037891	+0.015090			
2s		-0.119833	-0.168992	-0.170083	+0.992794	+0.964488	+0.968000	-0.202991	-0.181235	+0.034679			
3s			+0.063880	+0.069537		-0.194800	-0.170104	-0.978760	-0.982029	-0.042981			
4s				-0.005955			-0.043657		-0.036555	+0.998360			

²³ W. S. Wilson, Phys. Rev. **48**, 536 (1935); W. S. Wilson and R. B. Lindsay, Phys. Rev. **47**, 681 (1935).

²⁴ Green, Mulder, Lewis, and Woll, Phys. Rev. **93**, 757 (1954).

TABLE IV. Ground state of helium. Total energy in modified atomic units ($=e^2/a_0, \text{H}_e=2hc \text{ Ry}_{\text{H}_e}$) for the interrupted natural expansion (42) of rank $r=1, 2, \dots, M$, when only radial configurations are included; $\eta=2$.

$M=$	1	2	3	4
$r=1$	-2.750000	-2.837638	-2.861335	-2.8614151
$r=2$		-2.850225	-2.877236	-2.8776857
$r=3$			-2.878116	-2.8785000
$r=4$				-2.8785973

the form

$${}^3\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}}(\alpha_1\beta_2 + \alpha_2\beta_1)\Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (50)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{kl} C_{kl} \{\psi_k, \psi_l\}, \quad (51)$$

where

$$C_{kl} = \frac{1}{2}i(A_{kl} - A_{lk}), \quad (52)$$

and $\{\psi_k, \psi_l\}$ is an abbreviation for the "antisymmetrized product"

$$\{\psi_k, \psi_l\} = -\frac{1}{2}i[\psi_k(\mathbf{r}_1)\psi_l^*(\mathbf{r}_2) - \psi_k(\mathbf{r}_2)\psi_l^*(\mathbf{r}_1)]. \quad (53)$$

Here we have introduced the quantities ψ_l^* ($=\psi_l$ for real orbitals) in order to facilitate the later use of complex orbitals. We note that (50) corresponds to a triplet state with $S_z=0$, whereas the wave functions for the triplet states with $S_z=+1$ and $S_z=-1$ may be obtained by replacing the spin factor in (50) by the functions $\alpha_1\alpha_2$ and $\beta_1\beta_2$, respectively.

The coefficients C_{kl} in (51) may be found by the variational principle¹⁴ corresponding to the Schrödinger equation, which leads to a certain secular equation. The numerical solution is often presented in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k<l} \bar{C}_{kl} [\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2) - \psi_k(\mathbf{r}_2)\psi_l(\mathbf{r}_1)] / \sqrt{2}, \quad (54)$$

which gives

$$C_{kk}=0, \quad C_{kl} = -C_{lk} = i2^{-\frac{1}{2}}\bar{C}_{kl}. \quad (55)$$

The normalization condition for the total space function may then be written in the form $\sum_{k<l} |\bar{C}_{kl}|^2 = 1$ or

$$\text{Tr}(\mathbf{C}^\dagger \mathbf{C}) = \sum_{kl} |C_{kl}|^2 = 1. \quad (56)$$

(a) Triplet Wave Function as a Hermitean Quadratic Form. Diagonal Representation

By introducing the factor i in the definition (52) of the quantities C_{kl} , we have ensured that the elements C_{kl} form a Hermitean matrix \mathbf{C} having only real eigenvalues. However, this matrix with vanishing diagonal elements and purely imaginary elements has rather peculiar properties. The secular equation for the eigenvalues c contains either only odd or only even powers of c , and this implies that the eigenvalues occur in pairs, $\pm c_k$, and that a matrix \mathbf{C} of odd order has always an additional eigenvalue $c_k=0$.

Since the "antisymmetrized product" (53) fulfils the relation $\{\psi_l, \psi_k\} = \{\psi_k, \psi_l\}^*$, the total space function (51) must be equivalent to a *Hermitean quadratic form*. In

carrying out the transformation

$$\psi_k = \sum_m \psi_m' a_{mk}, \quad (57)$$

we obtain

$$\{\psi_k, \psi_l\} = \sum_{mn} \{\psi_m', \psi_n'\} a_{mk} a_{nl}^*, \quad (58)$$

which gives

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{kl} C_{kl} \{\psi_k, \psi_l\} = \sum_{mn} C_{mn}' \{\psi_m', \psi_n'\}, \quad (59)$$

with

$$C_{mn}' = \sum_{kl} a_{mk} C_{kl} a_{ln}^\dagger,$$

or

$$\mathbf{C}' = \mathbf{a} \mathbf{C} \mathbf{a}^\dagger. \quad (60)$$

Let us choose $\mathbf{a} = \mathbf{U}^\dagger$, where \mathbf{U} is the unitary transformation which brings the Hermitean matrix \mathbf{C} to diagonal form $\mathbf{c} = \mathbf{U}^\dagger \mathbf{C} \mathbf{U}$, with the eigenvalues c_k . Introducing a new set of basic orbitals φ_k by the relation

$$\varphi = \psi \mathbf{U}^\dagger, \quad \varphi_k = \sum_m \psi_m U_{km}^*, \quad (61)$$

we then obtain

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_k c_k \{\varphi_k, \varphi_k\}, \quad (62)$$

which gives the "diagonal representation" of the total space function. We note that, in the odd case, the orbital φ_k belonging to the vanishing eigenvalue $c_k=0$ will not occur in this expansion. Because of the special properties of the eigenvalues c_k , the signature of the form (62) will always vanish: $s=0$.

Since $\mathbf{C}^* = -\mathbf{C}$, we can conclude from $\mathbf{C} \mathbf{U}_k = c_k \mathbf{U}_k$ that $\mathbf{C} \mathbf{U}_k^* = -c_k \mathbf{U}_k^*$. This implies that, if the function φ_k is associated with the eigenvalue $+c_k$, the function φ_k^* will be associated with the eigenvalue $-c_k$. In the sum in (62), the contribution from a negative eigenvalue will therefore be identical with the contribution from the corresponding positive eigenvalue:

$$-c_k \{\varphi_k^*, \varphi_k^*\} = +c_k \{\varphi_k, \varphi_k\}. \quad (63)$$

Hence we may write (62) in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=1}^{[M/2]} 2c_k \{\varphi_k, \varphi_k\}, \quad (64)$$

where we sum only over the positive eigenvalues c_k ; the number of terms is $[M/2]$, i.e., the integer equal to or nearest lower than $M/2$. The normalization of the total space function may then be expressed in the form:

$$\sum_{k=1}^{[M/2]} 2c_k^2 = \sum_k c_k^2 = \text{Tr}(\mathbf{c}^\dagger \mathbf{c}) = \text{Tr}(\mathbf{C}^\dagger \mathbf{C}) = 1. \quad (65)$$

After the reduction to diagonal form, we can now easily go back to a real representation of the total space function. Putting

$$\begin{aligned} \mathbf{U} &= \mathbf{R} + i\mathbf{S}, \\ \mathbf{u} &= \sqrt{2} \psi \mathbf{R}, \quad \mathbf{v} = \sqrt{2} \psi \mathbf{S}, \end{aligned} \quad (66)$$

we obtain $\varphi = 2^{-\frac{1}{2}}(\mathbf{u} - i\mathbf{v})$ and

$$\{\varphi_k, \varphi_k\} = \frac{1}{2} [u_k(\mathbf{r}_1)v_k(\mathbf{r}_2) - u_k(\mathbf{r}_2)v_k(\mathbf{r}_1)]. \quad (67)$$

Since φ_k and φ_k^* are associated with different eigenvalues, $+c_k$ and $-c_k$ ($c_k \neq 0$), they are orthogonal, i.e., $\int \varphi_k \varphi_k^* dv = 0$, and this implies that the functions u_k and v_k must be mutually orthogonal and have the same normalization integral, which is here chosen to be unity. In general, the functions $u_1, v_1, u_2, v_2, \dots, u_k, v_k, \dots$ therefore form an orthonormal set, or may be brought into this form in case of degenerate eigenvalues c_k . Substituting (67) into (64), we get then the real expansion

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k=1}^{[M/2]} c_k \begin{vmatrix} u_k(\mathbf{r}_1) & u_k(\mathbf{r}_2) \\ v_k(\mathbf{r}_1) & v_k(\mathbf{r}_2) \end{vmatrix}. \quad (68)$$

It should be noted that the functions u_k and v_k are here undetermined with respect to a linear transformation:

$$\begin{aligned} u_k' &= u_k \cos\theta + v_k \sin\theta, \\ v_k' &= -u_k \sin\theta + v_k \cos\theta, \end{aligned} \quad (69)$$

which corresponds to a multiplication of the unitary transformation U by a phase factor $\exp(-i\theta)$. In treating the eigenvalue equation $\mathbf{C}\mathbf{U} = \mathbf{U}\mathbf{c}$, we will sometimes separate it into its real and imaginary parts:

$$\mathbf{C}\mathbf{R} = i\mathbf{S}\mathbf{c}; \quad \mathbf{C}\mathbf{S} = -i\mathbf{R}\mathbf{c}. \quad (70)$$

These relations show that both \mathbf{R}_k and \mathbf{S}_k are eigenvectors to the symmetric Hermitean matrix \mathbf{C}^2 having the eigenvalues c_k^2 . Numerically, it is often convenient to solve the eigenvalue problem $\mathbf{C}\mathbf{U}_k = c_k \mathbf{U}_k$ by an iteration procedure based on (70).

(b) Natural Orbitals for the Triplet State

It is immediately clear that the complex functions $\varphi_k(\mathbf{r})$ form the *natural orbitals* of the triplet state under consideration. Using (1), (50), and (51), we obtain

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = (\alpha_1' \alpha_1 + \beta_1' \beta_1) \sum_{kl} \psi_k(\mathbf{r}_1') \psi_l(\mathbf{r}_1) \gamma_{lk}, \quad (71)$$

where

$$\gamma_{lk} = \sum_m C_{lm} C_{km}^*, \quad \gamma = \mathbf{C}\mathbf{C}^\dagger = \mathbf{C}^2. \quad (72)$$

If \mathbf{U} is the unitary transformation which brings \mathbf{C} to diagonal form, it will bring also the matrix γ to diagonal form with the eigenvalues $n_k = c_k^2$, i.e.,

$$\mathbf{U}^\dagger \gamma \mathbf{U} = \mathbf{n} = \mathbf{c}^2. \quad (73)$$

By carrying out the transformation (61), the first-order density matrix may then be expressed in the following forms:

$$\begin{aligned} \gamma(\mathbf{x}_1' | \mathbf{x}_1) &= (\alpha_1' \alpha_1 + \beta_1' \beta_1) \sum_k n_k \varphi_k^*(\mathbf{r}_1') \varphi_k(\mathbf{r}_1) \\ &= (\alpha_1' \alpha_1 + \beta_1' \beta_1) \sum_{k=1}^{[M/2]} n_k [\varphi_k^*(\mathbf{r}_1') \varphi_k(\mathbf{r}_1) \\ &\quad + \varphi_k(\mathbf{r}_1') \varphi_k^*(\mathbf{r}_1)] \\ &= (\alpha_1' \alpha_1 + \beta_1' \beta_1) \sum_{k=1}^{[M/2]} n_k [u_k(\mathbf{r}_1') u_k(\mathbf{r}_1) \\ &\quad + v_k(\mathbf{r}_1') v_k(\mathbf{r}_1)], \end{aligned} \quad (74)$$

and n_k may thus be interpreted as the occupation number for the natural orbitals $\varphi_k(\mathbf{r})$ and $\varphi_k^*(\mathbf{r})$, which are always simultaneously occupied.

According to (64) and (53), the total space function has the natural expansion

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= 2 \sum_{k=1}^{[M/2]} c_k \{ \varphi_k, \varphi_k \} \\ &= i \sum_{k=1}^{[M/2]} c_k [\varphi_k^*(\mathbf{r}_1) \varphi_k(\mathbf{r}_2) - \varphi_k^*(\mathbf{r}_2) \varphi_k(\mathbf{r}_1)], \end{aligned} \quad (75)$$

showing that, in the triplet state, two electrons with antiparallel or parallel spins may be considered as placed in pairs of conjugate complex orbitals φ_k and φ_k^* , which have the same charge distribution in space but which still are orthogonal to each other. The antisymmetry property in r_1 and r_2 is here sufficient to take account of the main part of the electronic correlation even when only one term in (75) is included. In the form (68), the quantity $n_k = c_k^2$ may be considered as the probability for the simultaneous occupation of the pair u_k, v_k .

(c) Example: Lowest Triplet State of Helium

The theory outlined above will be exemplified by an investigation of the lowest triplet state of helium. The total space function (54) was first derived by using configurations built up from the basic set (46), but only the results of the radial configurational interaction will be reported here. Starting from the s -functions ($1s, 2s, \dots, Ms$), we get $M(M-1)/2$ different configurations and a secular equation of the same order. After having obtained the $M(M-1)/2$ coefficients \tilde{C}_{kl} for the lowest triplet, we can easily form the antisymmetric Hermitean matrix \mathbf{C} of order M according to (55). The eigenvalues of \mathbf{C} form a maximum of $[M/2]$ non-vanishing pairs $\pm c_k$, and the normalization gives further $\sum_k c_k^2 = 1$.

In the case $M=3$, the matrix \mathbf{C} has the three eigenvalues $0, \pm 2^{-1/2}$, determined by the general properties of the matrix. The natural expansion (68) for the total space function consists then of a single term:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = 2^{-1/2} [u(\mathbf{r}_1)v(\mathbf{r}_2) - u(\mathbf{r}_2)v(\mathbf{r}_1)]. \quad (76)$$

For the best value of the adjustable effective charge, $\eta = 1.133$, this wave function gives an energy of -2.12906 , which is to be compared with the experimental value -2.1750 (see Table V).

TABLE V. Lowest triplet state of helium. Total energy in modified atomic units ($=e^2/a_0, H_0 = 2hc \text{ Ry}_{H_0}$) for the interrupted natural expansion (68). Experimental value = -2.1750 .

Number of terms	$M=3$ $\eta=1.133$	$M=4$ $\eta=1.11141$
1	-2.12906	-2.167620
2	...	-2.167636

In the case $M=4$, the total space function may be expressed in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = c_1 \begin{vmatrix} u_1(\mathbf{r}_1) & u_1(\mathbf{r}_2) \\ v_1(\mathbf{r}_1) & v_1(\mathbf{r}_2) \end{vmatrix} + c_2 \begin{vmatrix} u_2(\mathbf{r}_1) & u_2(\mathbf{r}_2) \\ v_2(\mathbf{r}_1) & v_2(\mathbf{r}_2) \end{vmatrix}, \quad (77)$$

and, for the best value of the adjustable effective charge, $\eta=1.11141$, the matrix \mathbf{C} has the four eigenvalues

$$c_{1,-1} = \pm 0.707105, \quad c_{2,-2} = \pm 0.001519. \quad (78)$$

The energy of (77) is then -2.167636 , which should be compared with the above-mentioned experimental value -2.1750 . The functions u_1, v_1, u_2, v_2 are given in Table VI; the angles θ_1 and θ_2 in (69) have been de-

TABLE VI. The natural orbitals of the lowest triplet of helium in a real representation.

	u_1	v_1	u_2	v_2
1s	+0.920687	+0.181063	-0.34569	+0.00709
2s	-0.059257	+0.924828	+0.32263	-0.19260
3s	+0.385358	-0.281968	+0.87863	-0.00071
4s	-0.018002	+0.180011	+0.06646	+0.98125

termined so that u_1 and u_2 have maximum overlap with the natural orbitals χ_1 and χ_3 , respectively, for the singlet ground state (for $M=4$). Table VII gives a survey of the overlap integrals between the triplet orbitals u_k, v_k and the corresponding natural orbitals χ_l for the singlet; we observe that the orbital χ_1 occurring in the conventional closed-shell structure $(\chi_1)^2$ for the ground state does not occur with any higher degree of accuracy in the description of the lowest triplet state, and this implies that one has to be careful in using the naïve orbital picture of a single excitation as obtained by an electronic jump from one orbital to another, whereas the others are left unchanged. An excitation is instead a transition of the system as a whole from one state to another and may imply changes for all the electrons—there may be a certain orbital correspondence,²⁵ but the accuracy is usually rather limited.

In conclusion, it should be observed that the second term in (77) has only a small importance; if it is dropped and the expansion renormalized by putting $c_1=2^{-\frac{1}{2}}$, the energy is changed from -2.167636 to -2.167620 . This value is probably rather close to the best energy obtainable by a $[u, v]$ wave function, which should strictly be calculated by a Hartree-Fock procedure. We note that the angular correlation energy does not amount to 0.0075, which is only half the value in the singlet case, and that most of the radial correlation is apparently taken into account already in the $[u, v]$ form.

²⁵ See, e.g., P.-O. Löwdin, Phys. Rev. **97**, 1490 (1955), particularly p. 1506.

TABLE VII. Overlap integrals between the natural orbitals for the lowest triplet and singlet states.

$\int u_1 \chi_1 dv = 0.941976$	(maximum overlap)
$\int v_1 \chi_2 dv = 0.967796$...
$\int u_2 \chi_3 dv = 0.93684$	(maximum overlap)
$\int v_2 \chi_4 dv = 0.97310$...

3. DISCUSSION

In the general quantum theory of many-particle systems,^{9,11} it was shown that the total wave function may be expressed as a superposition of configurations built up from a basic set of one-particle functions. By introducing the natural spin orbitals diagonalizing the first-order density matrix (1), the corresponding “natural expansion” of the total wave function may be obtained, and this series of configurations has then certain properties of maximum convergence.

In this paper, the case of $N=2$ has been investigated in greater detail. It has been shown that the total space function is equivalent with a quadratic form having a certain rank and signature and that the natural expansion of the wave function corresponds to the diagonal representation of this form. For the singlet, it has further been shown that the approximate wave function obtained by interrupting the natural expansion after r terms and renormalizing the series represents the *best* approximation of rank r , i.e., the function of rank r having the smallest total quadratic deviation from the exact wave function. A corresponding theorem holds also for the triplet. The case of $N=2$ is, of course, of particular simplicity, but the possibility of generalizing the results to many-electron systems is now being further investigated.

The theory has been exemplified by some results concerning the lowest singlet and triplet of the helium atom. Applications to the hydrogen molecule are now also in progress, but the results will be published elsewhere.

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