

Expansion Theorems for the Total Wave Function and Extended Hartree-Fock Schemes*

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1. EXPANSION THEOREMS

(a) Superposition of Configurations

IN order to solve the Schrödinger equation $\mathcal{H}\Psi = E\Psi$ for a system of N electrons, it is often convenient to use expansion theorems for the total wave function $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ where $\mathbf{x}_i = (\mathbf{r}_i, \zeta_i)$ is the combined space-spin coordinate for electron i . For this purpose, one may introduce a certain orthonormal and complete set of discrete one-electron functions or spin-orbitals $\psi_k(\mathbf{x})$ as a basis and assume the existence of an expansion theorem

$$\psi(\mathbf{x}) = \sum_k c_k \psi_k(\mathbf{x}) \quad (1)$$

for every normalizable function $\psi(\mathbf{x})$ of a single electronic coordinate. For a function of several electronic coordinates, one can then repeat the use of (1) for one coordinate at a time, which leads to an expansion of the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots) = \sum_{klm\dots} c_{klm\dots} \psi_k(\mathbf{x}_1) \psi_l(\mathbf{x}_2) \psi_m(\mathbf{x}_3) \dots \quad (2)$$

Every normalizable function of N particle coordinates can hence be expanded in Hartree-products built up from a complete basic set. This expansion can be further simplified for an electronic system, which obeys the Pauli exclusion principle mathematically equivalent to the antisymmetry requirement $P\Psi = (-1)^p\Psi$, where P is a permutation of the coordinates and p its parity. Introducing the antisymmetry projection operator

$$\Theta_{AS} = (N!)^{-1} \sum_P (-1)^p P, \quad (3)$$

fulfilling the relations

$$P\Theta_{AS} = (-1)^p \Theta_{AS}, \quad (\Theta_{AS})^2 = \Theta_{AS}, \quad (4)$$

we have $\Theta_{AS}\Psi = \Psi$, and, by applying operator (3) to both members of Eq. (2), we thus obtain

$$\begin{aligned} \Psi &= \Theta_{AS}\Psi \\ &= (N!)^{-1} \sum_{klm\dots} c_{klm\dots} \det\{\psi_k, \psi_l, \psi_m, \dots\} \\ &= \sum_{k<l<m\dots} c_{klm\dots} \det\{\psi_k, \psi_l, \psi_m, \dots\}. \end{aligned} \quad (5)$$

The relation shows that every normalizable antisymmetric wave function Ψ may be expanded in Slater determinants built up from a complete basic set, and this theorem forms the basis for the method of "super-

position of configurations." A selection K of N indices $k < l < m < \dots$ is called an "ordered configuration" and, introducing the notations

$$\Psi_K = (N!)^{-\frac{1}{2}} \det\{\psi_k, \psi_l, \psi_m, \dots\}, \quad C_K = (N!)^{+\frac{1}{2}} c_{klm\dots}, \quad (6)$$

one can write expansion (5) in the condensed form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sum_K C_K \Psi_K(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N). \quad (7)$$

In the N -electron configuration space, the Slater determinants Ψ_K form an antisymmetric basis fulfilling the orthonormality relation $\int \Psi_K^* \Psi_L(dx) = \delta_{KL}$. With respect to this basis, the Hamiltonian \mathcal{H}_{op} is represented by the matrix $\mathcal{H}_{KL} = \int \Psi_K^* \mathcal{H}_{op} \Psi_L(dx)$, where the elements are easily simplified.¹

In order to evaluate the coefficients C_K corresponding to the solutions of the Schrödinger equation $\mathcal{H}\Psi = E\Psi$, one conventionally applies the variation principle $\delta\langle \mathcal{H} \rangle_w = 0$, which leads to the equation system

$$\sum_L (\mathcal{H}_{KL} - E\delta_{KL}) C_L = 0, \quad (8)$$

where the eigenvalues E are determined by the secular equation

$$\det\{\mathcal{H}_{KL} - E\delta_{KL}\} = 0. \quad (9)$$

In principle, one can obtain any accuracy desired for an eigenfunction Ψ by means of an expansion of type (7). This fact was well known in the early days of wave mechanics but seems to have been almost forgotten during quite some time until the revival a decade ago by the work of Slater, Boys, Jucys, and others.

Convergency Problem

Even if the expansion (7) formally exists as soon as the basis $\{\psi_k\}$ is complete, the convergency may be exceedingly slow, and an important problem is hence to find the particular basis which leads to a most rapid convergency. This problem was first treated by Slater² who constructed the basis by solving a set of integro-differential equations similar to the Hartree-Fock equations.

The convergency problem can also be approached in a different way by studying the first-order density matrix.³ If the wave function Ψ is normalized so that

¹ J. C. Slater, Phys. Rev. **34**, 1293 (1929); **38**, 1109 (1931); E. U. Condon, *ibid.* **36**, 1121 (1930).

² J. C. Slater, Quarterly Progress Report of Solid-State and Molecular Theory Group at Massachusetts Institute of Technology, 6 (January 15, 1953) (unpublished); Tech. Rept. No. 3, 39 (February 15, 1953) (unpublished); Phys. Rev. **91**, 528 (1953).

³ P. O. Löwdin, Phys. Rev. **97**, 1474 (1955); *Advances in Phys.* **5**, 1 (1956); *Advances in Chemical Physics*, I. Prigogine, Editor (Interscience Publishers, Inc., New York, 1959), Vol. 2, p. 207.

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$\int |\Psi|^2(dx) = 1$, the first-order density matrix $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$ is defined by

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = N \int \Psi^*(\mathbf{x}_1' \mathbf{x}_2 \mathbf{x}_3 \cdots \mathbf{x}_N) \times \Psi(\mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_3 \cdots \mathbf{x}_N) dx_2 dx_3 \cdots dx_N. \quad (10)$$

By means of the basic set ψ_k and repeated use of (1), one can expand $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$ in the form

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = \sum_{kl} \psi_k^*(\mathbf{x}_1') \psi_l(\mathbf{x}_1) \gamma_{lk}, \quad (11)$$

where the coefficients γ_{lk} form an Hermitean matrix γ . By substituting (7) into (10) and carrying out the integrations, one finds relations between the quantities γ_{lk} and the coefficients C_K . For the diagonal elements, one obtains the simple formula

$$\gamma_{kk} = \sum_K^{(k)} |C_K|^2, \quad (12)$$

where the summation goes over all configurations K containing the specific index k . The diagonal element γ_{kk} may be interpreted as the "occupation number" of the spin-orbital ψ_k , and we note that it depends only on Ψ and ψ_k . Since the normalization gives $\sum_K |C_K|^2 = 1$, one has further the inequality $0 \leq \gamma_{kk} \leq 1$ which may be considered a consequence of the antisymmetry requirement and hence also of the Pauli principle.

Because of (12), there is a connection between the convergency property of expansion (7) and the diagonal elements of the matrix γ , and we now consider the optimum case. Let \mathbf{U} be the unitary matrix which brings γ to diagonal form:

$$\mathbf{U}^\dagger \gamma \mathbf{U} = \mathbf{n}, \quad (13)$$

where \mathbf{n} is a diagonal matrix with the eigenvalues $n_1 \geq n_2 \geq n_3 \geq \cdots$. Introducing a new basic set $\{\chi_k\}$ by the matrix formula $\chi = \psi \mathbf{U}$ or $\chi_k = \sum_\alpha \psi_\alpha U_{\alpha k}$, we obtain $\gamma = \mathbf{U} \mathbf{n} \mathbf{U}^\dagger$, $\psi = \chi \mathbf{U}^\dagger$, and

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = \sum_k \chi_k(\mathbf{x}_1') \chi_k(\mathbf{x}_1) n_k. \quad (14)$$

The basic set χ_k has hence the occupation numbers n_k , and, since they are the eigenvalues of γ , they have extremum properties. The first function χ_1 has the highest occupation number possible, the second function χ_2 has the same property within the class orthogonal to χ_1 , etc. The functions χ_k are called the "natural spin-orbitals" associated with the system and state under consideration.

Substituting the relation $\psi = \chi \mathbf{U}^\dagger$ or $\psi_k = \sum_\alpha \chi_\alpha U_{\alpha k}^\dagger$ into the Slater determinants of expansion (7) and using a theorem for evaluating the determinant of a matrix being a product of two rectangular matrices, we obtain an expansion of Ψ into configurations of the natural spin orbitals:

$$\Psi = (N!)^{-\frac{1}{2}} \sum_K A_K \det\{\chi_k, \chi_l, \chi_m, \cdots\}, \quad (15)$$

which are called the "natural expansion." This series has a certain optimum convergency property.

Let us consider the matrix γ and all possible submatrices $\gamma^{(r)}$ of order r along the diagonal which may be obtained by truncating the basis to finite order r . According to a well-known separation theorem,⁴ the r highest eigenvalues of γ are in order of magnitude larger than the corresponding eigenvalues of $\gamma^{(r)}$. The sum of the r highest eigenvalues of γ is hence always larger than the sum of the r eigenvalues of $\gamma^{(r)}$, i.e., larger than the sum of its r diagonal elements, which gives the general inequality

$$\sum_{k=1}^r n_k \geq \sum_{k=(1)}^{(r)} \gamma_{kk}, \quad (16)$$

where in the sum $k=(1) \cdots (r)$, one can take any r indices. By using (12), we obtain finally

$$\sum_{k=1}^r \sum_K^{(k)} |A_K|^2 \geq \sum_{k=(1)}^{(r)} \sum_K^{(k)} |C_K|^2, \quad (16')$$

for $r=1, 2, 3, \cdots$, which relation expresses the optimum convergency property of the natural expansion.

Case of Two-Electron Systems

In the special case of $N=2$, the properties of the natural expansion have been investigated in greater detail.⁵ The spin function may be taken out as a separate factor and, instead of (7), one obtains for the singlet state

$${}^1\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}} (\alpha_1 \beta_2 - \beta_1 \alpha_2) \sum_{k,l=1}^{\infty} C_{kl} \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2), \quad (17)$$

where $C_{lk} = C_{kl}$. The problem of diagonalizing the first-order density matrix $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$ is essentially a problem of diagonalizing the matrix \mathbf{C} , and the natural expansion takes the simple form

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

where $c_k = \pm n_k^{\frac{1}{2}}$. Hence the double sum in (17) has been reduced to a single sum in (18). A similar theorem holds also for the triplet state.

For $N=2$, the natural expansion (18) has in addition to (16) another important optimum convergency property. Let ${}^1\Psi_r(\mathbf{x}_1, \mathbf{x}_2)$ be any singlet wave function which may be built up from a basic orbital set of finite order r and consider the total quadratic deviation between the "exact solution" and such a trial function

$$\int |\Psi_{\text{exact}} - \Psi_r|^2 dx_1 dx_2. \quad (19)$$

⁴ E. A. Hylleraas and B. Undheim, *Z. Physik* **65**, 759 (1930); J. K. L. MacDonald, *Phys. Rev.* **43**, 830 (1933).

⁵ P. O. Löwdin and H. Shull, *Phys. Rev.* **101**, 1730 (1956).

It may be shown that this quantity has a minimum for

$${}^1\Psi_r(\mathbf{x}_1, \mathbf{x}_2) = 2^{-\frac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \times \sum_{k=1}^r c_k \chi_k(\mathbf{r}_1) \chi_k(\mathbf{r}_2) / \left\{ \sum_{k=1}^r c_k^2 \right\}^{\frac{1}{2}}, \quad (20)$$

which is actually the function obtained by truncating the natural expansion (18) after r terms and renormalizing the result. For two-electron systems, there are particularly two types of approximate wave functions which have been discussed,⁶ namely, the closed-shell or u^2 form and the split-shell or (u, v) form having $r=1$ and $r=2$, respectively. From the general theorem follows now that $(\chi_1)^2$ is the u^2 function which has the smallest quadratic deviation (19) from the exact eigenfunction. The first natural orbital χ_1 is hence closely related to the corresponding Hartree-Fock function and has actually only a slightly higher energy.⁷ The space function

$$(n_1^{\frac{1}{2}}\chi_1^2 - n_2^{\frac{1}{2}}\chi_2^2) / (n_1 + n_2)^{\frac{1}{2}} \quad (21)$$

is further the optimum function for $r=2$ and is easily transformed to (u, v) form⁸ by putting $u = n_1^{\frac{1}{2}}\chi_1 + n_2^{\frac{1}{2}}\chi_2$, $v = n_1^{\frac{1}{2}}\chi_1 - n_2^{\frac{1}{2}}\chi_2$.

The natural orbitals have so far been investigated in detail for the ground state of helium,⁹ for the long-range interaction between two hydrogen atoms,¹⁰ and for the hydrogen molecule,¹¹ and further work is in progress.

(b) Introduction of Correlation Factor

The first practical application of the method of superposition of configurations was carried out by Hylleraas¹² in connection with the helium problem, and he found that if the basic orbital set contained the spherical harmonics Y_{lm} in the conventional way, the expansion (7) converged comparatively slowly.¹³ Hylleraas¹⁴ suggested therefore that one should instead try to include the interelectronic distance r_{12} explicitly in the wave

function, and, for a two-electron system, r_{12} could actually be chosen as one of the basic coordinates. For the helium problem this led to a fruitful development which so far has culminated in the highly accurate calculations by Kinoshita¹⁵ and by Pekeris,¹⁶ the latter using perimetric coordinates. For the hydrogen molecule, the corresponding development started with James and Coolidge¹⁷ and has now reached the accurate level reported by Kolos¹⁸ at this conference.

Unfortunately this r_{12} coordinate approach cannot easily be generalized to a many-electron system. Another way of introducing r_{12} in the wave function was also suggested by Hylleraas¹⁴ who considered space functions of the form

$$g(r_{12})u(r_1)u(r_2), \quad (22)$$

where $g(r_{12})$ is a "correlation factor." By using the simple functions $g = \exp\{\alpha r_{12}\}$ and $g = 1 + \alpha r_{12}$, Hylleraas showed that one could obtain surprisingly good results. Both for the helium atom¹⁹ and the hydrogen molecule,²⁰ this idea has been extensively developed in the literature. In the more recent works, also quite a few nonlinear parameters have been varied, and excellent results have been obtained by the largest electronic computers available.

Here we would like to draw attention to the fact that the method with correlation factor can easily be combined with the method using superposition of configurations in such a way that very good results can be obtained without too extensive numerical calculations. If the correlation factor $g = g(r_{12})$ is nodeless and such that the function Ψ/g is still normalizable, one can apply the expansion theorems (17) and (18) to this function. For the symmetric space function associated with a singlet state for a two-electron system, this gives

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= g(r_{12}) \sum_{k,l=1}^{\infty} C_{kl} \psi_k(\mathbf{r}_1) \psi_l(\mathbf{r}_2) \\ &= g(r_{12}) \sum_{k=1}^{\infty} c_k \chi_k'(\mathbf{r}_1) \chi_k'(\mathbf{r}_2), \end{aligned} \quad (23)$$

where, for fixed g , the coefficients C_{kl} may be determined

¹⁵ T. Kinoshita, Phys. Rev. **105**, 1490 (1957); Phys. Rev. **115**, 366 (1959).

¹⁶ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); Phys. Rev. **115**, 1216 (1959).

¹⁷ H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

¹⁸ W. Kolos and C. C. J. Roothaan, Revs. Modern Phys. **32**, 205 (1960), this issue.

¹⁹ D. R. Hartree and A. L. Ingman, Mem. Proc. Manchester Lit. & Phil. Soc. **77**, 69 (1933); T. D. H. Baber and H. R. Hassé, Proc. Cambridge Phil. Soc. **33**, 253 (1937); P. Pluvinaige, Ann. Phys. **5**, 145 (1950); C. C. J. Roothaan, Colloq. intern. centre natl. recherche sci. (Paris) **82**, 49 (1958); L. C. Green, S. Matsushima, C. Stephens, E. K. Kolchin, M. M. Kohler, Y. Wang, B. B. Baldwin, and R. J. Wisner, Phys. Rev. **112**, 1187 (1958); C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. **32**, 194 (1960), this issue.

²⁰ A. A. Frost, J. Braunstein, and W. Schwemer, J. Am. Chem. Soc. **70**, 3292 (1948); W. Kolos and C. C. J. Roothaan, reference 18.

⁶ See, e.g., the contributions by R. S. Mulliken, M. Kotani, G. R. Taylor, and R. G. Parr in Proceedings of the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, Physics Branch of the Office of Naval Research (unpublished) (1951).

⁷ According to reference 9, the $(\chi_1)^2$ energy for the ground state of helium is -2.861530 a.u._{He} to be compared with the SCF energy -2.861673 a.u._{He}.

⁸ C. A. Coulson and I. Fischer, Phil. Mag. **40**, 386 (1949).

⁹ H. Shull and P. O. Löwdin, J. Chem. Phys. **30**, 617 (1959).

¹⁰ J. O. Hirschfelder and P. O. Löwdin, Mol. Phys. **2**, 229 (1959).

¹¹ H. Shull, Tech. Notes No. 17 (September 15, 1958) and No. 26 (June 5, 1959) from the Uppsala Quantum Chemistry Group (to be published).

¹² E. A. Hylleraas, Z. Physik **48**, 469 (1928).

¹³ Recent investigations (see reference 9) indicate that the energy limit for wave functions including f orbitals ($l=3$) would be -2.90332 a.u._{He} compared to the exact value -2.90372 a.u._{He}. Including angular terms up to $l=5$, D. H. Tycho, L. H. Thomas, and K. M. King, Phys. Rev. **109**, 369 (1958), obtained -2.90343 a.u._{He}, but they did not get any appreciable improvement by including additional terms up to $l=14$. A closer investigation of this convergence problem would certainly be of value.

¹⁴ E. A. Hylleraas, Z. Physik **54**, 347 (1929).

by the variation principle. By using the simple factor $g=1+\alpha r_{12}$, this method has so far been applied to the helium atom.²¹

This approach can now be generalized to a many-electron system. Let us introduce a "correlation factor" $g=g(r_{12}, r_{13}, r_{23}, \dots)$ which is a symmetric function of all the $N(N-1)/2$ interelectronic distances r_{ij} or, still more general, an even and symmetric function of the corresponding vectors $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. Let us further assume that g is nodeless and such that the quotient $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)/g$ is still normalizable. By applying the expansion theorem (7) to the function Ψ/g , we obtain the representation

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = g(r_{12}, r_{13}, r_{23}, \dots) \times \sum_K C_K \Psi_K(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N), \quad (24)$$

where, for fixed g , the coefficients C_K may be determined by the variation principle. The antisymmetric wave function Ψ is here described in a configuration space spanned by the basic vectors $g\Psi_K$, and the main practical difficulty is connected with the evaluation of such parts of the matrix elements \mathcal{H}_{KL} where the integrand contains three or more interelectronic distances r_{ij} . Convenient test problems are here provided by the lithium and beryllium atoms.

In this connection, I would also like to draw attention to the important work on the lighter atoms carried out by Jucys and his group in Vilna, Lithuania, by means of the method of superposition of configurations or modifications of this scheme by introducing self-consistency requirements or convenient correlation factors. Since 1947, the group has published more than 30 papers on this subject in various journals in U.S.S.R., but unfortunately only a few of them have been translated into English.

(c) Symmetry Properties and Projections

In studying the solution of the Schrödinger equation $\mathcal{H}\Psi=E\Psi$, we now consider the case when there exists an auxiliary operator Λ symmetric in all coordinates which commutes with the Hamiltonian \mathcal{H} so that $\Lambda\mathcal{H}=\mathcal{H}\Lambda$. For the sake of simplicity, the eigenvalue problem

$$\Lambda\Theta_l=\lambda_l\Theta_l \quad (25)$$

is assumed to have only a finite number of discrete solutions for $l=1, 2, 3, \dots, n$, where later we can let $n \rightarrow \infty$ provided our expressions remain convergent. Let Θ be an arbitrary trial function which is expandable in the form

$$\Theta = \sum_{l=1}^n a_l \Theta_l, \quad (26)$$

and let us now try to construct an operator Θ_k which, applied to Θ , selects only the term corresponding to $l=k$:

$$\Theta_k\Theta = a_k\Theta_k. \quad (27)$$

Since one can visualize the expansion (26) by considering a Hilbert space spanned by the basic vectors $\Theta_1, \Theta_2, \dots, \Theta_n$, in which it is required to resolve an arbitrary vector Θ into components along the axes, one can say that the meaning of Θ_k is to take the "parallel projection" of Θ on the axis Θ_k . Repeated use of Θ_k does not change the result, which leads to the relation $\Theta_k^2=\Theta_k$ characteristic for the projection operators.²² Since further, $\Theta_k\Theta_l=0$ for $k \neq l$, one has

$$\Theta_k\Theta_l = \Theta_k\delta_{kl}. \quad (28)$$

It is immediately clear that the product operator³

$$\Theta_k = \prod_{l \neq k} \frac{\Lambda - \lambda_l}{\lambda_k - \lambda_l}, \quad (29)$$

has the selective property (27) desired. Since

$$(\Lambda - \lambda_l)\Theta_l = 0,$$

all terms in (26) having $l \neq k$ are annihilated, whereas the term for $l=k$ survives the operation in an unchanged form. In (29) each eigenvalue λ_l appears only once, even if it is multiple, and, if the eigenvalue λ_k itself is degenerate, the operator Θ_k does not project on a specific axis but on the entire subspace associated with this eigenvalue.

In the following we assume that Λ is either self-adjoint or normal, i.e., commutes with its Hermitean adjoint operator Λ^\dagger so that $\Lambda\Lambda^\dagger=\Lambda^\dagger\Lambda$. This condition is fulfilled both by the operators corresponding to the physical observables and by the unitary operators associated with the basic symmetry operations. A normal operator Λ may be written as the sum of a Hermitean part and an anti-Hermitean part, which commute with each other and hence have simultaneous eigenfunctions Θ_l . These functions are then also simultaneous eigenfunctions to Λ and Λ^\dagger associated with the eigenvalues λ_l and λ_l^* , respectively. Since eigenfunctions Θ_k and Θ_l associated with different eigenvalues are now automatically orthogonal, the operators Θ_k describe orthogonal projections. The selection effect of the operator Θ_k^\dagger is identical with that of Θ_k , i.e., the operator is essentially self-adjoint. As a general rule self-adjoint projection operators select orthogonal projections, and reverse.

Since Λ commutes with \mathcal{H} , the same holds for the projection operators Θ_k formed by (29), instead of (28), we obtain now the more useful relations

$$\Theta_k^\dagger\mathcal{H}\Theta_l = \mathcal{H}\Theta_k\delta_{kl}, \quad \Theta_k^\dagger\Theta_l = \Theta_k\delta_{kl}, \quad (30)$$

which form the basis for the practical applications of the theory. Let Φ_I and Φ_{II} be two arbitrary trial functions which are identical or not. By means of the quantum mechanical "turnover rule" and (30), we

²¹ P. O. Löwdin and L. Redei, Phys. Rev. **114**, 752 (1959).

²² J. von Neumann, *Math. Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943), p. 41.

obtain for their projections

$$\begin{aligned} \int (\Theta_k \Phi_I)^* \mathcal{C}(\Theta_l \Phi_{II})(dx) &= \int \Phi_I^* \Theta_k^\dagger \mathcal{C} \Theta_l \Phi_{II}(dx) \\ &= \delta_{kl} \int \Phi_I^* \mathcal{C} \Theta_k \Phi_{II}(dx), \end{aligned} \quad (31)$$

$$\begin{aligned} \int (\Theta_k \Phi_I)^* (\Theta_l \Phi_{II})(dx) &= \int \Phi_I^* \Theta_k^\dagger \Theta_l \Phi_{II}(dx) \\ &= \delta_{kl} \int \Phi_I^* \Theta_k \Phi_{II}(dx), \end{aligned} \quad (32)$$

showing that, for $k \neq l$ the projections $(\Theta_k \Phi_I)$ and $(\Theta_l \Phi_{II})$ are not only *orthogonal* but also *noninteracting* with respect to \mathcal{C} .

Let us now consider an antisymmetric wave function $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ which is already an eigenfunction to Λ so that $\Lambda \Psi = \lambda \Psi$ and $\Theta \Psi = \Psi$, where for a moment we have dropped index k . Letting the operator Θ work on both members of (7), we obtain

$$\Psi = \Theta \Psi = \sum_K C_K (\Theta \Psi_K), \quad (33)$$

showing that a simultaneous eigenfunction to \mathcal{C} and Λ may actually be expanded into the projections $\Theta \Psi_K$ of the Slater determinants Ψ_K . The functions $\Theta \Psi_K$ usually are not linearly independent and expansion (33) often may be considerably condensed by eliminating the redundancies. Since Λ was assumed to be fully symmetric in the coordinates $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N$ and hence commutes with all the permutations P , the projection operator Θ defined by (29) commutes with the antisymmetrization operator Θ_{AS} defined by (3). The antisymmetric character of Ψ is hence undisturbed by the projection Θ .

The existence of an auxiliary normal operator Λ , which commutes with \mathcal{C} and Θ_{AS} , could be used to split the secular equation (9), but we note that a much more powerful approach could be obtained by splitting the basis $\{\Psi_K\}$ by the projection operators Θ_k into the orthogonal and noninteracting bases

$$\{\Theta_1 \Psi_K\}, \quad \{\Theta_2 \Psi_K\}, \quad \dots \{\Theta_n \Psi_K\}. \quad (34)$$

This leads automatically to a splitting of the secular equation (9), since we obtain a smaller secular equation for each one of the eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_n$, but for different values of λ_k , one could now actually choose different basic spin orbitals $\{\psi_j\}$ or different adjustable parameters describing this set. This new degree of freedom in the projection technique is particularly of importance in calculations using truncated sets.

Projection operators of the simple product type (29) have so far been successfully used for creating wave functions of pure total spin²³ and pure angular mo-

²³ P. O. Löwdin, Phys. Rev. **97**, 1509 (1955); Colloq. intern. centre natl. recherche sci. (Paris) **82**, 23 (1958).

menta²⁴ in general. They have also been used for constructing Bloch functions in the case of translational symmetry.²⁵ It is clear that a much more general class of projection operators or fundamental idempotents exist in the group algebra,²⁶ and that they could be used in exactly the same way, provided that they commute with the Hamiltonian and hence fulfill the relations (30). The antisymmetry projection operator (3) is a typical example. Many otherwise useful projection operators of this category are unfortunately ruled out since they do not commute with the Hamiltonian and Θ_{AS} , and particularly the treatment of degeneracies requires special consideration.²⁷

One can improve the speed of convergency of expansion (33) by introducing a correlation factor $g = g(r_{12}, r_{13}, r_{23}, \dots)$ which is totally symmetric. This leads to the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = g(r_{12}, r_{13}, r_{23}, \dots) \sum_K C_K (\Theta \Psi_K), \quad (35)$$

which is a combination of (24) and (33).

2. EXTENSION OF THE HARTREE-FOCK SCHEME

If the expansion (7) is truncated to a single Slater determinant D and the N spin orbitals involved are optimized to give the best total energy possible, one obtains the conventional Hartree-Fock scheme. Various extensions of this scheme are possible by starting out from the expansions (24), (33), and (35), and truncating them to a single dominant term. Hence we obtain, in order,

$$\begin{aligned} \Psi &\approx D, & \Psi &\approx gD, \\ \Psi &\approx \Theta D, & \Psi &\approx g\Theta D. \end{aligned} \quad (36)$$

Common features of all these approximations are that the number of spin orbitals involved equals the number of electrons, that, except for an irrelevant normalization factor, the total wave function is invariant under linear transformations of these basic functions, and that one can without loss of generality choose the basis $\psi_1, \psi_2, \dots, \psi_N$ orthonormal. The fundamental quantity in all four approximations is apparently the Fock-Dirac density matrix,

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{k=1}^N \psi_k^*(\mathbf{x}_1) \psi_k(\mathbf{x}_2), \quad (37)$$

which is also invariant under transformations of the basis.

Let us start by considering the case $\Psi \approx \Theta D$, where the total wave function is approximated by a projection of a single Slater determinant. This wave function is

²⁴ See a series of research reports from the Uppsala Quantum Chemistry Group 1956-1959 (unpublished).

²⁵ P. O. Löwdin, Advances in Phys. **5**, 56 (1956).

²⁶ See, e.g., E. P. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Vieweg und Sohn, Braunschweig, 1931); D. E. Littlewood, *Theory of Group Characters and Matrix Representations of Groups* (Clarendon Press, Oxford, 1950).

²⁷ Cf. P. O. Löwdin, reference 3, p. 290.

not only antisymmetric under permutations but is also an eigenfunction to the auxiliary operator Λ commuting with \mathcal{H} or fulfills certain additional symmetry requirements connected with Θ . The function ΘD could be expressed as a sum of determinants—a “codetor” according to Boys’s terminology—but the condensed projection form has several advantages, e.g., in showing the invariance under linear transformations of the basis $\{\psi_k\}$ and in connection with the use of the “turn-over rule” in (31) and (32). For the normalization integral, we obtain, according to (32),

$$c = \int |\Psi|^2(dx) = \int D^* \Theta D(dx), \quad (38)$$

and it turns out that for very important categories of projections (e.g., those connected with angular momenta), this quantity is a *constant* characteristic for the projection Θ under certain conditions on the spin orbitals $\{\psi_k\}$. By using (31), we obtain for the total energy

$$\langle \mathcal{H} \rangle = \int D^* (c^{-1} \mathcal{H}_{\text{op}} \Theta) D(dx), \quad (39)$$

which is exactly the same expression as in the conventional Hartree-Fock theory except that \mathcal{H}_{op} has been replaced by the composite Hamiltonian

$$\mathcal{H}_{\text{op}}' = c^{-1} \mathcal{H}_{\text{op}} \Theta. \quad (40)$$

It has been shown²⁸ that even in the case of complicated Hamiltonians containing many-particle interactions, the one-particle scheme based on a single determinant D leads to Hartree-Fock equations of the conventional form

$$H_{\text{eff}}(1) \psi_k(\mathbf{x}_1) = \sum_{l=1}^N \psi_l(\mathbf{x}_1) \lambda_{lk}, \quad (41)$$

where, according to Eq. (40) in reference 28, the effective Hamiltonian \mathcal{H}_{eff} depends only on the total Hamiltonian \mathcal{H}_{op} and the density matrix ρ defined in (37). Since H_{eff} is invariant under unitary transformations of $\{\psi_k\}$, the right-hand member can further be diagonalized to the form $\epsilon_k \psi_k$. This implies that the variation problem $\delta \langle \mathcal{H} \rangle_{\text{av}} = 0$ connected with (39) leads to extended Hartree-Fock equations of the type (41), where H_{eff}' now depends on the operator $c^{-1} \Theta$ in addition to \mathcal{H}_{op} and ρ . Hence the symmetry properties of the state under consideration influences now the effective Hamiltonian. Again the right-hand member can be diagonalized to the form $\epsilon_k \psi_k$, provided the normalization integral (38) remains invariant also under this unitary transformation.

So far, we have assumed that the normalization integral (38) is a constant c characteristic for the projection Θ . If this is not the case, one must, instead of

(39), consider the more general expression

$$\langle \mathcal{H} \rangle_{\text{av}} = \int D^* (\mathcal{H} \Theta) D(dx) / \int D^* \Theta D(dx), \quad (42)$$

and the variation principle $\delta \langle \mathcal{H} \rangle_{\text{av}} = 0$ leads again to one-dimensional eigenvalue problems²⁸ which are generalizations of the type (41). This approach is mathematically more complicated, but it has the advantage that there are no extra constraints on the basic spin orbitals $\{\psi_k\}$ which could prevent an optimum lowering of the energy.

The split-shell method for treating two-electron systems, frequently discussed in the current literature,⁶ may be considered as a special case of the general type $\Psi \approx \Theta D$. Two spin states are here possible—a singlet and a triplet—and, according to (29), the singlet projection operator takes the form ${}^1\Theta = 1 - S^2/1.2 = \frac{1}{2}(1 - P_{12}^t)$. Starting out from a single Slater determinant $D = \det\{u\alpha, v\beta\}$, one obtains

$${}^1\Theta D = \frac{1}{2}(\alpha_1\beta_2 - \beta_1\alpha_2)(u_1v_2 + u_2v_1),$$

which is the (u, v) form used in the split-shell theory. By using (38), one gets for the normalization integral $c = 1 + |\int u^*v(d\mathbf{r})|^2$, which is constant $c = 1$, if u and v are assumed to be orthogonal. In general, however, it is essential that u and v may be overlapping and, in such a case, the energy variation must be based on (42).

The results obtained so far on helium^{6,9}, lithium²⁹ and beryllium³⁰ seem very promising, and further applications on the lighter atoms are now in progress. For molecules and crystals, the exact solution of the extended Hartree-Fock equations is a rather cumbersome numerical problem which can be replaced by approximate schemes of a simpler type, like the alternant-molecular orbital method.³¹

In conclusion, we also consider the extended Hartree-Fock schemes based on the approximations $\Psi \approx gD$ and $\Psi \approx g(\Theta D)$, where g is a correlation factor

$$g = g(r_{12}, r_{13}, r_{23}, \dots).$$

The results on the helium atom²¹ and the hydrogen molecule²⁰ obtained by using wave functions of the form $g(u)^2$ and $g(u, v)$ and simple correlation factors g seem very promising, but, in order to extend this approach practically to many-electron systems, one has to master the energy integrals containing more than two inter-electronic distances r_{ij} . In this connection, it is inter-

²⁹ G. H. Brigman and F. A. Matsen, *J. Chem. Phys.* **27**, 829 (1957); R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, *Mol. Phys.* **1**, 189 (1958); E. A. Burke and J. F. Mulligan, *J. Chem. Phys.* **28**, 995 (1958).

³⁰ G. H. Brigman, R. P. Hurst, J. D. Gray, and F. A. Matsen, *J. Chem. Phys.* **29**, 251 (1958).

³¹ P. O. Löwdin, *Nikko Symposium on Molecular Physics*, 13 (Maruzen, Tokyo, 1954); *Phys. Rev.* **97**, 1509 (1955); T. Itoh and H. Yoshizumi, *J. Phys. Soc. Japan* **10**, 201 (1955); H. Yoshizumi and T. Itoh, *J. Chem. Phys.* **23**, 412 (1955); Busseiron Kenkyu **82**, 13 (1955) (in Japanese).

²⁸ P. O. Löwdin, *Phys. Rev.* **97**, 1490 (1955).

TABLE I. Different expansion methods and extended Hartree-Fock schemes with helium errors in kcal/mole.

Expansion	Principal term	Helium error ^a
$\Psi = \sum_K C_K \Psi_K$	$\Psi \approx D$	26.3
$\Psi = \sum_K C_K (\Theta \Psi_K)$	$\Psi \approx \Theta D$	16.0
$\Psi = g \sum_K C_K \Psi_K$	$\Psi \approx gD$	2.3
$\Psi = g \sum_K C_K (\Theta \Psi_K)$	$\Psi \approx g\Theta D$	1.2

^a The errors refer to a case where $g=1+\alpha r_{12}$ and Θ stands for a spin projection only.

esting to note that Krisement³² has pointed out that the form $\Psi \approx gD$ is closely connected both with Wigner's³³ classical theory for the electrons in an alkali metal and Bohm and Pines³⁴ plasma model.

3. DISCUSSION

In this paper, we have tried to show how the expansion (7) of configurations could be gradually changed by the introduction of a correlation factor

$$g = g(r_{12}, r_{13}, r_{23}, \dots)$$

or a projection operator Θ , or both. It is anticipated that this transformation would lead to an improvement in the rate of convergency, and, in Sec. 2, we have discussed the various Hartree-Fock schemes (36) which are obtained by truncating the expansions to a single dominant term. One gets an idea of the strength of the various methods from Table I, where we have listed the helium errors^{9,29} in kcal/mole for the optimized truncated wave functions.

Let us now discuss the physical reasons for the obvious improvement which comes from the introduction of Θ and g . The conventional Hartree-Fock scheme having $\Psi \approx D$ is originally based on the independent-particle model, in which one neglects the fact that the electrons actually repel each other, so that each electron is surrounded by a "Coulomb hole" with respect to all other electrons. Since the electrons apparently try to avoid each other, there is a certain correlation between their movements, and the omission of this effect causes a so-called "correlation error." This picture is partly changed by the introduction of the antisymmetry requirement through the use of (3), since each electron is now surrounded by a "Fermi

hole" with respect to all other electrons having the same spin.³⁵ The correlation error in the Hartree-Fock scheme can hence be essentially attributed to electrons having antiparallel spins, and 1.1 ev is a rather typical figure for a single electron pair. According to the virial theorem, this correlation error consists of an error of -1.1 ev in the kinetic energy, which comes out so low since the electrons are permitted to make simpler movements when they do not have to avoid each other, and an error of $+2.2$ ev in the Coulomb potential.

The pairing of electrons with antiparallel spins in the same orbital is a characteristic feature of the conventional Hartree-Fock scheme, which is mathematically convenient since it enables us to construct pure spin functions easily, but which is physically more doubtful since it introduces large correlation errors. If the pure spin functions are instead created by spin-projection operators, one can permit "different orbitals for different spins" and, since the electrons having antiparallel spins now get a possibility to avoid each other in space, the correlation error starts going down. A still better result can be obtained by also introducing other projection operators, e.g., in the helium case, the orbital angular-momentum operator creating S states.

If the correlation factor $g = g(r_{12}, r_{13}, r_{23}, \dots)$ is chosen so that it has its smallest value when any $r_{ij} = 0$, the form $\Psi \approx gD$ corresponds to the introduction of a "Coulomb hole" for both parallel and antiparallel spins. The correlation error goes then down essentially, and, by combining the use of g and Θ , one can apparently in the helium case approach a good "chemical" accuracy of about 1.2 kcal/mole even with the simple function $g = 1 + \alpha r_{12}$.

The main advantage of the Hartree-Fock schemes here described comes from the fact that they have a strong physical and chemical visuality which leads to a simple model of the system under consideration. On the other hand, the solution of the corresponding Hartree-Fock equations is usually a numerically extremely cumbersome procedure involving nonlinear integro-differential equations, and, in this connection, one should observe that it is usually considerably simpler to solve linear secular equations of the type (9). In the latter case, there are further no limitations on the accuracy obtainable, and the final results can always be simplified by going over to the natural expansions.

³² O. Krisement, *Phil. Mag.* **2**, 245 (1957).

³³ E. Wigner, *Phys. Rev.* **46**, 1002 (1934); *Trans. Faraday Soc.* **34**, 678 (1938).

³⁴ See, e.g., D. Pines, *Solid State Phys.* **1**, 368 (1957).

³⁵ E. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933); J. C. Slater, *ibid.* **81**, 385 (1951).