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The Solution of Schrödinger's Equation for Two-Electron Systems by an MCHF Procedure

CHARLOTTE FROESE FISCHER

Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada

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Assuming the existence of a complete set of orthonormal radial functions $\{P_{nl}(r), n = l + 1,...\}$, $l = 0, 1,...$ and an expansion of the exact total wavefunction for a two-electron system, it is shown that orthogonal transformations of the radial functions exist so that the expression can be reduced from a triple to a double sum. The exact form depends on the symmetry of the state.

A procedure is proposed for solving Schrödinger's equation using an MCHF approach to the reduced form. Convergence of the process is illustrated for the $1s^2\,{}^1S$, $1s2s\,{}^{1,3}S$, and $1s2p\,{}^{1,3}P$ states of He using numerical methods.

I. INTRODUCTION

With the work of Pekeris [1, 2] and his co-workers [3] the two-electron problem is effectively solved. They have shown that highly accurate solutions of Schrödinger's nonrelativistic equation can be obtained by expanding the wavefunction if terms of perimetric coordinates, which are linear combinations of r_1, r_2, and r_{12}, and solving an equivalent variational problem. Accurate results have been computed for most of the observed S and P states of two electron systems with atomic number $Z = 2$ to 10 [4].

The Hartree–Fock (HF) method [5] has been used successfully to provide a qualitative description of the atom. Though the accuracy is not anywhere near that obtained by Pekeris *et al.* for the two-electron system, it has the advantage that large atoms can be dealt with almost as readily as small ones with the computational time of a numerical procedure increasing roughly as the groups of equivalent electrons [6]. An improvement upon the HF scheme which retains many of its advantages, is the multiconfiguration Hartree–Fock (MCHF) approximation [7, 8]. In this paper, an MCHF scheme is proposed for solving the two-electron problem which reduces the number of configurations that need be considered. It is similar, but not identical, to Löwdin's [7] natural orbital expansion method and can be extended to systems with more than two electrons. The scheme is applied to $1s^2\,{}^1S$, $1s2s\,{}^{1,3}S$, and $1s2p\,{}^{1,3}P$ of Helium using a numerical MCHF approach: the results are presented and compared with the "exact" ones.

II. The Numerical MCHF Approach

The numerical MCHF approach is best illustrated by means of an example. Suppose we wish to approximate the exact total wavefunction ψ for the $1s^2\,{}^1S$ state by $\bar{\psi}$. The MCHF approach assumes that $\bar{\psi}$ can be expressed as a linear combination of wavefunctions for configurations or "configuration state functions"; in particular, a two-configuration approximation could be

$$\bar{\psi}(1s^2\,{}^1S) = a_1\Phi(1s^2\,{}^1S) + a_2\Phi(2s^2\,{}^1S), \tag{1}$$

where $\Phi(ns^2\,{}^1S)$ in this case is a single Slater determinant for the configuration ns^2, but in general would be a linear combination of determinants. The unknown quantities in $\bar{\psi}$ are the radial functions, $P_{1s}(r)$ and $P_{2s}(r)$, and the mixing coefficients, a_1 and a_2. These are to be determined such that the total energy,

$$E = \langle \bar{\psi} \mid H \mid \bar{\psi}\rangle / \langle \bar{\psi} \mid \bar{\psi}\rangle$$

is stationary.

An expression for the energy can readily be derived if we make the following assumptions:

(i) $\int_0^\infty P_{ns}(r)\, P_{ms}(r)\, dr \equiv \langle ns \mid ms\rangle = \delta_{nm}$

(ii) $a_1^2 + a_2^2 = 1$.

Then, in Slater's [10] notation,

$$E = a_1^2\{2I(1s) + F^0(1s, 1s)\} + 2a_1a_2G^0(1s, 2s) + a_2^2\{2I(2s) + F^0(2s, 2s)\}.$$

But before the variational principle can be applied Lagrange multipliers must be introduced for each constraint. In our example, the functional which must remain stationary is

$$W = E + \lambda_{1s1s}\langle 1s \mid 1s\rangle + \lambda_{1s2s}\langle 1s \mid 2s\rangle + \lambda_{2s2s}\langle 2s \mid 2s\rangle - \lambda(a_1^2 + a_2^2).$$

As in the single configuration approximation [10], the requirement that $\delta W = 0$ for variations in both $P_{1s}(r)$ and $P_{2s}(r)$ leads to the MCHF equations,

$$\begin{aligned} LP_{1s}(r) = {} & (2/r)[Y^0(1s, 1s; r)\, P_{1s}(r) + (a_2/a_1)\, Y^0(1s, 2s; r)\, P_{2s}(r)] \\ & + \epsilon_{1s1s}P_{1s}(r) + \epsilon_{1s2s}P_{2s}(r) \end{aligned}$$

and

$$\begin{aligned} LP_{2s}(r) = {} & (2/r)[Y^0(2s, 2s; r)\, P_{2s}(r) + (a_1/a_2)\, Y^0(1s, 2s; r)\, P_{1s}(r)] \\ & + \epsilon_{2s1s} P_{1s}(r) + \epsilon_{2s2s} P_{2s}(r), \end{aligned}$$

where

$$L = \frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2}$$

and

$$\epsilon_{nsns} = \lambda_{nsns}/a_n{}^2; \qquad n = 1, 2,$$

$$\epsilon_{1s2s} = \lambda_{1s2s}/(2a_1{}^2); \qquad \epsilon_{2s1s} = (a_1/a_2)^2\, \epsilon_{1s2s}\, .$$

The boundary conditions are $P_{ns}(0) = 0$ and $P_{ns}(\infty) = 0$. The requirement that $\delta W = 0$ for variations in a_1 and a_2 leads to the secular equations:

$$\begin{bmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

where $H_{nn} = 2I(ns) + F^0(ns, ns)$ and

$$H_{12} = H_{21} = G^0(1s, 2s).$$

The MCHF equations together with the secular equations define the stationary energy. Note that the equations defining the radial functions depend on the mixing coefficients and vice versa. As a result, these two problems must be solved simultaneously. Note also that for small values of a_2, the equation for $P_{1s}(r)$ is nearly the same as that for a single configuration but that the equation for $P_{2s}(r)$ is quite different. The dominant term is $Y^0(1s, 2s; r)\, P_{1s}(r)$ which originates from the interaction of $2s^2$ with $1s^2$.

In general, in the m-configuration approximation (which we shall denote by MCHF_m),

$$\psi(\gamma LS) = \sum_{i=1}^{m} a_i \Phi(\gamma_i LS),$$

where γ is the label for the state and γ_i the i-th configuration. The unknowns are the radial functions, $P_{nl}^{(i)}(r)$, which occur in the configuration state functions $\Phi(\gamma_i LS)$, and the mixing coefficients, a_i, $i = 1, 2, \ldots, m$. Orbitals with the same (nl) quantum numbers but in different configurations need not have the same radial function, but in order for the energy expression to have a suitable form, it is convenient to assume[1]

(i) $\int_0^\infty P_{nl}^{(i)}(r)\, P_{n'l}^{(i)}(r)\, dr = \delta_{nn'}$

(i.e., two radial functions with the same l dependence occurring within the same configuration state function are orthogonal).

(ii) $\langle \Phi(\gamma_i LS) \mid \Phi(\gamma_j LS) \rangle = \delta_{ij}$.

(iii) $\sum_{i=1}^{m} a_i^2 = 1$.

Condition (ii) often will be satisfied when radial functions belonging to two *different* configuration state functions are also orthogonal, but when the angular quantum numbers are different there is no need to introduce such a constraint. For example, the approximation

$$\psi(1s2p\,{}^1P) = a_1\Phi(1s2p\,{}^1P) + a_2\Phi(3p3d),$$

where $\langle 2p \mid 3p \rangle \neq 0$, satisfies all the above requirements.

Once an energy expression has been obtained, the variational procedure can be applied as in the single configuration approximation (see Slater [10]), resulting in a system of MCHF equations, one for each radial function in the approximation, and a system of secular equations of order m.

In order to obtain the energy expression, angular momentum integrals for the energy matrix element

$$H_{ij} = \langle \Phi(\gamma_i LS) \mid H \mid \Phi(\gamma_j LS) \rangle$$

must be evaluated, where H is the Hamiltonian for the system. For the two-electron system considered here,

$$H = H_1 + H_2 + V$$

where

$$H_\alpha = -(1/2)\,\nabla_\alpha^2 + Z/r_\alpha\,, \quad \alpha = 1, 2, \qquad \text{and} \qquad V = 1/r_{12}\,.$$

Let us assume

$$\gamma_i = (n_1 l_1 n_2 l_2), \quad l_1 \leqslant l_2\,, \qquad \text{and} \qquad n_1 \leqslant n_2 \quad \text{when} \quad l_1 = l_2\,,$$
$$\gamma_j = (n_3 l_3 n_4 l_4), \quad l_3 \leqslant l_4\,, \qquad \text{and} \qquad n_3 \leqslant n_4 \quad \text{when} \quad l_3 = l_4\,,$$

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[1] For larger atomic systems, the expression for interactions between configurations may become unwieldy unless it is also assumed that a common core of electrons have the same radial function.

then the one-electron part of the Hamiltonian, $H_1 + H_2$, will make a nonzero contribution only if $l_1 = l_3$ and $l_2 = l_4$ and $n_1 = n_3$ or $n_2 = n_4$, i.e., the two configurations are the same or differ only in the principal quantum number of one electron. Then

$$\langle \Phi(n_1l_1n_2l_2) \mid H_1 + H_2 \mid \Phi(n_1l_1n_2l_2)\rangle = I(n_1l_1) + I(n_2l_2)$$

and

$$\langle \Phi(n_1l_1n_2l_2) \mid H_1 + H_2 \mid \Phi(n_1l_1n_3l_3)\rangle = I(n_2l_2, n_3l_3),$$

$$\langle \Phi(nl^2) \mid H_1 + H_2 \mid \Phi(nln'l)\rangle = \sqrt{2}\, I(nl, n'l),$$

where

$$I(nl, n'l) = -(1/2)\langle nl \mid L \mid n'l\rangle \qquad \text{and} \qquad I(nl, nl) = I(nl).$$

The contribution from V can be obtained using Hibbert's [11] program for evaluating angular momentum integrals.

Given the expression for the energy, the radial functions and mixing coefficients, which define $\bar{\psi}$, can be calculated using the program, MCHF72 [6], modified to allow for contributions $I(nl, n'l)$ from interactions between configurations and extended to include g-electrons.

The MCHF72 program solves the MCHF problem iteratively. Given estimates of a_i (which should at least specify the dominant component) and estimates of radial functions (possibly screened hydrogenic functions), the program repetitively improves first the radial functions then the mixing coefficients, so that both converge simultaneously. The iterative solution of the MCHF equations incorporates procedures with improved stability [12]. The $\rho = \log(Zr)$ variable is used for solving the radial equation so that an equal step-size may be used throughout, and Numerov's method together with a deferred difference correction [13] is used for approximating the radial equation.

The numerical procedures have been checked using hydrogenic functions (see [6] for details). For $n \leqslant 2$, the relative errors tend to be 10^{-8} or less. In an actual MCHF calculation, the self-consistency of the radial functions is restricted by the accuracy of the total energy. As a result, a radial function for a configuration which contributes very little to the total energy cannot be determined to the same degree of self-consistency as one which contributes significantly; in fact it would be pointless to attempt such accuracy. For example, Table 2 shows that in an MCHF_{11} calculation for $1s^2\,{}^1S$ of He, the mixing coefficients for $5g^2$ is -0.001894. This calculation terminated when the last iteration lowered the energy by 4.0×10^{-8}, with the maximum change in $P_{5g} = 1.0 \times 10^{-2}$ and $\max(P_{5g}) = 1.26$; the change in the $5g^2$ mixing coefficient was 9.0×10^{-6}. Another indication of the overall accuracy, can be obtained from a direct calculation of both the total energy and the Kinetic energy. In this example,

$$\begin{aligned} E(\text{Total}) &= -2.9030331, \\ E(\text{Kinetic}) &= 2.9030165. \end{aligned}$$

In general, as the degree of self-consistency improves, E(Kinetic) tends to approach E(Total) which changes very little. For example, an earlier calculation which terminated when the maximum change in P_{5g} was 2.5×10^{-2}, gave

$$\begin{aligned} E(\text{Total}) &= -2.9030330, \\ E(\text{Kinetic}) &= 2.9029931. \end{aligned}$$

MCHF72 represents a significant improvement in accuracy over the earlier program [14].

As in single configuration calculations, difficulties tend to be associated with orthogonality constraints. In such cases it is better to perform a series of calculations, each time introducing a new configuration in the order of importance. For example, in the calculation for the MCHF_2 approximation of Eq. (1), it is clear that a_1 will be at least an order of magnitude greater than a_2. Then, as already mentioned, P_{1s} will be similar to that of a single configuration which provides a good initial estimate for the two-configuration calculation. In this way, at least one of a pair of orthogonal functions can be estimated reasonably accurately.

The MCHF approach itself provides no insight or guidance to the question of which configurations should be included in order to obtain a reasonably accurate approximate wavefunction $\tilde{\psi}(\gamma LS)$. In fact, simply adding configurations indiscriminately may lead to systems of equations which do not have a unique solution [15]. At the same time, the computational effort increases as the square of the number of configurations[2] and the problem rapidly can become unmanageable. In the next sections, a theory will be developed for two-electron systems which suggests a procedure for adding configurations in a manner that also reduces the number of configurations.

III. Expansion of the Total Wavefunction

The exact total wavefunction can be expanded in terms of a complete basis for the two-electron problem. In this paper, we want to consider transformations of

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[2] In a numerical calculation, the time required to improve a radial function is of the same order of magnitude as that for calculating an F^k, G^k, or R^k integral. The latter increase even more rapidly than the square of the number of configurations.

the radial functions defining the basis which have the effect of reducing the number of terms in the expansion. In order to study such transformations we shall first define a basis using the notation of Shore and Menzel [16].

Let $\{\phi(nlm\mu \mid \cdot)\}$ be a complete orthonormal set of spin-orbitals which are eigenfunctions of a one-electron Hamiltonian, i.e.,

$$\phi(nlm\mu \mid i) = r_i^{-1} P_{nl}(r_i)\, Y_{lm}(\theta_i, \phi_i)\, \chi(1/2, \mu_i)$$

The set of all possible products

$$\Phi(ab \mid 12) = \phi(a \mid 1)\, \phi(b \mid 2), \qquad a \neq b,$$

then form a basis for the two-electron Hilbert space, where a and b each represent a set of four quantum numbers, say $a \equiv \{nlm\mu\}$ and $b \equiv \{n'l'm'\mu'\}$. But the total angular momentum operators, L^2 and L_0, the total spin operators, S^2 and S_0, and the parity operator all commute with the Hamiltonian. Hence an eigenfunction of H is also simultaneously an eigenfunction of these operators. Let us consider the LSM-coupling scheme and denote the total wave function for a state by $\psi(n_1 l_1 n_2 l_2\ \gamma L M_L S M_S)$ where γ is a seniority number. Then, an orthonormal basis for the state, is a set of functions

$$\Psi(nln'l'\ \gamma L M_L S M_S \mid 12) = (r_1 r_2)^{-1} P_{nl}(r_1)\, P_{n'l'}(r_2) \mid ll'\ \gamma L M_L S H_S\rangle \tag{2}$$

where $l + l'$ has the same parity as $l_1 + l_2$. Here $\mid ll'\ \gamma L M_L S M_S\rangle$ represents the coupling of the momenta to yield the indicated eigenstate: electron 1 is associated with the first orbital, and electron 2 with the second. An antisymmetrized basis element will be given by

$$\begin{aligned}\tilde{\Psi}(nln'l'\ \gamma L M_L S H_S) &= (1 - p_{12})\, \Psi(nln'l'\ \gamma L M_L S H_S \mid 12) \\ &= \Psi(nln'l'\ \gamma L M_L S H_S \mid 12) - \Psi(nln'l'\ \gamma L M_L S M_S \mid 21),\end{aligned} \tag{3}$$

where p_{12} is an exchange operator. The eigenstates of the angular momenta have the property that

$$\mid ll'\ \gamma L M_L S M_S\rangle = (-1)^{l+l'-L+1-S} \mid l'l\ \gamma L M_L S M_S\rangle.$$

For $l' = l$, it is then easy to verify that the basis element,

$$\begin{aligned}\tilde{\Psi}(nln'l\ \gamma L M_L S M_S) = (r_1 r_2)^{-1}\{&P_{nl}(r_1)\, P_{n'l}(r_2) - (-1)^{l+l'-L+1-S} P_{n'l}(r_1)\, P_{nl}(r_2)\} \\ &\times \mid l^2\ \gamma L M_L S M_S\rangle,\end{aligned} \tag{4}$$

is antisymmetric. In other words, the space part is *symmetric* when the angular and spin parts are antisymmetric, and vice versa. Note that these antisymmetrized basis elements have not been normalized. We shall see later that, because the normalization factor differs for equivalent and nonequivalent electrons, this form simplifies the arguments.

From now on, since the energy of our state is independent of the M_L and M_S values, we shall omit the designation of these quantum numbers. Then, expanding the exact wavefunction in terms of our basis we get

$$\psi(n_1 l_1 n_2 l_2\ \gamma LS) = (1 - p_{12}) \sum_{\substack{nl,n'l' \\ n'l' \geqslant nl}} a_{nl,n'l'} \Psi(nln'l'\ \gamma LS \mid 12), \tag{5}$$

where the sum is over all possible configuration (or pairs of nl quantum numbers) of the proper parity for which the angular and spin momenta may couple to yield the designated eigenstates. In order not to include a given configuration twice, an ordering of the $\{nl\}$ quantum numbers is assumed: the inequality $n'l' \geqslant nl$ implies that the nl quantum number appears before $n'l'$ in the ordering.

IV. THE $1s^2\,{}^1S$ STATE

For the $1s^2\,{}^1S$ state $l = l'$ and the space part of Eq. (3) is symmetric. Upon substituting Eqs. (2)–(4) into (5), we get

$$\psi(1s^2\,{}^1S) = (r_1 r_2)^{-1} \sum_{l=0}^{\infty} \left\{ \sum_{n,n'} (1 + \delta_{nn'})\, a_{nl,n'l} P_{nl}(r_1)\, P_{n'l}(r_2) \right\} \mid l^2\,{}^1S\rangle \tag{6}$$

with $a_{n'l,nl} = a_{nl,n'l}$. Let $\mathbf{P}_l(r)$ be the column vector of radial functions, $\{P_{nl}(r)\}^T$, and $\mathbf{A}^{(l)}$ the matrix of coefficients. Then the inner sum of Eq. (6) may be rewritten, in matrix vector form, as

$$\sum_{n,n'} (1 + \delta_{nn'})\, a_{nl,n'l} P_{nl}(r_1)\, P_{n'l}(r_2) = \mathbf{P}_l^T(r_1)\, \mathbf{A}^{(l)} \mathbf{P}_l(r_2) \tag{7}$$

But $\mathbf{A}^{(l)}$ is a symmetric matrix. Hence an orthogonal matrix $\mathcal{O}$ exists such that $\mathcal{O}^T \mathbf{A}^{(l)} \mathcal{O} = \mathbf{D}^{(l)}$ is diagonal. Let $\tilde{\mathbf{P}}_l = \mathcal{O}^T \mathbf{P}_l$, then $\mathbf{P}_l = \mathcal{O} \tilde{\mathbf{P}}_l$. Substituting for $\mathbf{P}_l$ in Eq. (7) we get

$$\begin{aligned} \mathbf{P}_l^T(r_1)\, \mathbf{A}^l \mathbf{P}_l(r_2) &= \tilde{\mathbf{P}}_l^T(r_1)\, \mathcal{O}^T \mathbf{A}^{(l)} \mathcal{O} \tilde{P}_l(r_2) \\ &= \tilde{\mathbf{P}}_l^T(r_1)\, \mathbf{D}^{(l)} \tilde{\mathbf{P}}_l(r_2) \\ &= \sum_n d_n^{(l)} \tilde{P}_{nl}(r_1)\, \tilde{P}_{nl}(r_2). \end{aligned} \tag{8}$$

This result shows that by transforming the radial functions for a given l, the doubly infinite sum in Eq. (6) can be reduced to a single infinite sum. Though the notation did not indicate this explicitly, there is one such orthogonal transformation for each l. In this case, the functions $\tilde{P}_{nl}(r)$ are the radial part of the natural orbitals defined by Löwdin [9].

Let $\Phi(nl^2\,{}^1S) = (r_1 r_2)^{-1} \tilde{P}_{nl}(r_1) \tilde{P}_{nl}(r_2) \mid l^2\,{}^1S\rangle$ which is both normalized and antisymmetric. Transforming each set of radial functions, so that the sum in Eq. (7) assumes the diagonal form of Eq. (8) we obtain the doubly infinite sum

$$\psi(1s^2\,{}^1S) = \sum_{l=0}^{\infty} \left\{ \sum_{n=l+1} d_n^{(l)} \Phi(nl^2\,{}^1S) \right\}. \tag{9}$$

A systematic MCHF procedure can now be defined. Starting with $l = 0$, for each l increase the number of (nl^2) configurations until the change in the energy ΔE_{nl} is sufficiently small. Let the improvement associated with this value of l be $\Delta E^{(l)}$. Increase l until $\Delta E^{(l)}$ is also sufficiently small. This procedure was applied to the $1s^2\,{}^1S$ state of helium using a numerical MCHF approach described in the earlier section. No fixed criterion for "sufficiently small" was used: instead configurations were introduced in turn until $n = 4$. Table 1 shows the convergence of the process, where at each stage one new configuration is added to the approximation in an accumulative manner. Note that for a given n, the largest ΔE_{nl} is associated with the largest l. It is clear that the most important configuration omitted from the

TABLE 1

Convergence of an MCHF Procedure for $1s^2\,{}^1S$ of He

m	Configuration	E_{total}	ΔE_{nl}			
			$n = 2$	$n = 3$	$n = 4$	$n = 5$
1	$1s^2$	−2.861680				
2	$+2s^2$	−2.877997	0.016317			
3	$+3s^2$	−2.878871		0.000874		
4	$+4s^2$	−2.878990			0.000119	
5	$+2p^2$	−2.898554	0.019564			
6	$+3p^2$	−2.900150		0.001599		
7	$+4p^2$	−2.900399			0.000249	
8	$+3d^2$	−2.902179		0.001780		
9	$+4d^2$	−2.902523			0.000344	
10	$+4f^2$	−2.902909			0.000386	
11	$+5g^2$	−2.903033				0.000124
E_{exact}[2]		−2.903724				
$E - E_{\text{exact}}$		0.000691				

systematic study is $5g^2$: the latter was then added to determine the extent of its contribution. The value of 2.902909 for the ten configuration approximation is in good agreement with that of -2.90289 obtained by Sabelli and Hinze [17] for the same configurations. Their paper includes a detailed analysis of this MCHF approximation.

In Table 2, the mixing coefficients, $d_n^{(l)}$ are given. Note that for a particular l, the coefficients all have the same sign and that the coefficient for $5g^2$ is appreciable.

TABLE 2
Mixing Coefficients $d_n^{(l)}$ for $1s^2\,{}^1S$ of He for the Eleven Configuration Approximation

Configuration	$d_n^{(l)}$
$1s^2$	0.995967
$2s^2$	-0.061750
$3s^2$	-0.007847
$4s^2$	-0.001707
$2p^2$	0.062046
$3p^2$	0.011044
$4p^2$	0.002691
$3d^2$	-0.012793
$4d^2$	-0.003467
$4f^2$	0.004103
$5g^2$	-0.001894

V. THE $1s2s\,{}^1S$ STATE

The symmetry properties of $1s2s\,{}^1S$ are exactly the same as those of $1s^2\,{}^1S$ and so the expansion for $\psi(1s2s\,{}^1S)$ has the same form as Eq. (6): orthogonal transformations exist which reduce it to the diagonal form of Eq. (9). However, in this form no single configuration will dominate. In the original expansion of Eq. (6) we would expect the coefficients $a_{1s2s} = a_{2s1s}$ to dominate. When the matrix for a single configuration approximation,

$$\mathbf{A} = a_{1s2s}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},$$

is diagonalized, by the rotations,

$$\mathcal{O} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix},$$

we find

$$\mathcal{O}^T \mathrm{A} \mathcal{O} = a_{1s2s}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

In other words, the diagonal entries have opposite sign. This form was first observed by Seaton [18] but numerical attempts at computing a function of this form failed, possibly because the stationary solution is numerically unstable. Certainly there is considerable cancellation in the calculation of the total energy.

Intuitively, we would like to retain the $1s2s\,{}^1S$ configuration since this represents a dominant component for the state. It is easy to show that, as long as two diagonal entries have opposite sign, say d_1 and $-d_2$, that an orthogonal matrix exists such that

$$\mathcal{O}^T \begin{pmatrix}d_1 & 0\\ 0 & -d_2\end{pmatrix} \mathcal{O} = \begin{pmatrix}d_1 - d_2 & (d_1d_2)^{1/2}\\ (d_1d_2)^{1/2} & 0\end{pmatrix}. \tag{10}$$

In other words an orthogonal transformation of $\tilde{P}_{1s}$ and $\tilde{P}_{2s}$ exists which allows us to replace one "diagonal" configuration by a "nondiagonal" one so that,

$$\psi(1s2s\,{}^1S) = c_{11}^{(0)}\Phi(1s^2\,{}^1S) + c_{12}^{(0)}\Phi(1s2s\,{}^1S) + \sum_{n=3}^{\infty} c_{n,n}^{(0)}\Phi(ns^2\,{}^1S) + \sum_{l=1}^{\infty}\left\{\sum_{n=l+1}^{\infty} c_{nn}^{(l)}\Phi(nl^2\,{}^1S)\right\}. \tag{11}$$

TABLE 3

Convergence of an MCHF Procedure for $1s2s\,{}^1S$ for He

Configuration	E_{total}	ΔE_{nl}			
		$n = 1$	$n = 2$	$n = 3$	$n = 4$
$1s2s$	-2.169854				
$+1s^2$	-2.143474	-0.026380			
$+3s^2$	-2.144138			0.000664	
$+4s^2$	-2.144188				0.000050
$+2p^2$	-2.145235		0.001047		
$+3p^2$	-2.145645			0.000410	
$+4p^2$	-2.145736				0.000081
$+3d^2$	-2.145773			0.000037	
$+4d^2$	-2.145866				0.000093
$+4f^2$	-2.145873				0.000007
⋮					
E_{exact}[2]	-2.145974				
$E - E_{\text{exact}}$	0.000101				

The mixing coefficients $c_{nn}^{(l)}$ are directly related to the $d_n^{(l)}$'s. An earlier correlation study for $1s2s\,^1S$ [15] has shown that the MCHF approximation given by the first two configurations is equivalent to a nonorthogonal Hartree–Fock approximation. Furthermore, of the set of possible rotations, this approximation has the property of minimizing the energy of the ion.

An MCHF procedure for finding solutions of the form given by Eq. (11) was applied to He: results showing convergence of the energy are given in Table 3. The changes ΔE_{nl} do not appear to vary as systematically as those for $1s^2$. The mixing coefficients are given in Table 4. It is evident that there are still changes of sign in the mixing coefficients for a given l. In particular the coefficients of $2p^2$ and $3p^2$, as well as $3d^2$ and $4d^2$ have opposite sign. Transformations such as those of Eq. (9) could be employed to replace these configurations by $2p^2$, $2p3p$ and $3d^2$, $3d4d$, respectively. The earlier study in which $4s^2$, $4p^2$, and $4f^2$ were omitted, had proceeded in this fashion.

TABLE 4

Mixing Coefficients $c_{nn'}^{(l)}$ for $1s2s\,^1S$ of He

Configuration	$c_{nn'}^{(l)}$
$1s2s$	0.993636
$1s^2$	0.109762
$3s^2$	−0.013178
$4s^2$	−0.001931
$2p^2$	0.013711
$3p^2$	−0.015810
$4p^2$	0.002317
$3d^2$	0.003615
$4d^2$	−0.002252
$4f^2$	−0.001341

VI. THE $1s2s\,^3S$ STATE

From Eq. (3) it follows that the space part of the total wavefunction for the $1s2s\,^3S$ state is now antisymmetric. As a result, the expansion of the exact wavefunction given in Eq. (5) becomes

$$\psi(1s2s\,^3S) = (r_1r_2)^{-1} \sum_l \left\{ \sum_{\substack{n,n' \\ n\neq n'}} a_{nl,n'l} P_{nl}(r_1)\, P_{n'l}(r_2) \right\} \mid nln'l\,^3S\rangle$$

where now $a_{n'l,nl} = -a_{nl,n'l}$. Thus the matrix of coefficients, $\mathbf{A}^l = (a_{nl,n'l})$ is antisymmetric.

Consider $\mathbf{G} = i\mathbf{A}^{(l)}$. This matrix is Hermitian, hence there exists a unitary matrix $\mathbf{U}$ such that

$$\mathbf{U}^\dagger\mathbf{G}\mathbf{U} = \mathbf{D}$$

where $\mathbf{D}$ is diagonal and real. Consequently,

$$\mathbf{A}\mathbf{U} = \mathbf{U}(-i)\mathbf{D}$$

which implies that the eigenvalues of $\mathbf{A}$ are pure imaginary. But $\mathbf{A}$ is real, and so the eigenvalues must occur in complex conjugate pairs. Let $i\lambda_1$, $-i\lambda_1$ be one such pair. It is easy to verify that if $\mathbf{U}_1$ is an eigenvector for the first, $\mathbf{U}_1^*$, is the eigenvector for the second. From the orthogonality of eigenvectors of hermitian matrices, it follows that $\mathbf{U}_1^T\mathbf{U}_1 = 0$. Now let $\mathbf{U}_1 = \mathbf{X}_1 - i\mathbf{Y}_1$, then

$$\mathbf{A}\mathbf{X}_1 = \lambda_1\mathbf{Y}_1$$
$$\mathbf{A}\mathbf{Y}_1 = -\lambda_1\mathbf{X}_1 .$$

Also $\mathbf{X}_1^T\mathbf{Y}_1 = 0$ and $\mathbf{X}_1^T\mathbf{X}_1 = \mathbf{Y}_1^T\mathbf{Y}_1$ since $\mathbf{U}_1^T\mathbf{U}_1 = 0$. As a result the real matrix of vectors

$$\mathbf{B} = [\mathbf{X}_1, \mathbf{Y}_1, \mathbf{X}_2, \mathbf{Y}_2, \ldots]$$

defines an orthogonal transformation of the radial functions such that

$$\mathbf{P}_l = \mathbf{B}\tilde{\mathbf{P}}_l$$

and

$$\mathbf{P}_l^T(r_1)\,\mathbf{A}\mathbf{P}_l(r_2) = \sum_{\substack{n=l+1\\ \Delta n=2}} d_n^{(l)}\{\tilde{P}_{nl}(r_1)\,\tilde{P}_{n+1l}(r_2) - \tilde{P}_{n+1l}(r_1)\,\tilde{P}_{nl}(r_2)\}$$

where the notation $\Delta n = 2$ is used to indicate that n increments by 2. Hence the expansion for $\psi(1s2s\,^3S)$ becomes

$$\psi(1s2s\,^3S) = \sum_{l=0} \sum_{\substack{n=l+1\\ n'=n+1\\ \Delta n=2}} c_{nn'}^{(l)}\Phi(nln'l\,^3S). \tag{12}$$

Table 5 shows the convergence of an MCHF procedure for He based on this form. Notice that radial correlation is exceedingly small and that the addition of only four configurations has accounted for 98.9 % of the correlation energy, even though the correlation energv was small to begin with. The mixing coefficients are given in Table 6.

TABLE 5

Convergence of an MCHF Procedure for $1s2s\ {}^3S$ of He

Configuration	E_{total}	$\Delta E_{nl,n'l}$		
		$n = 2$ $n' = 3$	$n = 3$ $n' = 4$	$n = 4$ $n' = 5$
$1s2s$	−2.174251			
$+3s4s$	−2.174264		0.000014	
$+2p3p$	−2.175166	0.000902		
$+4p5p$	−2.175171			0.000005
$+3d4d$	−2.175218		0.000047	
E_{exact}[2]	−2.175229			
$E - E_{\text{exact}}$	0.000011			

The calculations for this case were particularly simple. Because the space part is antisymmetric, any orthogonal transformation of a pair of radial functions $\tilde{P}_{nl}$, $\tilde{P}_{n'l}$ into a new basis, leaves the configuration state function $\Phi(nln'l\ {}^3S)$ unchanged. As in the single configuration approximation, one can then select that basis for which the Lagrange multiplier associated with the orthogonality constraint is zero.

TABLE 6

Mixing Coefficients $c_{nn'}^{(l)}$ for $1s2s\ {}^3S$ of He

Configuration	$c_{nn'}^{(l)}$
$1s2s$	0.999812
$3s4s$	−0.001398
$2p3p$	0.019055
$4p5p$	−0.000689
$3d4d$	0.003230

VII. THE $1s2p\ {}^{1,3}P$ STATES

In considering transformations of the radial functions for this case it is necessary to restrict the transformation to the set of functions with a particular l. In the case of $1s2s\ {}^{1,3}P$ states, the expansion must have the form

$$\psi(1s2p\ {}^{1,3}P) = (1 - p_{12})(r_1 r_2)^{-1} \sum_{nl} \sum_{n'l'} a_{nn'}^{(l+l')} P_{nl}(r_1)\, P_{n'l'}(r_2) \mid ll'\ {}^{1,3}P\rangle \quad (13)$$

where $l + l'$ is odd and $l' - l = 1$. Here we have assumed arbitrarily that $l < l'$. As a result the space part contains products of radial functions with different l. For this reason, it is more convenient to deal with a form in which the space part has *not* been antisymmetrized.

Let us rewrite Eq. (13). Let $l' = l + 1$, then

$$\psi(1s2p\ {}^{1,3}P) = (1 - p_{12})(r_1 r_2)^{-1} \sum_{l=0}^{\infty} \left\{ \sum_{n,n'} a_{nn'}^{(l+l')} P_{nl}(r_1)\ P_{n'l'}(r_2) \right\} \mid ll'\ {}^{1,3}P\rangle.$$

Now let $\mathbf{P}_l = \{P_{nl}\}^T$ and $\mathbf{P}_{l'} = \{P_{n'l'}\}^T$ be column vectors of radial functions and define $\mathbf{A}^{(l+l')}$ to be the matrix of coefficients,

$$\mathbf{A}^{(l+l')} = (a_{n,n'}^{(l+l')}).$$

Then there exist *two* orthogonal matrices $\mathcal{O}_1$ and $\mathcal{O}_2$ [19] such that

$$\mathcal{O}_1{}^T \mathbf{A}^{(l+l')} \mathcal{O}_2 = \mathbf{D}$$

where $\mathbf{D}$ is a diagonal matrix. Let $\tilde{\mathbf{P}}_l = \mathcal{O}_1{}^T \mathbf{P}_l$ and $\tilde{\mathbf{P}}_{l'} = \mathcal{O}_2{}^T \mathbf{P}_l$. Then

$$\begin{aligned} \sum_{n,n'} a_{n,n'}^{(l+l')} P_{nl}(r_1)\ P_{n'l'}(r_2) &= \mathbf{P}_l{}^T(r_1)\ \mathbf{A}^{(l+l')} \mathbf{P}_{l'}(r_2) \\ &= \tilde{\mathbf{P}}_l{}^T(r_1)\ \mathbf{D} \tilde{\mathbf{P}}_{l'}(r_2). \end{aligned}$$

But the first entry in $\tilde{\mathbf{P}}_l$ is $\tilde{P}_{nl}$ where $n = l + 1$ and the first in $\tilde{\mathbf{P}}_{l'}$ is $P_{n'l'}$ where $n' = n + 1$ since $l' = l + 1$. As a result

$$\tilde{\mathbf{P}}_l{}^T(r_1)\ \mathbf{D} \tilde{\mathbf{P}}_{l'}(r_2) = \sum_{n=l+1} d_{nn'}^{(l+l')} \tilde{P}_{nl}(r_1)\ \tilde{P}_{n'l'}(r_2)$$

where $n' = n + 1$ and $l' = l + 1$. The expansion for $\psi(1s2p\ {}^{1,3}P)$ then assumes the form

$$\psi(1s\ 2p\ {}^{1,3}P) = \sum_{l=0}^{\infty} \sum_{n=l+1} c_{nn'}^{(l+l')} \Phi(nln'l'\ {}^{1,3}P).$$

However, it is important to remember how this form was arrived at. Unlike the previous ${}^1S$ cases, the vector $\mathbf{P}_l$ occurred (in general) in *two* sums on l. The orthogonal transformations which diagonalize $\mathbf{A}^{(l+l')}$ in fact depend on $(l + l')$ and hence there really will be *two* sets of basis functions, $\tilde{\mathbf{P}}_l$ and $\tilde{\mathbf{P}}_l{}'$. Within each set the radial functions must be orthogonal but they need not be orthogonal between sets. This is the primary difference between the transformations considered here and Löwdin's natural orbitals.

The convergence of an MCHF procedure based on this form is shown in Table 7 for $1s2p\ {}^1P$, and Table 9 for $1s2p\ {}^3P$. Table 7 also shows the tremendous advantage

TABLE 7

Convergence of an MCHF Procedure for $1s2p\,^1P$ of He

Configurations	E_{total}	$\Delta E_{nl,n'l'}$	
		$n = 2$ $n' = 3$	$n = 3$ $n' = 4$
$1s2p\,^1p$	−2.122464		
$+2s3p$	−2.122587	0.000123	
$+2p'3d$	−2.123653	0.001066	
$(2p3d)$	(−2.122708)	(0.000121)	
$+3d'4f$	−2.123766		0.000113
E_{exact}[3]	−2.123843		
$E - E_{\text{exact}}$	0.000077		

TABLE 8

Mixing Coefficients $c_{nn'}^{(l+l')}$ for $1s2p\,^1p$ of He

Configuration	$c_{nn'}^{(l+l')}$
$1s2p$	0.999754
$2s3p$	0.007411
$2p'3d$	0.020392
$3d'4f$	0.004705

TABLE 9

Convergence of an MCHF Procedure for $1s2p\,^3p$ of He

Configuration	E_{total}	$\Delta E_{nl,n'l'}$	
		$n = 2$ $n' = 3$	$n = 3$ $n' = 4$
$1s2p$	−2.131437		
$+2s3p$	−2.132337	0.000900	
$+3s4p$	−2.132367		0.000030
$+2p'3d$	−2.133054	0.000687	
$+3d'4f$	−2.133086		0.000032
E_{exact}[3]	−2.133164		
$E - E_{\text{exact}}$	0.000078		

TABLE 10

Mixing Coefficients $c_{nn'}^{(l+l')}$ for $1s2p\ ^3p$ of He

Configuration	$c_{nn'}^{(l+l')}$
$1s2p$	0.999639
$2s3p$	−0.020943
$3s4p$	−0.002241
$2p'3d$	0.016467
$3d'4f$	−0.002565

that has been gained by not restricting the $2p$ radial function for $\Phi(1s2p)$ and $\Phi(2p3d)$ to be the same. When they are the same, the improvement in the correlation energy, ΔE_{2p3d}, is 0.000121 whereas for different $2p$ radial functions it is 0.001066. This is the largest contribution of any configuration. Of course, the number of radial functions which have to be computed increases when the two are not the same but the amount of computation tends to increase linearly with the number of radial functions and as the square of the number of configurations. In addition, no additional terms enter into the energy expression when $P_{2p'}$ is not orthogonal to P_{3p} and so the improvement in the correlation energy has been achieved with only a small increase in the amount of computation. The restricted calculation was not repeated for $1s2p\ ^3P$ but the effects are likely to be similar. The mixing coefficients for $1s2p\ ^1P$ and ^3P are given in Tables 8 and 10, respectively.

VIII. GENERALIZATION AND CONCLUSION

The four states—$1s^2\ ^1S$, $1s2s\ ^1S$, $1s2s\ ^3S$, $1s2p\ ^1P$ (or ^3P)—illustrate the four different cases which may arise in the study of two electron states. In general, the exact wavefunction may be expressed as a sum over all possible coupling schemes. With each coupling scheme is associated a doubly infinite sum over all possible pairs of principle quantum numbers n and n'. When the angular coupling is such that $l' \neq l$, an analysis like the one for $1s2p\ ^{1,3}P$ shows that orthogonal transformations of the radial basis exist which reduce this double sum to a single sum, though it may then be necessary to have more than one basis for a given l. When $l' = l$, two cases may occur: either the space part is symmetric or antisymmetric. In either case, orthogonal transformations again exist which reduce the double sum to a single sum. Finally, as in $1s2s\ ^1S$, when $l' = l$, the space part is symmetric, and the diagonal form contains two configurations for which the mixing coefficients are nearly equal but of opposite sign, then one of the "diagonal" configurations can be replaced by a "nondiagonal" one. These transformations are useful in determining a "reduced" functional form for the exact wavefunction which contains a minimum of configurations.

An MCHF procedure can now be defined for computing such two-electron correlated functions which considers each coupling scheme in turn. For each coupling scheme configurations are added in accordance with the reduced form, and the radial functions and mixing coefficients computed until the change in energy (or the mixing coefficients for the added configuration) is sufficiently small.

For a many-electron atomic system with $N > 2$ electrons, the exact total wavefunction is again a sum over all possible coupling schemes. But with each spin-angular factor there are now N sums over all possible values of the N principle quantum numbers $n_1, n_2, ..., n_N$. By keeping all but two of the indices fixed, and possibly recoupling the spin-angular factor, the double sum on the remaining two indices may be reduced to a single sum. The sum over all possible couplings of this pair of electrons, the coupling of the remaining $N - 2$ electrons remaining unchanged, defines a pair correlation function, similar in concept to the pair correlation functions which form the basis of Sinanoglu's extremely successful many-electron theory (for a recent review, see [20]). Pair correlated functions have been used, for example, by Byron and Joachain [21] in the study of Be, but they restricted the coupling of electron pairs to being of ^1S type.

In an N-electron system the number of pair correlated functions rapidly increases. Since an MCHF approach to correlation in effect expresses the correlated function as a linear combination of configurations, it is highly desirable to minimize the number of such configurations. Table 11 presents some data on the efficiency of representation. Ideally one would like to compare the various methods at the same level of accuracy. This was not possible, and so the accuracy is included in the table. For the perimetric coordinate expansion (PC) method of Pekeris *et al.* [2, 3], m is the number of terms in their sum. The CI results are those of Green *et al.* [22] and m refers to the number of configurations when each radial function is an optimized Slater orbital. The multiconfiguration frozen core (MCFC) results of Calvert and Davison [23] are in a sense similar to the MCHF ones, except that in each configuration, one of the radial functions is part of a "frozen core" and the second is determined variationally. Thus electrons are treated in a nonequivalent manner and several radial functions with the same nl may be present. In both MCHF and MCFC, m refers to the number of configurations.

For ^1P or ^3P, Table 11 shows immediately that with a similar set of configurations the MCHF results are more accurate than the MCFC ones. For $1s^2\,^1S$, the MCFC approach has an advantage since the single configuration, nonequivalent approximation has a lower energy than the Hartree–Fock one. If in Table 11, we take the energy of the 8-configuration approximation, and subtract the contributions ΔE_{nl} for $3s^2$, $4s^2$, $4p^2$, we get an approximate energy for the same 5-configuration approximation with $(E - E_{\text{exact}}) \simeq 0.00278$. This result is in agreement with that

TABLE 11

A comparison of the Number of Terms m in a Pair Correlated Function for Various Methods

PC — perimetric co-ordinate expansion (Pekeris [2, 3])
CI — configuration interaction
(Slater orbitals) (Green et al [22])
MCHF — multi-configuration Hartree-Fock
MCFC — multi-configuration frozen core (Calvert and Davison [23])

1. $1s^2\,^1S$	m	$E_{\text{exact}} - E$
(i) PC	95	0.000001
(ii) CI	50	0.00034
(iii) MCHF	10	0.00081
	11	0.00069
(iv) MCFC	5	0.00339
2. $1s2p\,^1P$		
(i) PC	20	0.000049
(ii) CI	42	0.000062
(iii) MCHF	4	0.000077
(iv) MCFC	5	0.00010
3. $1s2p\,^3p$		
(i) PC	20	0.000052
(ii) CI	42	0.000036
(iii) MCHF	5	0.000078
(iv) MCFC	5	0.00012

obtained by subtracting ΔE_{3s} from Sabelli and Hinze's 6-configuration result to yield $(E - E_{\text{exact}}) \simeq 0.000273$ for the 5-configuration approximation. It is clear that MCHF has the faster rate of convergence and that by the time five configurations have been added, it is the more accurate approximation.

The CI results of Green *et al.* are consistently more accurate than the MCHF ones presented here. But for $1s^2\,^1S$, the $5g^2\,^1S$ contribution alone accounts for about 25% of the difference between the 10-configuration MCHF approximation and the CI result. Because of the simple form of the radial functions, the CI results are bound to require far more configurations.

For $1s^2\,^1S$, the Pekeris result with 95 terms is too accurate for a reasonable comparison. But for ^1P and ^3P, the 20 term result has an error of roughly half of the 4 and 5 configuration MCHF one, respectively.

The MCHF method has the advantage that it retains the simple configuration concept of an atom and, at the same time can represent the pair correlation function efficiently with a relatively few configurations. It is not certain that the high accuracy of Pekeris *et al.* can be achieved with present numerical methods. On the otherhand an MCHF pair correlation study of the outer shell of, say, $1s^2\, 2s^2\, 2p^6\, 3s\, nl\, LS$, can be performed as readily as the two electron study reported here.

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