APPLICATIONS OF A METHOD FOR THE ANALYSES OF MANY-ELECTRON WAVEFUNCTIONS

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ABSTRACT

We show how the method of successive partial orthogonalizations can be used to obtain approximate Hartree-Fock (HF) pair functions directly from the hydrogenic pair functions. The method is more practical than accurate but with the explicit Z-dependence of the bar -nuclei pair functions just eleven such pair functions are needed to obtain an approximate HF pair function by this method for any pair of orbitals in any first row atom. We use the same method of analysis to extract HF orbitals directly from suitable trial functions for the He-He system at several internuclear distances and and also for the auto-ionizing $2s^2$ $2p^2$ states of helium. This approach avoids a separate variational calculation for the HF wave function and furthermore it provides approximate HF pair functions for these auto-ionizing states.

I. INTRODUCTION

The method of successive partial orthogonalizations was introduced by Sinanoğlu in his development of the many-electron theory.[1] The method can be used; (a) to analyze a trial function of arbitrary form for a many-electron system into its various correlation effects each involving a specific number of electrons and (b) to obtain a Hartree-Fock wavefunction directly from accurate trial functions which bypass a Hartree-Fock (HF) calculation. This avoids a separate variational calculation for the HF wave function. The applications illustrated in this paper indicate the ability of this method not only to aid physical interpretation but also to provide a simple way of obtaining some useful and practical information concerning atomic pair correlation functions. The results are certainly more practical than highly accurate.

A brief review of the necessary theory is presented in Sec. II. In Sec. III we describe how one can obtain approximate Hartree-Fock pair functions $\hat{u}_{ij}$ by first solving for the hydrogenic pair functions u_{ij}, which determine the first-order correction $\psi^{(1)}$ to the zeroth-order hydrogenic eigenfunction, and then analyzing that wavefunction $\psi^{(0)} + \psi^{(1)}$ into its various HF correlation components by successive partial orthogonalizations. The hydrogenic wavefunction accurate to first order in the entire inter-electron repulsion $H_1 = \sum_{i<j}^{N} 1/r_{ij}$ is not a terribly accurate wavefunction but in this way it can provide useful estimates of HF pair functions. The hydrogenic pair functions u_{ij} are solutions to simpler nonhomogeneous differential equations than are the HF pair functions and they can be obtained independently and with explicit Z-dependence. One just needs

eleven such two-electron functions in order to write down the wavefunction for any first row atom accurate to first order in the perturbation $H_1 = \sum_{i<j}^{N} 1/r_{ij}$.

In Secs. IV and V we illustrate how good HF wavefunctions can be obtained by this method of analysis from existing accurate trial functions without a separate variational calculation. Examples include the HF wavefunction for the He_2 molecule as a function of R extracted from Phillipson's 1962 wavefunction[2] and approximate SCF functions for the auto-ionizing $2s^2$ and $2p^2$ (^1S) states of He. These auto-ionizing states are of particular interest since the variational foundation of the Hartree-Fock method is no longer valid and in fact no true variational principle exists for such states. Nevertheless fairly accurate wavefunctions for such systems can be obtained by a scaling-variation orthogonalization procedure.[3,4] Analysis of these functions provides not only the SCF functions but also approximate pair correlation functions for such doubly excited states of the two-electron system.

II. THEORY

The exact wavefunction for a many-electron system can be written as[1,5]

$$\Psi = \Phi_0 + \sum_{i=1}^{N} \{\hat{f}_i\} + \sum_{i>j}^{N} \{\hat{U}'_{ij}\} + \sum_{i>j>k} \{\hat{U}'_{ijk}\} + \cdots \tag{1}$$

with the one- and two-electron clusters defined as

$$\{\hat{f}_i\} = A(\phi_1^{(0)} \phi_2^{(0)} \cdots \phi_{i-1}^{(0)} \hat{f}_i \phi_{i+1}^{(0)} \cdots \phi_N^{(0)}) \tag{2a}$$

$$\{\hat{U}'_{ij}\} = \frac{1}{\sqrt{2}} A(\phi_1^{(0)} \cdots \phi_{i-1}^{(0)} \hat{U}'_{ij} \phi_{j+1}^{(0)} \cdots \phi_N^{(0)}) , \tag{2b}$$

and Φ_0 is the orbital approximation to Ψ

$$\Phi_0 = A(\phi_1^{(0)} \; \phi_2^{(0)} \cdots \phi_N^{(0)}). \tag{3a}$$

The best orbital approximation of the form Eq. (3a) is the Hartree-Fock wavefunction Φ

$$\Phi = A(\phi_1 \phi_2 \cdots \phi_N) . \tag{3b}$$

The form of the wavefunction, Eq. (1), can be derived in different ways including the method of successive partial orthogonalizations.[1] The derivation of this expansion for $\Psi - \Phi_0$, [Eq. (1)], by the method of successive partial orthogonalizations formally assumes that Ψ is the exact many-electron function. Clearly a meaningful decomposition[1] can be obtained for any trial function $\tilde{\Psi}$ that is a good approximation to Ψ. Hence, given an orbital approximation Φ_0 any accurate trial function of arbitrary functional form can be decomposed into the form of Eq. (1). The meaning and magnitude of each term in the decomposition depends on the orbital approximation Φ_0. If one chooses the Hartree-Fock approximation for Φ_0 then the only important terms[6] in the decomposition of $\Psi - \Phi$ are the pair functions $\hat{U}'_{ij}$.

First Φ_0 is removed from Ψ

$$\chi = \Psi - \Phi_0 \tag{4}$$

and Ψ is normalized so that $\langle \Psi, \Phi_0 \rangle = 1$ and $\langle \Phi_0 , \chi \rangle = 0$. If Φ_0 is the HF wavefunction then χ is the correlation wavefunction and it simply represents what is left in Ψ after Φ_0 has been removed. Next one orthogonalizes χ to products of (N-1) orbitals obtained from the orbital product of Φ_0 by dropping one spin orbital at a time. The result is some portion of χ, i. e.,

$$\chi' = \chi - (N!)^{\frac{1}{2}} \sum_{i=1}^{N} A\Big[\phi_1^{(0)} \cdots \phi_{i-1}^{(0)} \Big\langle \chi, \phi_1^{(0)} \cdots \phi_{i-1}^{(0)}\, \phi_{i+1}^{(0)} \cdots \phi_N^{(0)} \Big\rangle_{\ldots x_{i-1} x_{i+1} \cdots}$$

$$\phi_{i+1}^{(0)} \cdots \phi_N^{(0)} \Big] . \qquad (5)$$

Note that in the orbital product of Eq. (5) the orbital $\phi_i^{(0)}$ has been replaced by a one-electron function, $\hat{f}_i$, defined by a partial integral over (N-1) electron coordinates, i. e.,

$$\hat{f}_i(\underset{\sim}{x}_i) = (N!)^{\frac{1}{2}} \int \chi^* (\underset{\sim}{x}_1, \underset{\sim}{x}_2 \cdots \underset{\sim}{x}_N)\, \phi_1^{(0)}(\underset{\sim}{x}_1) \cdots \phi_{i-1}^{(0)}(\underset{\sim}{x}_{i-1})\, \phi_{i+1}^{(0)}(\underset{\sim}{x}_{i+1}) \cdots$$

$$\cdots \phi_N^{(0)}(\underset{\sim}{x}_N)\, d\underset{\sim}{x}_1 \cdots d\underset{\sim}{x}_{i-1}\, d\underset{\sim}{x}_{i+1} \cdots d\underset{\sim}{x}_N \qquad (6)$$

The second term on the right hand side of Eq. (5) are just the $\{\hat{f}_i\}$ clusters of Eq. (1). One can continue this analysis by orthogonalizing χ' to products of (N-2) orbitals obtained from the orbital product of Φ_0 by dropping two spin orbitals at a time. The result is χ''

$$\chi'' = \chi' - (N!)^{\frac{1}{2}} \sum_{i<j}^{N} A\Big[\phi_1^{(0)} \cdots \phi_{i-1}^{(0)} \phi_{j-1}^{(0)} \Big\langle \chi', \phi_1^{(0)} \cdots \phi_{i-1}^{(0)}\, \phi_{j-1}^{(0)}\, \phi_{i+1}^{(0)}\, \phi_{j+1}^{(0)} \cdots$$

$$\cdots \phi_N^{(0)} \Big\rangle_{\ldots x_{i-1} x_{j-1} x_{i+1} x_{j+1} \cdots} \cdots \phi_{i+1}^{(0)} \phi_{j+1}^{(0)} \cdots \phi_N^{(0)} \Big] .$$

$$(7)$$

Again orbitals $\phi_i^{(0)}$ and $\phi_j^{(0)}$ are replaced by a two-electron function $\hat{U}'_{ij}(\underset{\sim}{x}_i, \underset{\sim}{x}_j)$, defined by a partial integral over (N-2) electron coordinates[7], i. e.,

$$\hat{U}'_{ij}(\underset{\sim}{x}_i, \underset{\sim}{x}_j) = \frac{(N!)^{\frac{1}{2}}}{\sqrt{2!}} \int \chi^{*\prime}(\underset{\sim}{x}_1 \cdots \underset{\sim}{x}_N)\, \phi_1^{(0)}(\underset{\sim}{x}_1) \cdots \phi_{i-1}^{(0)}(\underset{\sim}{x}_{i-1})\, \phi_{j-1}^{(0)}(\underset{\sim}{x}_{j-1})$$

$$\phi_{i+1}^{(0)}(\underset{\sim}{x}_{i+1})\, \phi_{j+1}^{(0)}(\underset{\sim}{x}_{j+1}) \cdots \phi_N^{(0)}(\underset{\sim}{x}_N)$$

$$\cdots d\underset{\sim}{x}_1 \cdots d\underset{\sim}{x}_{i-1}\, d\underset{\sim}{x}_{j-1}\, d\underset{\sim}{x}_{i+1}\, d\underset{\sim}{x}_{j+1} \cdots d\underset{\sim}{x}_N \,. \tag{8}$$

The second term on the right-hand side of Eq. (7) is the cluster term $\{\hat{U}'_{ij}\}$ of Eq. (1). This procedure is continued by orthogonalizing each new remainder, e. g., χ'' to all the orbital products from which one more orbital has been dropped.

These results are sufficient to illustrate how we will go about obtaining approximate HF pair functions $\hat{u}_{ij}$ indirectly starting from the bare-nuclei (i. e., hydrogenic) pair functions, u_{ij}. But it has also been shown that this same method provides a way of obtaining Hartree-Fock orbitals directly from a good trial function without a separate variational calculation.[1, 8] If Φ_0 is the Hartree-Fock wavefunction the dominant term in the correlation wavefunction χ will be the pair functions $\hat{U}'_{ij}$. In particular the $\hat{f}_i$'s have been shown to be small in typical closed-shell systems.[6, 9] Suppose that we have both a good trial function $\tilde{\Psi}$ which is close to Ψ and an arbitrary orbital approximation Φ_0. With these orbitals $\phi_i^{(0)}$ and Eqs. (5), (6) and (7) one can calculate the $\hat{f}_i^{(0)}$ for each orbital

$\phi_i^{(0)}$. But the $\hat{f}_i$ are negligible for HF orbitals so each $\hat{f}_i^{(0)}$ is simply trying to turn the approximate orbital $\phi_i^{(0)}$ into a HF orbital ϕ_i. Each orbital can therefore be improved by adding to it its $\hat{f}_i^{(0)}$ obtained from the trial function $\widetilde{\Psi}$

$$\phi_i^{(0)} \rightarrow \widetilde{\phi}_i = \frac{\phi_i^{(0)} + \hat{f}_i^{(0)}}{(1 + \langle \hat{f}_i^{(0)}, \hat{f}_i^{(0)} \rangle)^{\frac{1}{2}}} \tag{9}$$

and reorthogonalizing the set of orbitals $\{\widetilde{\phi}_i\}$. If all the orbitals $\phi_i^{(0)}$ are replaced by orbitals $\widetilde{\phi}_i$ and this procedure successively repeated the orbitals should converge to the generalized SCF orbitals. These generalized SCF orbitals are very close to the HF orbitals. This method for obtaining approximate HF orbitals is particularly applicable if $\widetilde{\Psi}$ is a CI wavefunction generated with an orthogonal basis set. After the first iteration the form of the orbitals $\{\widetilde{\phi}_i\}$ is limited to a linear combination of the CI basis set, and if this basis is orthogonal the integrations become very simple.

III. APPROXIMATE HF PAIR FUNCTIONS

From the many-electron theory[5, 6] the total correlation energy of an N-electron closed-shell system is, to a very good approximation

$$E_{\text{corr}} \approx \sum_{i<j}^{N} \widetilde{\varepsilon}'_{ij} \tag{10}$$

where $\widetilde{\varepsilon}'_{ij}$ is the exact pair energy[10]

$$\tilde{\varepsilon}'_{ij} \cong \frac{2\langle B(\phi_i\phi_j),\, m_{ij}\,\hat{u}_{ij}\rangle + \langle \hat{u}_{ij},\, (e_i + e_j + m_{ij})\,\hat{u}_{ij}\rangle}{1 + \langle \hat{u}_{ij},\, \hat{u}_{ij}\rangle} \tag{11}$$

with

$$m_{ij}(1,2) = 1/r_{12} - \overline{S}_i(1) - \overline{S}_i(2) - \overline{S}_j(2) - \overline{S}_j(1) + J_{ij} - K_{ij} \tag{12}$$

and

$$\overline{S}_i(2) = S_i(2) - R_i(2)\,. \tag{13}$$

$S_i(2)$ and $R_i(2)$ are the Coulomb and exchange potential of orbital ϕ_i. The operator B is the two-electron antisymmetrizer.[11] The pair function in Eq. (11) is denoted by lower case $\hat{u}_{ij}$ so as to distinguish it from the $\hat{U}'_{ij}$ which is the function formally obtained by the method of successive partial orthogonalizations. These $\hat{u}_{ij}$'s are obtained by minimizing a very large portion of the correlation energy using a correlation wavefunction which contains only the $\hat{u}_{ij}$'s and their unlinked clusters. The $\hat{U}'_{ij}$'s depend in principle on the other cluster terms, e.g., $\{\hat{f}_i\}$, $\{\hat{U}'_{ijk}\}$, etc.[12] From the many-electron theory the functions $\hat{u}_{ij}$ and $\hat{U}'_{ij}$ should be almost identical. For the practical considerations of this paper we need not distinguish between such functions.

The pair functions $\hat{u}_{ij}$ can be obtained by minimizing each $\tilde{\varepsilon}'_{ij}$ with respect to the variational parameters in some trial function $\tilde{\hat{u}}_{ij}$ or by direct numerical integration of its equivalent effective Schrödinger equation[13]

$$(e_i + e_j)\hat{u}_{ij} + Q\, m_{ij}[B(\phi_i\, \phi_j) + \hat{u}_{ij}] = \mathcal{E}_{ij}\ \hat{u}_{ij} \tag{14}$$

where Q makes a two-electron function orthogonal to all occupied HF orbitals and $\mathcal{E}_{ij}$ is the extremum value of $\tilde{\mathcal{E}}'_{ij}$, i. e.,

$$\epsilon_{ij} = \langle B(\phi_i\, \phi_j), \frac{1}{r_{12}}\ \hat{u}_{ij}\rangle . \tag{15}$$

If very accurate pair functions and energies are required one must eventually solve Eq. (14) or its variational equivalent, Eq. (11), for every pair of orbitals ϕ_i and ϕ_j. For many purposes pair functions of lower order may be sufficient in which case we may solve for a first-order pair function $\hat{u}_{ij}^{(1)}$. These $\hat{u}_{ij}^{(1)}$'s determine the total first-order correction to the zeroth-order HF wavefunction. Each $\hat{u}_{ij}^{(1)}$ satisfies the differential equation

$$(e_i + e_j)\,\hat{u}_{ij}^{(1)} = -\ Q\ m_{ij}\, B(\phi_i\, \phi_j) \tag{16}$$

and determines its pair energy $\mathcal{E}_{ij}^{(2)}$

$$\mathcal{E}_{ij}^{(2)} = \langle B(\phi_i\, \phi_j), \frac{1}{r_{12}}\ \hat{u}_{ij}^{(1)}\rangle . \tag{17}$$

One can always use $\hat{u}_{ij}^{(1)}$ in Eq. (11) to obtain an estimate of the exact pair energy $\tilde{\mathcal{E}}'_{ij}$.

Every pair function $\hat{u}_{ij}$ for every pair of HF orbitals ϕ_i and ϕ_j in any atom is a separate problem. For many purposes one may need only approximate information about a set of pair functions. In such cases the effort required to solve for $\hat{u}_{ij}$ or $\hat{u}_{ij}^{(1)}$ may not seem worthwhile. Examples of such cases can include (a) calculations in which one may want pair energies to within 15% to 20%; (b) an investigation of the effects of electron correlation on properties other than the energy, e. g., transition moments (here the pair energy may be of secondary importance), (c) the behavior of a given $\hat{u}_{ij}$ in an isoelectronic series and (d) estimates of the exclusion effect of outer electrons on inner-shell correlation energies.[14] The pair functions of Eqs. (14) and (16) represent corrections to the Hartree-Fock orbital approximation and these functions therefore depend explicitly on the medium through the HF potentials in the operators e_i and the exclusion effect requiring each $\hat{u}_{ij}$ to be orthogonal to occupied HF orbitals. Instead of starting from a HF Φ_0 one can apply the same formalism used to obtain the pair functions satisfying Eq. (16) to a hydrogenic orbital approximation Φ_0. The first-order correction can then be written[15]

$$\Psi^{(1)} = \frac{1}{\sqrt{2}} \sum_{i<j}^{N} A(\phi_1^{(0)} \cdots \phi_{i-1}^{(0)} \phi_{j-1}^{(0)} u_{ij} \phi_{i+1}^{(0)} \phi_{j+1}^{(0)} \cdots \phi_N) . \qquad (18)$$

The function $\Psi^{(1)}$ satisfies the usual first-order equation

$$(H_0 - E_0)\Psi^{(1)} = (E_1 - H_1)\Phi_0 \qquad (19)$$

where H_0 is the bare-nuclei Hamiltonian and H_1 the entire interelectronic repulsion. A pair function u_{ij} of Eq. (18) satisfies the differential equation

$$(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} - \epsilon_i - \epsilon_j)u_{ij}$$

$$= [J_{ij} - K_{ij} - \frac{1}{r_{12}}] B[\phi_i^{(0)}(1)\phi_j^{(0)}(2)] \qquad (20)$$

for an atom[16] of nuclear charge Z. Here ϵ_i, J_{ij} and K_{ij} are the hydrogenic orbital eigenvalues, the Coulomb and exchange integrals over hydrogenic orbitals respectively. The HF Φ_0 plus its correlation function does have the advantage of greater accuracy than the bare-nuclei Φ_0 plus its first-order correction. The expressions for the energy corrections are much simpler starting from a HF Φ_0 due to the nature of the HF potential. But the pair functions of Eq. (18) are totally independent of the medium and represent first-order corrections to the actual states of real two-electron systems. They can be obtained with explicit Z-dependence through a Z-expansion of the wavefunction and only eleven such u_{ij}'s determine the first-order corrections for all the atoms and ions of the first row. This is a feature that cannot be easily dismissed. The functions u_{ij} satisfy simpler differential equations than do the functions $\hat{u}_{ij}^{(1)}$. We are currently solving by direct numerical integration the differential equations which determine all eleven pair functions u_{ij} of the first row atoms and ions,[17] i. e., $1s^2$, $1s\,2s\,(^1S$ and $^3S)$, $1s\,2p\,(^1P$ and $^3P)$, $2s\,2p\,(^1P$ and $^3P)$, $2s^2$ and $2p^2\,(^1S)$, $2p^2\,(^3P$ and $^1D)$.

We now propose that for certain purposes, e. g., as discussed above, one can combine the advantages of the hydrogenic pair functions with the method of successive partial orthogonalizations to obtain approximate Hartree-Fock pair functions[18] $\hat{u}_{ij}$ in a straightforward and simple way. One just assumes that the trial wavefunction $\tilde{\Psi}$

$$\tilde{\Psi} = \Psi^{(0)} + \Psi^{(1)} \tag{21}$$

where $\Psi^{(0)}$ is the hydrogenic orbital approximation and $\Psi^{(1)}$ its first-order correction, is a good enough approximation to the exact wavefunction to yield a meaningful decomposition by the method of successive partial orthogonalizations. With a simple coordinate transformation one obtains the explicit Z-dependence of $\Psi^{(1)}$ and therefore of the u_{ij}'s in Eq. (18). Next we take the $\tilde{\Psi}$ of Eq. (21) and a Hartree-Fock Φ_0 and begin to extract approximations to the functions $\hat{f}_i$ and $\hat{u}_{ij}$ by the simple integrations indicated by Eqs. (6) and (8). We do not expect these functions to be highly accurate but at the same time very little effort is required to obtain them. For many purposes they may be satisfactory. The Hartree-Fock functions Φ_0 are readily available and accurate numerical solutions to the differential equations, Eq. (20), are now being obtained.[17] For more accurate pair functions one must solve Eq. (14) or Eq. (16) for $\hat{u}_{ij}$ or $\hat{u}_{ij}^{(1)}$ respectively. We have already shown that the same numerical techniques[13] used to solve Eq. (20) for u_{ij} are applicable to the equation for $\hat{u}_{ij}$ or $\hat{u}_{ij}^{(1)}$.

Although these approximate functions could be of independent interest we normally want estimates of the pair correlation energies $\tilde{\mathcal{E}}'_{ij}$. The numerical solutions for u_{ij} of Eq. (18) will just give approximate values of a HF $\hat{u}_{ij}$ at a discrete number of points, i. e., tabular values. With all quadratures by a trapezoidal rule and the appropriate difference expansion of the differential operators we can estimate the pair energy of Eq. (11) quite easily. Extrapolation of such estimates for $\tilde{\mathcal{E}}'_{ij}$ corresponding to numerical solutions at various mesh sizes can yield better estimates[13] of $\tilde{\mathcal{E}}'_{ij}$. But perhaps the accuracy desired may not justify doing even this. A less accurate alternative can be as follows. The $\tilde{\mathcal{E}}'_{ij}$ of Eq. (11) attains its minimum value if the $\hat{u}_{ij}$ in this equation is the solution of the effective Schrödinger equation Eq. (14). For the exact $\hat{u}_{ij}$ $\tilde{\mathcal{E}}'_{ij}$ of Eq. (11) is equal to $\mathcal{E}_{ij}$ of Eq. (15). In our approach we have an approximate $\hat{u}_{ij}$ and we should use the variational expression, $\tilde{\mathcal{E}}'_{ij}$, to estimate the pair energy $\mathcal{E}_{ij}$. However for crude estimates it is not unreasonable to use Eq. (15) directly. One clearly loses the advantage of Eq. (11), i.e., $\tilde{\mathcal{E}}'_{ij} \geqslant \mathcal{E}_{ij}$. Equation (15) is extremely simple to evaluate and this approach may yet yield estimates within 20% of the correct values.

We now illustrate the above procedure using the helium atom pair function as an example. The results for this example are encouraging and we give reasonable arguments to suggest that similar results can be obtained for pair functions of other atoms. In this example we did not use the numerical solutions for the $u(1s^2)$ but just evaluated the pair function directly using a basis set of ten associated Laguerre polynomials. The general form of these orbitals[19]

$$(n\ell m) = (2\eta)^{\frac{3}{2}}\{(n+\ell+1)!\}^{-\frac{3}{2}}\{(n-\ell-1)!\}^{\frac{1}{2}}(2\eta r)^{\ell}\, e^{-\eta r}$$

$$\cdot L^{2\ell+2}_{n+\ell+1}(2\eta r)\, Y_{\ell m}(\theta,\phi) \qquad (22)$$

where $L^{2\ell+2}_{n+\ell+1}$ are Laguerre functions of order $(2\ell+2)$, η is a scale factor and $Y_{\ell m}$ is a spherical harmonic. This set of orbitals is similar to the hydrogenic orbitals but they form a complete discrete set. Our basis set contains the 1s, 2s, 3s, 4s, 2p, 3p, 4p, 3d, 4d, and 4f orbitals. The pair function $u(1s^2)$ is most conveniently expressed in terms of normalized two-electron functions formed from this basis set. In our tables the function denoted by 1s2s actually is $\frac{1}{\sqrt{2}}$ [1s (1) 2s (2) + 1s (2) 2s (1)] $\frac{1}{\sqrt{2}}$ $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ and that for $1s^2$ is 1s (1) 1s (2) $\frac{1}{\sqrt{2}}$ $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. The 1s orbital of Eq. (22) is the same as the hydrogenic 1s orbital and therefore $\Phi_0 = B[1s(1)\alpha(1)\, 1s(2)\beta(2)]$. The function $u(1s^2)$ is obtained by straightforward solution of the matrix equation arising from Eq. (20) with Z = 2, $\epsilon_i = \epsilon_j = -2$ a. u., $J_{1s\,1s} =$ = 1.25 a. u. The approximate HF pair function determined from this trial function, i. e., $\Phi_0 + u(1s^2)$, (the bare-nuclei approximation plus its first-order correction), by the method of successive partial orthogonalizations is listed in the first column of Table I. In the next column we give the first-order HF pair function $\hat{u}_{ij}^{(1)}$ obtained by direct solution of Eq. (16) with the same basis functions. For further comparison we also list in the third column of this table the approximate HF $\hat{u}_{ij}$ extracted from the configuration interaction wavefunction, i. e., diagonalization of the total Hamiltonian in this basis. The Φ_0 used in the analysis was the best approximation to the HF wavefunction using the same basis set. The HF orbital is therefore expanded in terms of the 1s, 2s, 3s and 4s basis functions of Eq. (22). The coefficients of this expansion are listed in Table II. This basis set gives an orbital eigenvalue of - 0.91768 and a Hartree-Fock energy of -2.86158 a. u. compared to the very accurate values of -0.91795 and -2.86167 a. u., respectively.[20] The hydrogenic orbital product plus its first-order correction obtained with this basis set gives an upper bound[21] to the total energy of -2. 89305 a. u. while the configuration interaction wavefunction gives an upper bound of -2. 90099 a. u. This energy of -2. 90099 is the best value obtainable with this basis set.

To compare these various approximate pair functions we evaluate their corresponding pair energies. The first column of Table III gives estimates of the exact pair energies $\tilde{\mathcal{E}}'_{ij}$ obtained by using these three pair functions directly in Eq. (11). In the second column we list the values obtained by inserting the approximate pair functions directly into the expression for the extremum value of the exact pair energy, Eq. (15). For the first-order HF $\hat{u}^{(1)}_{ij}$ this is just the second-order pair energy $\varepsilon^{(2)}_{ij}$ since $\hat{u}^{(1)}_{ij}$ solves Eq. (16). For the first pair function $\hat{u}_{ij}$ (MSPO) one does not have a variational estimate but the other $\hat{u}_{ij}$ (MSPO) must essentially give a variational estimate.[22] The best value for the exact pair energy obtainable with these basis functions is -0. 0394 a. u. compared to the accurate value of -0. 0419 a. u.[23] The approximate $\hat{u}_{ij}$ extracted by this simple analysis from a hydrogenic Φ_0 plus its u_{ij} gives a variational estimate of -0. 0359 and a non-variational but very direct estimate of -0. 0444. In view of the advantages of this simple approach to obtaining approximate Hartree-Fock pair functions these results are very encouraging. Reliable estimates of the second and third order coefficients of the Z-expansion of the energy derived by empirical analysis of atomic energies indicate that the energy to third order in hydrogenic perturbation theory for 3 to 10 electron atoms can be sufficient for many purposes.[24] This is just the energy obtainable from $\Psi^{(0)} + \Psi^{(1)}$ of Eq. (21) and this does indicate that such functions are suitable for the kind of analysis we are proposing. In this procedure we take a very simple zero-order Hamiltonian and find its $\Psi^{(1)}$ but with the method of successive partial orthogonalizations we regain the many advantages of the simple expressions for the correlation energy resulting from a Hartree-Fock choice for Φ_0. One also has the advantages of the explicit Z-dependence of the bare-nuclei u_{ij}'s.

It is also interesting to compare the estimates of the second-order pair energy obtainable with these two approximate $\hat{u}_{ij}$'s. A variational estimate of the second-order pair energy $\varepsilon_{ij}^{(2)}$ is given by

$$\varepsilon_{ij}^{(2)} \leqslant 2\,\langle B(\phi_i\,\phi_j),\ m_{ij}\,\hat{u}_{ij}\rangle + \langle \hat{u}_{ij},\,(e_i + e_j)\,\hat{u}_{ij}\rangle . \qquad (23)$$

This is a minimum for $\hat{u}_{ij} = \hat{u}_{ij}^{(1)}$. The $\varepsilon_{ij}^{(2)}$ also breaks down into a sum over partial wave contributions. The partial wave contributions obtained with the approximate $\hat{u}_{ij}$ extracted from the bare-nuclei u_{ij} compare quite well with those given by the first-order HF pair function $\hat{u}_{ij}^{(1)}$. The agreement for the $\ell = 1$ and 2 waves is particularly good. The largest error occurs in the $\ell = 0$ partial wave. The $\ell = 0$ component of the bare-nuclei u_{ij} is by far the largest in its partial wave expansion since most of this is orbital average polarization which is trying to turn the hydrogenic orbitals into HF orbitals. One can start with screened hydrogenic orbitals so as to reduce the size of this term but for the present purposes the agreement between the first two columns of Table IV is encouraging.

In analyzing these trial functions one obtains not only the pair functions $\hat{u}_{ij}$ but also the $\hat{f}_i$'s. A good trial function should give negligible $\hat{f}_i$ terms in such an analysis and any trial function that yields non-negligible $\hat{f}_i$ terms can be improved by simply dropping them.[9] The bare-nuclei Φ_0 plus its u_{ij} in this basis gives an energy[21] of -2.89305 a.u. and the approximate $\hat{u}_{ij}$ extracted from this function gives a pair energy of -0.0359 a.u. Therefore removal of the $\hat{f}_i$ terms now gives an energy $E_{HF} + \tilde{\mathcal{E}}'_{ij} = -2.89748$ a.u. which is 0.00443 a.u. lower than the energy (-2.89305 a.u.) originally obtained with the trial function containing the $\hat{f}_i$'s.

IV. EXTRACTION OF THE HARTREE-FOCK WAVEFUNCTIONS FROM A GOOD TRIAL FUNCTION

We have already discussed how this method of analysis provides a way of obtaining Hartree-Fock orbitals directly from a good many-electron trial function without a separate variational calculation.[1, 8] We take a trial function and an arbitrary orbital approximation and find the $\hat{f}_i^{(0)}$. But the $\hat{f}_i$'s are negligible for HF orbitals so a non-negligible $\hat{f}_i^{(0)}$ is simply trying to turn the approximate orbitals of $\Phi_i^{(0)}$ into HF orbitals. Each orbital can therefore be improved by adding to it its $\hat{f}_i^{(0)}$ [see Eq. (9)].

To illustrate this application we have obtained a good HF wavefunction directly from Phillipson's extensive configuration interaction wavefunction for the He-He system at several internuclear separations.[2] The most extensive CI function contained 64 components constructed out of a 1s, 1s$'$, 2pσ, 2pπ STO basis set. Our choice for the initial orbitals at all internuclear distances is the sum and difference of 1s Slater orbitals centered on each nucleus with the exponent optimized for the unperturbed helium atom:

$$\begin{aligned} 1\sigma_g &= N_g(1s_a + 1s_b) \\ 1\sigma_u &= N_u(1s_a - 1s_b) \\ 1s &= N \exp(-1.6875r) \\ \Phi_0 &= A(1\sigma_g^2\, 1\sigma_u^2)\,. \end{aligned} \tag{24}$$

The vectors for the improved σ_g and σ_u orbitals for three successive iterations are listed in Table V. For comparison we also list the vectors obtained by direct solution of the SCF equations. Convergence to the SCF orbitals is rapid despite the poor initial guess for the starting orbitals. These starting orbitals were just the molecular orbitals formed from the single Slater atomic orbitals appropriate to the noninteracting atoms. In Table VI we list the electronic energies for the initial orbital approximation and the three successive iterations and compare these with the SCF value obtained directly. The energy at each iteration, including the final, has been computed in this example specifically for purposes of comparison. The results of Tables V and VI clearly illustrate that good HF wavefunctions can be obtained by this method of analysis without a separate variational calculation. If the accurate trial wavefunction is obtained within a given basis set then the resulting HF orbitals are the best obtainable within that basis. One can then tell "how much" of the correlation energy has actually been obtained. This would have been particularly useful at the time of Phillipson's calculation.[25] The results of extensive calculations which bypass the HF Φ_0, e.g., in calculating potential energy surfaces,[26] can be easily analyzed not only to yield the Hartree-Fock orbitals but also to display explicitly the correlation effects contained in the wavefunction.

As another example we have extracted an approximate HF function for Be from Boys' 1953 CI wavefunction.[27] Boys' function is not very accurate but there is some historical interest in using it here. At the time of his calculation the only convenient and accurate method for finding atomic HF functions was direct numerical integration. Boys suggested using functions of simple analytic form to generate accurate many-electron functions in the form of a CI expansion. Such functions were more convenient than tabular values of a numerical solution but they did bypass the HF wavefunction. At that time no attempt was made to generate a HF Φ_0 in the same basis. This method of analysis can provide such a HF Φ_0 which should be essentially identical to those now obtained by matrix HF techniques. In this analysis the dominant term in Boys' function[27] was chosen as the initial orbital product. The resulting orbitals were orthogonalized after each iteration. In Table VII the energy of the improved orbital product after three iterations is compared to the energy of the SCF function in the same basis and to the accurate HF energy.

V. APPLICATIONS TO AUTO-IONIZING STATES

There are no assumptions in the theory of successive partial orthogonalizations which limit either the analysis of a wavefunction into the form of Eq. (1) or the extraction of a HF function from an accurate trial function to the lowest state of a given symmetry. We now illustrate how this method of analysis can be used to obtain both approximate HF functions and pair correlation functions for the doubly-excited auto-ionizing $2s^2$ and $2p^2$ (^1S) states of He. These auto-ionizing states are of interest since the variational foundation of the HF equations is no longer valid. For auto-ionizing states truncated diagonalization of the Hamiltonian is no longer justified by the variational proof since there is an infinite number of states of identical symmetry and lower energy. Nevertheless the truncated diagonalization method can be justified for other reasons[3, 4, 28] and Holoien[3] has demonstrated the stabilizing ability of particular roots corresponding to auto-ionizing levels as the basis is enlarged if orthogonalization is effectively achieved. Pair functions for these states are of interest since it is intuitively clear that correlation effects are quite important in auto-ionization transitions. Part of the interelectronic repulsion term is actually responsible for the auto-ionization transition itself.

For the analysis of the $2s^2$ and $2p^2$ doubly-excited states of helium the many-electron wavefunctions were those derived by Holoien using his scaling-variation orthogonalization procedure. With the basis functions of Eq. (22) the secular equation is solved and the scale parameter η varied until the energies of the roots which probably correspond to the $2s^2$ and $2p^2$ states are minimized. The optimum scale parameters are 0.76 and 0.8125 for the $2s^2$ and $2p^2$ states respectively. The optimum scale parameter for the ground state in the same basis is 2.222 and the lowest eigenvalue increases by 0.0837 a.u. when η is changed to 0.76. The overlaps of the approximate $2s^2$ ($\eta = 0.76$) and

$2p^2$ ($\eta = 0.8125$) states with the best ground state in this basis ($\eta = 2.222$) are 0.0033 and 0.00012 respectively which indicate that the nonorthogonality problem may not be too serious. The approximate HF orbitals for these two states were extracted from Holoien's twenty component-trial function and are listed in Table VIII. The orbital and HF energy for the $2s^2$ state agree well with previous HF results obtained by direct integration of Hartree-Fock-like equations for this state. The agreement for the $2p^2$ state is not as good, e.g., an orbital energy of -0.1504 a.u. compared to Wilson's value of -0.1931 a.u.. In view of the agreement for the $2s^2$ state we feel that our results for the $2p^2$ state are reliable. With these approximate HF functions in the orbital products Φ_0 the approximate pair functions for the $2s^2$ and $2p^2$ states were extracted from the trial functions and are listed in Table IX.

CONCLUSIONS

We have illustrated that the method of successive partial orthogonalizations provides a simple way of obtaining useful and practical information concerning both Hartree-Fock and pair correlation functions. With an example we have shown how one can obtain approximate HF pair functions by taking the hydrogenic pair functions which determine the wavefunction accurate to first-order in the entire interelectron repulsion and analyzing it into its various Hartree-Fock correlation components by successive partial orthogonalizations. The method is more practical than accurate but it can provide pair energies to within 15% to 20% of the exact values. The bare-nuclei u_{ij} can be obtained with explicit Z-dependence and therefore just eleven such u_{ij}'s are needed in order to obtain an approximate HF $\hat{u}_{ij}$ for any pair of orbitals in any first-row atom. We have also suggested some simple and direct ways for estimating the pair energies using these approximate functions. Reliable empirical estimates of the second and third order coefficients of the Z-expansion of the energy indicate that the general approach is adequate for three to ten-electron atoms.

The method does provide a simple iterative scheme for extracting HF orbitals from accurate trial functions directly and without a separate variational calculation. With this technique we obtained SCF orbitals for the He-He system at several internuclear distances directly from Phillipson's CI calculation and could then tell "how much" of the correlation energy was actually included in the original function. These results indicate that this same approach should be used to interpret the results of extensive calculations which may bypass the HF Φ_0. The method can also be used to analyze and study various trial functions for auto-ionizing states. In this way we have obtained not only SCF functions for the $2s^2$ and $2p^2$ (^1S) states of helium but also approximate pair functions for these doubly excited states.

TABLE I. Comparison of various approximate pair functions[a].

	$\hat{u}_{ij}$(MSPO)[b]	$\hat{u}^{(1)}_{ij}$ [c]	$\hat{u}_{ij}$[d](MSPO)
$1s^2$	-0.001856	-0.001490	-0.001922
1s2s	-0.015506	-0.011610	-0.014924
$2s^2$	-0.065559	-0.046284	-0.058915
1s3s	-0.000090	0.002074	0.002805
2s3s	-0.003565	0.007504	0.011848
$3s^2$	-0.005831	-0.008756	-0.008686
1s4s	0.001658	0.000411	0.000637
2s4s	0.008310	0.002195	0.003371
3s4s	-0.004080	-0.000835	-0.001195
$4s^2$	-0.003378	-0.002854	-0.002364
$2p^2$	-0.053346	-0.053534	-0.060749
2p3p	-0.024647	-0.011873	-0.014146
$3p^2$	-0.013767	-0.012081	-0.010658
2p4p	-0.002972	0.000067	0.000722
3p4p	-0.009632	-0.006118	-0.006229
$4p^2$	-0.007237	-0.005992	-0.005134
$3d^2$	-0.009092	-0.011996	-0.009729
3d4d	-0.009076	-0.007276	-0.007485
$4d^2$	-0.007261	-0.006998	-0.005950
$4f^2$	-0.002644	-0.006022	-0.002981

[a] This table gives the coefficients of the normalized components indicated in the left-hand column, e.g., 1s2s stands for

Table I continued

$\frac{1}{\sqrt{2}}$ $[1s(1)2s(2) + 1s(2)2s(1)] \cdot \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. All the basis functions have $\eta = 2$.

[b]These coefficients specify the approximate Hartree-Fock $\hat{u}_{ij}$ determined from a hydrogenic orbital product plus its u_{ij} by the method of successive partial orthogonalizations.

[c]This is the first-order Hartree-Fock pair function $\hat{u}_{ij}^{(1)}$ obtained by solving Eq. (16) with the same basis functions.

[d]This column gives the approximate HF pair function determined from the configuration interaction wavefunction by the method of successive partial orthogonalizations.

TABLE II. Hartree-Fock orbital used in this analysis.

	Eigenvector[a]
1s	0.98384
2s	-0.16735
3s	0.06360
4s	-0.00406
ε_{1s}	-0.91768
E_{HF}	-2.86158

[a] These are the coefficients of the basis functions shown in Eq. (22).

TABLE III. Estimates of the pair energy (in a. u.)

	$\tilde{\mathcal{E}}'_{ij}$	$\langle B[\phi_i(1)\phi_j(2), \frac{1}{r_{12}} \hat{u}_{ij}(1,2)]\rangle$
$\hat{u}_{ij}$(MSPO)	-0.0359[a]	-0.0444[b]
$\hat{u}^{(1)}_{ij}$	-0.0384	-0.0346
$\hat{u}_{ij}$(MSPO)	-0.0394	-0.0394

[a] Estimates of the pair energies obtained by evaluating Eq. (11). The three values correspond to the three pair functions listed in Table I. See footnotes b, c, and d of Table I respectively.

[b] These estimates are obtained by using the approximate pair functions directly in the equation for the extremum value of $\tilde{\mathcal{E}}'_{ij}$, i. e., $\mathcal{E}_{ij}$. See Eq. (15). The first value is not a variational estimate but the third value should be very close to being one--the difference here is concerned with the presence of small $\{\hat{f}_i\}$ terms.

TABLE IV. Partial wave contributions to $\mathcal{E}_{ij}^{(2)}$ (in a. u.) for the various pair functions

ℓ	$\hat{u}_{ij}(\mathrm{MSPO})^{a}$	$\hat{u}_{ij}^{(1)\,b}$	$\hat{u}_{ij}(\mathrm{MSPO})^{c}$	$\hat{u}_{ij}^{(1)\,d}$
0	-0. 00885	-0. 01318	-0. 01230	-0. 01347
1	-0. 01763	-0. 01926[e]	-0. 01894	-0. 01894
2	-0. 00199	-0. 00204	-0. 00201	-0. 00317
3	-0. 00011	-0. 00016	-0. 00012	-0. 00092
Total	-0. 02858	-0. 03464	-0. 03336	-0. 03650

[a] See footnote b of Table I for description of this approximate $\hat{u}_{ij}$.

[b] Approximate $\hat{u}_{ij}^{(1)}$ obtained with this basis and Eq. (23).

[c] See footnote d of Table I for a description of this approximate $\hat{u}_{ij}$.

[d] Accurate results of F. W. Byron, Jr. and C. J. Joachain, Phys. Rev. **157**, 1 (1967). Inclusion of higher ℓ-values gives their final value of -0. 03725 a. u.

[e] This value does seem slightly lower than expected. This may be due to a small error in some particular integral.

TABLE V. Approximate HF orbitals for He_2 obtained by iterative analysis of a CI wavefunction[a]

R		0.5A		0.75A		1.0A		2.0A	
1s		$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$	$1\sigma_g$	$1\sigma_u$
	1	.54772	.06984	.53242	.31811	.35788	.26472	.23968	.24618
	2	.54624	.15011	.52869	.35467	.35581	.27354	.24861	.25222
	3	.54505	.14427	.52775	.35205	.35564	.27298	.24986	.25175
	SCF	.54531	.14090	.52984	.35556	.35866	.27327	.24980	.25009
$1s^1$									
	1	.01686	2.1884	.06979	.95390	.27805	.67340	.46671	.50313
	2	.01201	2.0233	.06960	.89002	.27754	.65893	.45841	.49711
	3	.01387	2.0346	.07071	.89385	.27775	.65959	.45885	.49758
	SCF	.01349	2.0389	.06863	.88718	.27509	.65907	.45741	.49895
$2p\sigma$									
	1	.01854	-.00166	.01285	-.00697	.00847	-.00587	.00131	.00361
	2	.03447	-.01449	.02490	-.01349	.01757	-.01151	.00215	.00561
	3	.03353	-.01401	.02440	-.01366	.01737	-.01157	.00215	.00562
	SCF	.03364	-.01471	.02435	-.01469	.01730	-.01183	.00115	-.00102
orbital exponents[b]									
1s		2.25		2.05		2.25		2.39	
$1s^1$		0.84		0.99		1.24		1.33	
$2p\sigma$		3.4		2.8		2.5		2.5	

[a] These are the coefficients of the normalized atomic orbitals centered on nucleus a and b respectively. The coefficients are listed in order of the first, second and third iterations followed by the SCF orbitals computed directly (Nesbet-Stevens SCF program).

[b] The orbital exponents were varied with internuclear distance. See Ref. 2.

TABLE VI. The electronic energy (in a. u.) of the successive orbital approximations for the He-He system[a]

R	0. 5 A	0. 75 A	1. 0 A	2. 0A
Initial	-8. 277068	-7. 990395	-7. 635261	-6. 751438
Iteration				
1	-8. 901508	-8. 130661	-7. 679876	-6. 777663
2	-8. 918400	-8. 135249	-7. 681278	-6. 777657
3	-8. 918564	-8. 135230	-7. 681276	-6. 777657
SCF	-8. 918584	-8. 135269	-7. 681300	-6. 778196
Δ^b	0. 000020	0. 000020	0. 000032	0. 000533
CI Energy[c]	-8. 96695	-8. 18023	-7. 72183	-6. 81759
$E_{corr}{}^d$	-0. 0484	-0. 0450	-0. 0405	-0. 0394

[a] An additional calculation was done R = 0. 625 A but the error in the results was so much larger (Δ = 0. 007 a. u.) that we believe there must be a misprint in the coefficients listed in Ref. 2.

[b] Δ is the difference between the best energy of the improved orbital approximation and the SCF energy with the same basis set.

[c] These are the total energies for the CI wavefunction as given in Ref. 2.

[d] The difference between the energy after the third iteration and the CI energy, i. e., the correlation energy contained in Phillipson's CI wavefunction.

TABLE VII. Analysis of a trial function for Be.

	Boys' CI function[a]	Exact
Improved orbital product	-14.5667	
SCF	-14.5674	-14.5730
Δ[b]	0.0007	
Total energy	-14.637	-14.6674

[a] The CI wavefunction used in this analysis. See Ref. 7.

[b] Δ is the difference between the best energy of the improved orbital approximation and the SCF energy with the same basis set.

TABLE VIII. Approximate Hartree-Fock orbitals for the $2s^2$ and $2p^2\,(^1S)$ states.

	$2s^2$		$2p^2\,(^1S)$
1s	-0.6397[a]	2p	0.9866
2s	0.7450	3p	-0.0848
3s	0.1687	4p	0.1391
4s	0.0854		
orbital energy[b]	-0.2239	orbital energy[b]	-0.1504
HF energy	-0.7185	HF energy[d]	-0.6216
orbital energy[c]	-0.2302	orbital energy[e]	-0.1931
HF energy	-0.7197	HF energy	-0.6162

[a] These are the coefficients of the basis functions of Eq. (22).

[b] Orbital energy and HF energy for the Φ_0 extracted from the trial function of Ref. 3.

[c] Hartree-Fock approximation to the $(ns^2)\ ^1S$ auto-ionizing states of helium. D. E. Ransker, R. E. Stevenson and D. M. Schrader (preprint 1968).

[d] The energies of the trial functions for the $2s^2$ and $2p^2$ states are -0.7738 and -0.6189 a.u. respectively. That the energy of the approximate HF function for the $2p^2\,(^1S)$ state comes out slightly lower than the energy of the original function reflects the absence of a true variational principle for these states. Furthermore in the perturbation sum for E_2 for states that are not the lowest of a given symmetry some terms will be positive.

[e] W. S. Wilson, Phys. Rev. **48**, 536 (1935). The results of this reference for the $2s^2$ state are almost identical to those of footnote c above.

TABLE IX. Pair functions for the $2s^2$ and $2p^2$ auto-ionizing states[a]

	$2s^2$	$2p^2$
$1s^2$	-0.00871	0.21515
1s2s	-0.02411	-0.41745
$2s^2$	-0.02264	0.42488
1s3s	0.03674	0.15142
2s3s	0.03305	-0.12506
$3s^2$	-0.01061	-0.12114
1s4s	0.04550	-0.09868
2s4s	0.03350	0.10895
3s4s	0.01649	-0.00430
$4s^2$	0.01133	-0.00194
$2p^2$	-0.61353	-0.00214
2p3p	-0.03579	-0.02499
$3p^2$	0.03896	-0.18762
2p4p	-0.00092	0.00626
3p4p	0.01886	0.01543
$4p^2$	0.00198	-0.02472
$3d^2$	0.01487	-0.22695
3d4d	0.01547	-0.05913
$4d^2$	0.00858	-0.03473
$4f^2$	-0.00023	-0.03849

Table IX continued

[a] This table gives the coefficients of the normalized components indicated in the left-hand column, e.g., 1s2s represents

$$\frac{1}{\sqrt{2}}\left[1s(1)2s(2) + 1s(2)2s(1)\right] \cdot \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right].$$

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