[29] The original subroutine was written by F. Prosser and H. H. Michels, Program 62: 1, Quantum Chemistry Program Exchange, Indiana University. Rewritten in double precision by G. Sperber, Quantum Chemistry Group, Uppsala University, Sweden.

[30] It should be noted that the scale factors are defined in completely different ways in Eqs. (13) and (22), and need not *a priori* be the same. The computations were, however, carried out in such a manner that they become identical.

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Perturbation-Theoretic Approach To Atoms and Molecules

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A general perturbation-theoretic procedure for obtaining accurate wave functions for atoms and molecules is developed in detail for an arbitrary separable H_0, and the explicit equations satisfied by the various parts of the first- and second-order perturbed wave functions are given. It is shown how the solutions for the nth-order perturbed function can be found in terms of solutions to partial differential equations in only $n+1$ variables for atoms, and in terms of solutions to sets of coupled equations in the same $n+1$ variables for molecules. It turns out that for atoms the number of pair equations that need be solved to give Ψ_1 and the major part of Ψ_2 is roughly proportional to N, the number of electrons; while for molecules of no symmetry, with paired electrons, it is proportional to $N(N+2)/8$ as distinguished from the $N^2/4$ expected previously. This reduction in the number of necessary pairs may be of some practical use if the pair equations are integrated numerically. Various Hamiltonians are discussed, and an "exchangeless" Hamiltonian is introduced, which can serve to simplify the computations relative to the usual Hartree-Fock procedure, and might serve to increase the rate of convergence. Numerical calculations are performed for the helium-atom ground state in order to illustrate the procedure and to examine the rates of convergence of the expansions based on several different H_0's. Results differing from the exact result by 2–9×10^{-4} are obtained for the different calculations through third order, and this error cannot be reduced by changing H_0. The angular expansion and the numerical integration technique used on the two-dimensional equations are sufficiently accurate that the third-order energy agrees to within 7×10^{-6} of Knight and Scherr's value.

I. INTRODUCTION

Calculations on atoms and molecules, with the exception of those on two-electron systems,[1–5] have for the most part been restricted to single-determinant "self-consistent field" independent-particle solutions which describe the individual electrons moving in the average Coulomb and exchange fields of the remaining electrons.[6–10] As is well-known, such solutions only provide energy eigenvalues to an accuracy of ~1%, so that the inherent errors are never less than an electron volt and thus are always of spectroscopic (and hence astrophysical) importance, to say nothing of chemical or solid state importance. This error, is generally called "correlation error" as it is due to the part of the electron-electron interaction that cannot be treated in the smoothed-out approximation. It was only recently, with the work of Brueckner and Kelly[11] and Sinanoğlu[12] that the inherent simplicity of the correlation problem within a perturbation framework was recognized. These authors pointed out that when the Hartree-Fock solution is taken as Ψ_0, the first correction Ψ_1 and hence the leading two terms of the correlation energy can be determined by calculating the various two-particle correlation corrections to the wave function—a series of helium-atom-like problems.

Perturbation-theoretic calculations based on the Hartree-Fock self-consistent field (SCF) Ψ_0 have since been performed to varying degrees of accuracy by Sinanoğlu and Tuan[13] and Geller,[14] Kelly[11] and Byron and Joachain,[15] for the atoms Be, Be, and O, and He and Be, respectively. Perturbation-theoretic calculations based on the hydrogenic Ψ_0 have been recently performed through second-order by Chisholm and Dalgarno[16] and by Seung and Wilson[17] on Li, and by Safronova and Tolmachev[18] on Be. Nesbet[19] has recently performed a number of calculations using a nonperturbative cluster expansion and Conkie[20] has performed a different type of perturbative calculation for Li.

The present paper is devoted to several aspects of the many-electron problem.[21] In Sec. II a new set of equations is derived for the pair functions[22] which contribute to Ψ_1, and since no spin-symmetry restrictions are included, the number of interorbital correlation functions is exactly half that heretofore considered necessary. This section also contains the first explicit consideration of the equations to be solved for the pair and three-particle functions of Ψ_2, and some details in addition to a comparison with the theory of Sinanoğlu[12,23] are presented in the Appendix. Section III. A is devoted to a discussion of various possible H_0's which can either enhance the rate of convergence or simplify the computations, and Sec. III. B and C point out the advantages in expanding the perturbed wave functions in spherical harmonics. Finally, in Sec. IV a numerical procedure for directly solving the pair equations is described and applied to the helium-atom ground state in order to test the convergence of the energy through third-order for several H_0's.

It should be noted that the scheme presented in this paper avoids the variety of terms, such as those due to integral operators, orthogonality corrections, and certain single-particle diagrams, which have been treated approximately, for one reason or another, in the past. The only real approximation that we make is the neglect of higher-order terms in a perturbation expansion which is based on the assumption that the perturbation theory converges. This assumption is, of course, supported for both atoms and nuclei by the experimental verification of the validity of the relevant shell models. We hope, however, to demonstrate quantitatively this convergence for many-electron systems, so that, for example, the contributions from three-electron interactions which first occur in the fourth-order energy can indeed be shown to be small. This should then contribute to the realization of the goal set forth by Sinanoğlu in his pioneering papers of 1960 and 1961,[12] namely the solution of accurate wave functions in terms of their independent and pair-correlated parts. The fact that we find it desirable to avoid "self-consistent" Ψ_0's should not be of particular concern since recent experience[24,25] has indicated that these independent-particle solutions can give results which cannot be uncritically extrapolated to the real physical problems of interest.

II. GENERAL PROCEDURE

In order to be able to describe a perturbation expansion of atomic (and molecular) wave functions we define a Hamiltonian as a function of

$$H(\lambda) \equiv H_0 + \lambda H_1 \qquad (1)$$

as a sum of two terms, one independent of λ and one linear in λ, which coincides with the true Hamiltonian of the physical system for $\lambda = 1$, the separation into H_0 and H_1 being otherwise arbitrary. With this definition, each exact eigenfunction and eigenvalue of the model Schrödinger equation

$$[H(\lambda) - E(\lambda)]\Psi(\lambda) = 0, \qquad (2)$$

which coincides with the Schrödinger equation of the physical problem for $\lambda = 1$ can be expanded as

$$\Psi(\lambda) = \Psi_0 + \lambda\Psi_1 + \cdots, \qquad (3a)$$

and $$E(\lambda) = E_0 + \lambda E_1 + \cdots, \qquad (3b)$$

and these in turn coincide with the wave functions and energies of interest also for $\lambda = 1$.

The fact that Eq. (2) is a well-defined equation for all values of λ and $\Psi(\lambda)$ and $E(\lambda)$ being continuous functions of λ enables the solution of the desired problem, for which $\lambda = 1$, perturbatively, even though there is no variable linear parameter such as Z^{-1} or ϵ within H_1 itself. The present treatment argues that if the expansions (3) converge for $\lambda \leq \rho$ and $\rho > 1$, they converge for $\lambda = 1$ to the unique eigenfunction and eigenvalue, respectively. We have given the same argument elsewhere[26] in treating intermolecular forces where the equation analogous to (2) is not even an eigenvalue equation except for $\lambda = 1$.

Note that the expansion of $\Psi(\lambda)$ and $E(\lambda)$ in powers of λ does not require these functions to be analytic in λ, but is based on the Weierstrass theorem, and thus is not affected by the observation of Mendelsohn[27] that the expansion can contain terms in $\log\lambda$.

It is important to notice that the choice of H_0, the unperturbed Hamiltonian, can only affect:

(1) the radius of convergence or semiconvergence of the expansions, i.e., whether they converge or semiconverge for $\lambda = 1$,

(2) the rate of convergence of the expansions, i.e., how many terms are necessary to give the desired accuracy; and

(3) the ease with which each of the individual terms can be calculated, which determines the amount of labor necessary to give results to the desired accuracy.

In other words it is desirable to choose an H_0 such that

$$R_n(E) \equiv |E_n/E_{n-1}| \ll \lambda^{-1} = 1$$

for small values of n, and such that the number of terms in each expansion that are necessary for the desired accuracies can be calculated with reasonable ease.

The class of choices of H_0 which we have called in a particular sense separable,[22] so that

$$H_0 = \sum_{i=1}^{N} h_0(i), \qquad (4)$$

with h_0 a completely arbitrary operator on the space and spin variables of one electron only, provides *all* the tractable orthodox perturbation theoretic expansions for many-electron problems. With this class of choices of H_0, the perturbation term in $H(\lambda)$ can therefore be written as a sum of identical two-electron terms, or symbolically, as

$$\lambda H_1 \equiv \lambda \sum_{i<j} g(i,j). \tag{5}$$

The use of separable Hamiltonians leads to two essential simplifications of the procedure for calculating the terms in the expansion of Ψ. The first is that the Ψ_0 which is an eigenfunction of H_0 satisfying

$$(H_0 - E_0)\Psi_0 = 0 \tag{6}$$

can be written as a determinant (unnormalized)

$$\Psi_0 = \mathrm{Det}\,|a(1)b(2)c(3)\cdots| \tag{7}$$

(or a linear combination of degenerate determinants of eigenvalue E_0) constructed from spin-orbitals a, b, etc., which are eigenfunctions of the one-particle operator h_0, satisfying

$$[h_0(1) - \epsilon_a]a(1) = 0. \tag{8}$$

The second basic simplification, which was first pointed out by Sinanoğlu,[12] is that the nth-order corrections, Ψ_n, can be obtained by solving sets of uncoupled inhomogeneous partial differential equations involving at most $n+1$ electrons. This enables the energy to be calculated through third order after having solved equations for no more than two electrons at a time. As discussed below, this can be reduced still further to a set of coupled equations in two variables r_1 and r_2 which decouple[22] for atoms and ions.

Before examining the specific form of Ψ_1, Ψ_2, etc., we note[21] that it is solely because of the use of a separable H_0 that Ψ_0 is an independent-particle function, that Ψ_1 is constructed from pair-correlation corrections, and Ψ_2 from two- and three-electron correlation corrections, etc., independent of the particular choice which is made for H_0.

In order to obtain an explicit expression for Ψ_1, the solution to the first-order perturbation theory equation

$$(H_0 - E_0)\Psi_1 = (E_1 - H_1)\Psi_0 \tag{9}$$

we write $-H_1\Psi_0$ as

$$\begin{aligned} -H_1\Psi_0 &= -\sum_{i<j} g(ij)\mathcal{A}\, a(1)b(2)\cdots \\ &= -\mathcal{A}\Big[\sum_{i<j} g(ij)a(1)b(2)\cdots\Big]. \end{aligned} \tag{10}$$

We observe that immediately there is a contribution to Ψ_1 arising from each term on the right-hand side of (10) introduced by the two operations $\mathcal{A}$ and $\sum$, so that Ψ_1 can actually be written as

$$\Psi_1 = \mathcal{A} \sum_{a<b} u_{ab}(12)c(3)\cdots, \tag{11}$$

where the spin-pair function u_{ab} is the solution to

$$\begin{aligned} [h_0(1) + h_0(2) - \epsilon_a - \epsilon_b]u_{ab}(12) \\ = -g(12)a(1)b(2) \\ + \text{boundary-condition (b.c.) terms}. \end{aligned} \tag{12}$$

This derivation differs from those in the literature[12] as discussed in detail in the Appendix. Since $g(12)$ is usually spin-independent, u_{ab} will have electron 1 and 2 in the same spin-state respectively as they are in the spin-orbitals $a(1)$ and $b(2)$. The boundary condition terms are necessary for the solution u_{ab} to exist; namely, they are such that the total inhomogeneity is orthogonal to the solutions of the homogeneous equation. The latter are linear combinations of all pairs of orbitals of energy $\epsilon_a + \epsilon_b$. If, for example, both a and b are different s states or arbitrary spin and h_0 is not the pure hydrogenic Hamiltonian (which introduces s-p degeneracy), the boundary condition terms are seen to be

$$\begin{aligned} &\langle a(1)b(2)|g(12)|a(1)b(2)\rangle a(1)b(2) \\ &+ \langle b(1)a(2)|g(12)|a(1)b(2)\rangle b(1)a(2), \end{aligned}$$

where only the spatial orbitals are included in the integrals. It can be verified that these boundary condition terms multiplied by the appropriate minors of Ψ_0 and summed over all the pair equations add up to the term $E_1\Psi_0$ of the first-order perturbation theory equation. Notice that the u_{ab} are not restricted to be one-electron orthogonal to any of the unperturbed orbitals.

The second- and third-order perturbation theory energies can be obtained by substituting this Ψ_1 into equations for E_2 and E_3 and the former is given explicitly in the Appendix.

It is significant to note that Ψ_1 is described in terms of pair functions $u_{ab}(ij)$ which possess no symmetry, whereas in the literature[12,15] the description is always in terms of antisymmetric pair functions, and has led to considerable complications.[28] The present nonsymmetric description shows that these complications are, in fact, unnecessary, since the singlet and triplet pair functions in the usual scheme are simply related.[22] To illustrate this point, it can be seen, for example that only one nonsymmetric pair function $u_{1s\,2s}(12)$ need be calculated in order to obtain both the so-called singlet and triplet pair-correlation functions[14,15,28]

$$u_\pm(12)[\alpha(1)\beta(2) \mp \beta(1)\alpha(2)] \equiv u_\pm(12)\Sigma_{1,3} \tag{13}$$

between $1s$ and $2s$ doubly-occupied orbitals of beryllium. The partial differential equations defining these functions are

$$\begin{aligned} [h_0(1) + h_0(2) - \epsilon_{1s} - \epsilon_{2s}]u_\pm(12) \\ = [k_\pm - g(12)][(1 \pm P_{12})1s(1)2s(2)], \end{aligned} \tag{14}$$

where $k_\pm$ are the usual boundary condition constants and the spin functions $\Sigma_{1,3}$ have been divided from both sides of the equation. When the two equations are added and divided by 2, we obtain

$$\begin{aligned} [h_0(1) + h_0(2) - \epsilon_{1s} - \epsilon_{2s}][\tfrac{1}{2}(u_+ + u_-)] \\ = [-g(12) + k]1s(1)2s(2) \\ + k'2s(1)1s(2), \end{aligned} \tag{15}$$

where we have set

$$k = \tfrac{1}{2}(k_+ + k_-) = J_{1s\,1s} \tag{16}$$

and $k' = \frac{1}{2}(k_+ - k_-) = K_{1s1s}$. (17)

This is just the Eq. (12) for the spatial part of $u_{1s2s}(12)$, so that

$$u_{1s2s}(12) = \tfrac{1}{2}[u_+(12) + u_-(12)]. \tag{18}$$

In a similar way, by subtracting the second equation from the first we obtain an equation for

$$u_{2s1s}(12) = \tfrac{1}{2}[u_+(12) - u_-(12)], \tag{19}$$

and this equation is precisely P_{12} times the Eq. (12) for u_{1s2s}, so that we have

$$u_{2s1s}(12) = P_{12} u_{1s2s}(12) \tag{20}$$

and so that the functions $u_\pm(12)$ are given by

$$u_\pm(12) = (1 \pm P_{12}) u_{1s2s}(12). \tag{21}$$

Excited states of helium have been considered perturbatively by several authors,[29-31] as has the $1s$-$2s$ pair correlation in Be[15], all using treatments which obtain the pair functions variationally. In such variational calculations, the Hamiltonian to be diagonalized can be symmetry blocked, and the use of our nonsymmetric pairs offers no particular advantage and might even prove less favorable than solving for the projected pairs themselves. On the other hand, if the pair equations are to be integrated numerically as described below, the loss of symmetry is of lesser importance, and the decreased algebra attending a smaller number of nonsymmetric pairs might make the latter advantageous. Generalizing from the helium example, it can be seen that if the N electrons are in $N/2$ different spatial orbitals, the maximum number of pair functions that must be determined is $N(N+2)/8$ as distinguished from the $N^2/4$ presumably expected previously. This number will be reduced still further to $M(M+1)/2$ for atoms with electrons in M shells (each at least doubly-occupied) since h_0 can be taken as a function of r only so that the radial parts of the pair functions are independent of azimuthal quantum number m. Thus for Ne, Ar, and Kr, respectively, radial functions need only to be calculated for 6, 15, and 36 independent pairs, and the size of the calculation of Ψ_1 increases roughly in proportion to N.

In order to obtain an explicit expression for Ψ_2, the solution to

$$(H_0 - E_0)\Psi_2 = (E_1 - H_1)\Psi_1 + E_2\Psi_0 \tag{22}$$

we write $-H_1\Psi_1$ as

$$\begin{aligned} -H_1\Psi_1 &= -\sum_{i<j} g(ij)\,\mathcal{A} \sum_{a<b} u_{ab}(12)c(3)\cdots \\ &= -\mathcal{A}\Big[\sum_{i<j}\sum_{a<b} g(ij)u_{ab}(12)c(3)\cdots\Big]. \end{aligned} \tag{23}$$

Analogously to the derivation of (11) above, we can see that Ψ_2 can be written in terms of second-order spin-pair functions, three-electron spin-functions, and products of spin-pair functions, as

$$\begin{aligned} \Psi_2 = \mathcal{A} &\sum_{a<b} u_{ab}^{(2)}(12)c(3)d(4)\cdots \\ &+ \mathcal{A} \sum_{a<c} \sum_b u_{abbc}(123)d(4)\cdots \\ &+ \mathcal{A} \sum_{\substack{a<b \\ c<d}} u_{ab}(12)u_{cd}(34)e(5)\cdots. \end{aligned} \tag{24}$$

The equations satisfied by the $u_{ab}^{(2)}$ and u_{abbc} are

$$\begin{aligned} &[h_0(1) + h_0(2) - \epsilon_a - \epsilon_b]u_{ab}^{(2)}(12) \\ &\qquad = -g(12)u_{ab}(12) + \text{b.c. terms} \end{aligned} \tag{25}$$

and

$$\begin{aligned} &\Big[\sum_{i=1}^{3} h_0(i) - \sum_{i=a}^{c} \epsilon_i\Big]u_{abbc}(123) \\ &\qquad = -g(12)a(1)u_{bc}(23) - g(23)u_{ab}(12)c(3) \\ &\qquad\qquad + \text{b.c. terms}, \end{aligned} \tag{26}$$

where the generalized boundary-condition terms are added as appropriate. As shown elsewhere,[22b] assuming the singularities can be properly taken care of, the three-electron function u_{abbc} can be written as

$$\begin{aligned} u_{abbc}(123) &= u_{ab}(12)u_{bc}(23)b(2)^{-1} \\ &\quad + u'_{abbc}(123) \end{aligned} \tag{27}$$

in terms of known pair functions. The parts of Ψ_2 expressed as products of spin-pair functions can be seen to occur since clearly

$$\varphi(1234) = u_{ab}(12)u_{cd}(34) \tag{28}$$

is the solution to

$$\begin{aligned} &\Big[\sum_{i=1}^{4} h_0(i) - \sum_{i=a}^{d} \epsilon_i\Big]\varphi(1234) = \\ &\qquad = -g(12)a(1)b(2)u_{cd}(34) \\ &\qquad\quad - g(34)u_{ab}(12)c(3)d(4) + \text{b.c. terms} \end{aligned} \tag{29}$$

whose inhomogeneity occurs in the breakup of (22) and (23).

The functions $u_{ab}^{(2)}$ form the first corrections to u_{ab}. Thus, in an exact-pair scheme analogous to that of Sinanoğlu,[32] where we define $u_{ab}^{(\infty)}$ as the solution to

$$\begin{aligned} &[h_0(1) + h_0(2) - \epsilon_a - \epsilon_b]u_{ab}^{(\infty)} \\ &\qquad = g(12)[a(1)b(2) + u_{ab}^{(\infty)}(12)] + \text{b.c. terms}, \end{aligned} \tag{30}$$

we have in the λ expansion

$$u_{ab}^{(\infty)} = u_{ab} + \lambda u_{ab}^{(2)} + O(\lambda^2).$$

The recent work of Byron and Joachain[15] has shown the importance of including such terms at least for outer-shell electrons. The functions $u_{ab}u_{cd}$, first discussed by Sinanoğlu[23] and called "unlinked clusters," provide a significant contribution to the fourth-order energy,[23] even though they only require a knowledge of functions appearing in the first-order wave function. That they contribute more to the total energy than the "true" four-electron clusters, i.e., those which require the solution of four-electron partial differential equations, is easy to see, since the latter only appear in Ψ_0 and contribute first to E_6, well beyond any expected accuracy in atomic calculations. We prefer not to use the terms "exact pairs" and "unlinked clusters"[33] since the actual functions depend on the particular choice of separable Hamiltonians H_0.

The problem of finding Ψ and E using perturbation theory thus reduces to choosing an appropriate separable H_0 to satisfy the three criteria of goodness described above: solving for the spin-orbitals a, b, etc., the spin-pair functions $u_{ab}(12)$, etc., and perhaps the functions $u_{abbc}(123)$ and $u_{ab}^{(2)}(12)$, etc., and at the last step evaluating a number of integrals over these orbitals, pair functions, etc. We now discuss the choice of H_0, following which we briefly discuss some of the methods of computation and give our results.

III. METHOD OF CALCULATION

A. Choice of H_0

A general separable H_0 for an atom can be defined in terms of the one-electron operators

$$h_0(i) = -\tfrac{1}{2}\nabla_i^2 - Z/r_i + V(i) + \int d\tau_j V(ij) P_{ij}, \tag{31}$$

where the potentials $V(i)$ and $V(ij)$ include spin-projection operators and P_{ij} permutes the coordinates of electron i and j.

In addition to the hydrogenic Hamiltonian for which $V(i) = V(ij) = 0$ and the screened-hydrogenic Hamiltonian for which $V(i) = \sigma/r_i$ and $V(ij) = 0$, calculations have been usually performed using the unrestricted Hartree-Fock Hamiltonian,[34]

$$h_0^{\mathrm{UHF}}(i) = -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{\rho=1}^{N} \{[-a_\rho \mid -a_\rho] - [-a_\rho \mid a_\rho -]\} \tag{32}$$

and certain "restricted" variants thereof. The spin-orbitals a_ρ are those occurring in

$$\Psi_0 = \mathcal{A}\, a_1(1) a_2(2) \cdots, \tag{33}$$

and the "exchange" operators include integration over spin. Recently calculations have been performed using Hamiltonians[35-39] which replace the exchange operators in h_0^{UHF} by an effective Thomas-Fermi exchange potential first discussed by Slater[35] with

$$h_0^{\mathrm{TF}}(i) = -\tfrac{1}{2}\nabla_i^2 - Z/r_i + \textstyle\sum_\rho [-a_\rho \mid -a_\rho] - k\left(\sum_\rho |a_\rho|^2\right)^{1/2}, \tag{34}$$

where the two choices of the constants k differ multiplicatively by $\frac{3}{2}$. The avoidance of "exchange" terms in h_0 not only simplifies the calculation of Ψ_0, but also that of Ψ_1 and of electromagnetic properties when performed numerically.[40,41] As another class of Hamiltonians we have suggested[21] the use of "exchangeless" Hamiltonians of the form

$$h_0^{\mathrm{EL}}(i, \alpha) = -\tfrac{1}{2}\nabla_i^2 - Z/r_i + \alpha \sum_{\rho=1}^{N} [-a_\rho^0 \mid -a_\rho^0], \tag{35}$$

where a_ρ^0 are single-particle spin-orbitals which should simulate the actual orbitals a_ρ of Ψ_0, but need not be the self-consistent solutions. In particular, it will be convenient for open-shell systems to take a_ρ^0 as the spherical and spin average of the approximate eigenfunctions of h_0^{EL}, there being no advantage, in the perturbative scheme discussed here, to carry out the iteration to self-consistency. (These arguments could be applied to modify h_0^{TF} in the same way.) This enables h_0 to commute with l^2, l_z, s^2, and s_z, so that H_0 commutes with L^2, L_z, S^2, S_z, J^2, and J_z. Thus Ψ_0 can be constructed as either an eigenfunction of L^2, L_z, S^2, and S_z, or as the linear combination of a number of determinants of J^2, J_z, S^2, and S_z; and since H_1 also commutes with all these operators, Ψ_1, Ψ_2, etc., are also exact eigenfunctions of the appropriate angular momentum operators. For example, the $^1Sp^2$ state of carbon can be written as the sum of three determinants (unnormalized),

$$\begin{aligned}\Psi_0 = {} & \mathrm{Det}\,|(1s)^2(2s)^2 2p_0\alpha 2p_0\beta| \\ & + \mathrm{Det}\,|(1s)^2(2s)^2 2p_+\alpha 2p_-\beta| \\ & + \mathrm{Det}\,|(1s)^2(2s)^2 2p_-\alpha 2p_+\beta|,\end{aligned} \tag{36}$$

where the three p states are degenerate eigenfunctions of the same h_0^{EL}; and equivalently as

$$\begin{aligned}\Psi_0 = {} & \mathcal{A}\, 1s\,\alpha(1) 1s\,\beta(2) 2s\,\alpha(3) 2s\,\beta(4) \\ & \times R_2^1(r_5) R_2^1(r_6) Y_1(\theta_{56}) \alpha(5)\beta(6),\end{aligned} \tag{37}$$

where $Y_1(\theta_{56})$ is the first spherical harmonic of the interelectronic angle θ_{56}, and R_2^1 is the radial part of the three $2p$ functions ($n = 2$, $l = 1$). Thus open-shell atoms can be treated on exactly the same footing as closed-shell atoms, which is not possible in one of the Restricted Hartree-Fock theories of Roothaan.[42] It is possible to treat them equally in the hydrogenic theory of Layzer,[43] Linderberg and Shull[44] and Safronova and Tolmachev[18] except that here there is the extra Coulomb degeneracy as well. Notice that for partially-filled shells the effect of the exclusion principle becomes particularly transparent when E_2 is written in the form (A.4).

The variable parameter α which appears in h_0^{EL} of (35) can be chosen based on a variety of criteria — such as to simulate h_0^{UHF}, to minimize the pair operator $g^{\mathrm{EL}}(ij)$ asymptotically in some region of space, etc. We propose without further discussion the choice

$$\alpha = (N-1)/N, \tag{38}$$

so that the total screening terms do not completely screen the nuclear attraction term. As an alternative choice, which might actually prove useful in increasing the rate of convergence for large atoms, we also propose the choice

$$\alpha = (N-1)/2N, \tag{39}$$

which makes $g(ij)$ asymptotically

$$g^{\mathrm{EL}}(ij) \sim 1/r_{ij} - 1/2r_i - 1/2r_j, \tag{40}$$

where the number of repulsions exactly cancels the number of attractions. This would correspond to an asymptotic h_0^{EL} of the form

$$h_0^{\mathrm{EL}}(i) \sim -\tfrac{1}{2}\nabla_i^2 - [(N+1)/2]/r_i \tag{41}$$

in which each electron is screened from the nucleus by an average Coulomb field arising from the remaining $N-1$ electrons. Our first choice (38) has the advantage of enabling h_0^{EL} to reduce to the exact Hamiltonian for a hydrogen atom, whereas the h_0^{UHF} of the hydrogen atom is[45]

$$h_0^{\mathrm{UHF}} = -\tfrac{1}{2}\nabla^2 - 1/r + [-1s \mid -1s] - [-1s \mid 1s-], \tag{42}$$

and the convergence of the perturbation corrections to the electric polarizability using this h_0 has been shown[40] to be quite slow. For helium, the h_0^{EL} with α of (38) reduces to the Hartree h_0, the convergence of whose perturbation expansion has been demonstrated by Byron and Joachain.[15]

B. Partial-Wave Expansions

When the spherically symmetric h_0^{EL} is used, the equations for the spin-orbitals, the spin-pair functions, and three-electron functions, etc., can be separated into uncoupled equations for each of the partial waves. Thus the solution to the one-particle equations (8) can be written as

$$a_{nlms}(r, \theta, \varphi, s) = [A_{nl}(r)/r] Y_l^m(\theta, \varphi)\sigma(s), \tag{43}$$

where Y_l^m is a spherical harmonic and σ a spin function; the radial function $A_{nl}(r)$ is independent of m and is the solution to

$$[-\tfrac{1}{2}d^2/dr^2 - (1/r)d/dr + V(r) + l(l+1)/2r^2 - \epsilon_a] \times (A_{nl}/r) = 0. \tag{44}$$

This type of solution has been used in all single-particle atomic calculations, for historical reasons, in order to make hand computations practicable, even for so-called SCF calculations on open-shell atoms, which serve as an orbital restriction on self-consistency.[46]

Similarly, the spin-pair function $u_{ab}(1, 2)$ can be expanded as[22]

$$u_{ab}(12) = \sigma(1)\sigma(2) \sum_{ll'mm'} U_{ll'mm'}^{ab}(r_1, r_2) \times Y_l^m(1) Y_{l'}^{m'}(2)(r_1 r_2)^{-1} \tag{45}$$

with the $U_{ll'mm'}(r_1,r_2)$ solutions to the two-demensional equations

$$\left\{(1+P_{12})\left[-\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} + V(r_1)\right] + \frac{l(l+1)}{2r_1^2} + \frac{l'(l'+1)}{2r_2^2} - \epsilon_a - \epsilon_b\right\} \times (r_1 r_2)^{-1} U_{ll'mm'}^{ab}(r_1, r_2) = Q_{ll'mm'}^{ab}(r_1, r_2), \tag{46}$$

where $Q_{ll'mm'}^{ab}$ is defined by the partial-wave expansion of the inhomogeneity of (12)

$$g(12)a(1)b(2) + \text{b.c. terms} = \sigma(1)\sigma(2) \sum_{ll'mm'} Y_l^m(1) Y_{l'}^{m'}(2) Q_{ll'mm'}^{ab}. \tag{47}$$

It is seen that the operator of (46) is independent of m and m' and therefore the pair corrections for *all* pairs of orbitals a and b, which differ only by azimuthal quantum numbers (e.g., all pairs of p_+, p_-, and p_0 of the same quantum number n) can be obtained from the U's for an individual pair merely by including the appropriate angular factors and Clebsch-Gordon coefficients.

For a and b, both s states the right-hand side of (47) can be written as

$$\sigma(1)\sigma(2) \sum_{l=0}^{\infty} Y_l(\theta_{12}) Q_l^{ab}(r_1, r_2) \tag{48}$$

with

$$Q_l^{ab}(r_1, r_2) \propto [A(r_1)B(r_2)/r_1 r_2] r_<^l / r_>^{l+1} \tag{49}$$

for $l \neq 0$ and the $U_{ll'mm'}^{ab}$ of (46) can be replaced by U_l^{ab}.

The one-dimensional eigenvalue equations and the two-dimensional inhomogeneous equations can be solved by linear-expansion techniques equivalent to the usual variational procedure, by nonlinear-expansion techniques using the appropriate variational principle, or by numerical integration techniques. We have chosen the direct numerical integration procedure for the present study to obviate the problem of choosing a complete, but not overcomplete basis.[47] Cohen and Coulson[48] have indicated the ease of performing such numerical calculations for molecular spin-orbitals, and we have suggested using these numerical procedures for large molecules.[21] The application of numerical techniques to the two-dimensional inhomogeneous equations was suggested to us by V. McKoy.[49] The calculations, which are presented in the next section, have been performed using solely numerical techniques and do not fit the results to analytic functions in order to evaluate the integrals analytically. Had we been interested in simple polynomial fits of the radial pair functions and been willing to evaluate the analytic integrals, we could have solved the problem variationally in the first place and obtained exactly the same results as can be obtained by solving numerically and then fitting, and have also managed to avoid the extrapolation problems inherent in the numerical procedures. While we might actually treat the pair functions of larger atoms variationally for reasons of convenience, we are content here with performing calculations which are at every stage numerical and contain no analytic fits whatsoever; and we claim an error in the energy which can be estimated directly from arguments of numerical analysis. As such, there are no questions of limits of basis size, and the errors due to finite boundaries or finite such size can be estimated quantitatively.

C. Molecules

While the present discussion has been centered on atomic problems, it is pertinent to sketch briefly the application to molecules since we believe that exchangeless H_0's, single-center expansions, and numerical methods may be a useful combination of techniques for molecular calculations.

When the Hamiltonian contains many Coulomb interactions, it will probably not be possible to write an h_0 as a function of r measured from some center in the molecule such that a perturbation procedure will converge, although this might be possible for some diatomics and some illustrative calculations have been made by Hauk, Parr, and Hameka[50] and Dvořáček and Horák[51] along these lines. What we expect should be done is an expansion of some exchangeless or even screened bare nuclear[21, 52] h_0 about a point,

$$h_0=\sum_{lm}h_0^{lm}(r)Y_l^m(\theta,\varphi), \tag{50}$$

and a numerical solution[20] of the coupled set of equations for each of the eigenfunctions

$$a_n(r,\theta,\varphi,s)=\sigma(s)\sum_{lm}[A_{lm}(r)/r]Y_l^m(\theta,\varphi) \tag{51}$$

as has already been done for H_2^+ in its ground and excited states by Cohen and Coulson[48] some years ago. The advantage of not having a self-consistent or even pseudo-self-consistent (e.g., fully iterated exchangeless) scheme, becomes apparent when one realizes that for these functions this could require a double-iteration scheme. Experience seems to indicate that convergence of the "single iteration" necessary to obtain the A_{lm} will be relatively rapid, although a fairly large number of individual A_{lm} may be needed. The calculations previously performed on single-center expansions other than those of Cohen[48] cannot, however, be compared with such calculations for a number of reasons, principally because they did not deal with numerical solutions of one-electron eigenvalue equations. Notice, however, that despite the relative complexity of the form of the orbitals, one has the opportunity for greater precision than in the usual limited basis set schemes.

Similarly the pair-equations arising from the first-order perturbation theory equations can be solved by expanding the U_{ab} in partial waves as for atoms, except that now the equations for the different partial waves do not separate and the $U_{ll'mm'}{}^{ab}$ must be solved for iteratively. Again, even despite the labor involved, this procedure may prove tractable where the configuration interaction (CI) type is not.

IV. APPLICATION TO THE HELIUM-ATOM GROUND STATE

A. Equations Resulting from Partial-Wave Expansions

The helium-atom ground state has a single, symmetric pair function for the spatial part of its first-order wave function; and it is a natural system on which to test both the various choices of H_0 and the accuracy of the computational method because of its simplicity and because variational solutions for Ψ_1 already exist for the hydrogenic[4,5,15] and Hartree[15] H_0's. In this section are given the explicit expressions for E_2 and E_3. The numerical procedures are described in Sec. IV.B, and the energies calculated through third order for five different H_0's are given in Sec. IV.

With h_0 defined as in (31), we take the spatial part of Ψ_0 as

$$1s(1)1s(2)=(4\pi r_1r_2)^{-1}P(r_1)P(r_2) \tag{52}$$

and, using (12), solve for Ψ_1 which is itself simply a spatial pair function, u_{1s1s}, times a spin function. Using Eqs. (45)–(49) and writing

$$u=\sum_l\left[\frac{(2l+1)}{4\pi}\right]u_l(r_1,r_2)P_l(\cos\theta_{12})(r_1r_2)^{-1}, \tag{53}$$

the equations that must be solved for the μ_l^- are

$$\left\{(1+P_{12})\left[-\frac{1}{2}\frac{\partial^2}{\partial r_1^2}-\frac{2}{r_1}+\frac{l(l+1)}{2r_1^2}+V(r_1)\right]-2\epsilon_{1s}\right\}u_l$$
$$=\left\{[1s1s\,|\,1s1s]\delta_{l0}+[V(r_1)+V(r_2)]\delta_{l0}\right.$$
$$\left.-\left(\frac{1}{2l+1}\right)\frac{r_<^{\,l}}{r_>^{\,l+1}}\right\}P(r_1)P(r_2), \tag{54}$$

where $[1s1s\,|\,1s1s]$ is the usual two-electron Coulomb integral. Notice that the term in E_1 which is required for the inhomogeneity to be orthogonal to all solutions of the homogeneous equation enters only in the $l=0$ case, since there are no eigenfunctions of energy ϵ_{1s} for $l>0$.

As pointed out by Schwartz,[3] E_2 decouples into a sum of terms

$$E_2=\sum_{l=0}^{\infty}E_2(l), \tag{55}$$

where

$$E_2(l)=\iint P(r_1)P(r_2)\left\{\frac{r_<^{\,l}}{r_>^{\,l+1}}-[V(r_1)+V(r_2)+E_1]\delta_{l0}\right\}$$
$$\times u_l dr_1dr_2. \tag{56}$$

The third-order energy can be obtained by substitution of the Ψ_1 and $r_{12}{}^{-1}$ expansions into

$$E_2=\langle 1|H_1-E_1|1\rangle-2\langle 1|0\rangle E_2 \tag{57}$$

and is given by

$$E_3=\sum_{l_1,l_2=0}^{\infty}\sum_k\frac{(2l_1+1)(2l_2+1)}{2}C_{l_1l_2k}$$
$$\times\iint\left\{\frac{r_<^{\,k}}{r_>^{\,k+1}}-[V(r_1)+V(r_2)+E_1]\delta_{k0}\right\}$$
$$\times u_{l_1}u_{l_2}dr_1dr_2-2E_2\iint P(r_1)P(r_2)u_0dr_1dr_2 \tag{58}$$

where

$$C_{l_1l_2k}=\int_0^{\pi}P_{l_1}(\cos\omega)P_{l_2}(\cos\omega)P_k(\cos\omega)\sin\omega d\omega. \tag{59}$$

A general formula for this integral is given in Condon and Shortley.[53] The range of k for given l_1 and l_2 is limited to a finite number of values by a triangle condition; on the other hand the sums over l_1 and l_2 are infinite. It is hoped, and this hope seems to be borne out in this work and that of Byron and Joachain,[15] that for chemical accuracy these expansions can be truncated after the first few terms.

B. Numerical Solution of the Differential Equations

The applications of numerical techniques to solving the ordinary differential equations of atomic and molecular physics are well-known, having been applied to the eigenvalue problem for atomic orbitals by the Hartrees[6] and to inhomogeneous perturbation equations by Sternheimer[54] in connection with one-electron perturbations. Numerical methods for partial differential equations have not received the attention they deserve in atomic calculations[55]—most workers preferring the use of variational procedures[56]—although they are regularly used in engineering and have been suggested by Bartlett[57] as a method of direct solution to the helium-atom Schrödinger equation.

The advantages of the use of numerical methods are (1) there is no problem of incomplete basis sets; (2) analytic evaluation of integrals over basis functions is avoided; (3) the problem of absolute minima versus local minima in variational solutions is avoided; and (4) the solutions are obtained in easy visualizable form as amplitudes over a two-dimensional domain.

To begin the numerical solution, the single-particle radial equations (44) were solved by the Hartree[6,58] method using Numerov successive point-by-point integration. Five or six decimal accuracy in the orbitals and eigenvalues is readily obtained, to give Ψ_0, E_0, and E_1, with the latter being obtained to the same accuracy by two-dimensional numerical integration using the trapezoidal rule.[59]

To obtain numerical solutions to the pair equations (54), a square domain in the r_1-r_2 plane was chosen with both r_1 and r_2 running from zero to some sufficiently large value n. The square was partitioned by a mesh of N^2 points ($N \sim 40$) at whose intersections the continuous variables r_1, r_2, V, P, and U were defined. Conversion of the partial differential equation to a discrete algebraic equation was completed by substitution for the second derivatives of the simple five-point finite difference formula[59] where h, the mesh size, is the difference between adjacent points (n/N) in either the r_1 or r_2 direction, and $U(i,j)$, $i,j = 1,\cdots N$, is the value of the pair function at $r_1 = ih$, $r_2 = jh$.

Taking cognizance of the boundary conditions for the partial differential equations (54) we impose on the discrete problem the condition that U vanish on the boundary of the square $n \times n$ domain. For the exact problem, U should be small (but nonzero) at $r_1, r_2 = n$, if at these points the one-particle solutions are themselves quite small.

The pair equation is turned into a set of simultaneous equations summarized by the matrix relation $MU = Q$ where U and Q are N^2 vector approximations to the pair functions and inhomogeneities, respectively, and M is the $N^2 \times N^2$ matrix representation of the operator of (54). The off-diagonal elements of M arise only from the finite difference approximation to the derivatives and can all be trivially reduced to unity by multiplying the equation through by h^2. Matrix M is then reduced to a matrix of $N \times N$ submatrices of which only the diagonal submatrices ($M_i; i = 1,\cdots, N^2$) and two adjacent strips or bands of $N \times N$ identity submatrices contain nonzero elements (Fig. 1). Such a matrix is sometimes referred to as block-tridiagonal.[60] The fact that it contains very few nonzero elements in this particular arrangement facilitates solution for U, since the large size of M (greater than 10^6 when N has the typical value 40) precludes it from being stored intact and inverted.

Matrix M can be set equal to the product of two matrices L and U also having block-tridiagonal character but with zero elements above and below the diagonal submatrices, respectively (Fig. 2). Such L-U decompositions allow solution for U by a two-step process using forward substitution with L followed by back substitution with U.

M can also be seen to be a band matrix of width $2N+1$, namely one in which all nonzero elements lie in a band symmetric to the diagonal, and any element M_{ij} of M vanishes for $|i-j| > N$. The band-matrix viewpoint[49] does not take account of the block-tridiagonal character of M and therefore, although allowing for a L-U decomposition, does so at the cost of larger storage than the block-tridiagonal L-U method of Fig. 2. In fact, by observing that $\mathrm{L}_i = \mathrm{U}_i^{-1}$, the storage is reduced to the N^2-1U matrices.

Although the results given in the following section were obtained by the L-U method, we have also found Gauss-Seidel iteration[60] to be convergent, and capable of yielding eight decimal place agreement with the direct L-U decomposition in only slightly larger computer times. This method starts with an initial solution U^0, readily obtained by inverting the diagonal part of M[e.g., $U^0 = (\text{diag. } M)^{-1}Q$]; and it has a number of advantages over the L-U method, the most important being its neglible storage requirements. Various extrapolation and relaxation techniques[60] can be introduced to accelerate convergence, and these are under current investigation.

The finite difference approximation is the largest source of error in Ψ_1 and in the E_2 and E_3 computed using the trapezoid rule. This error may be

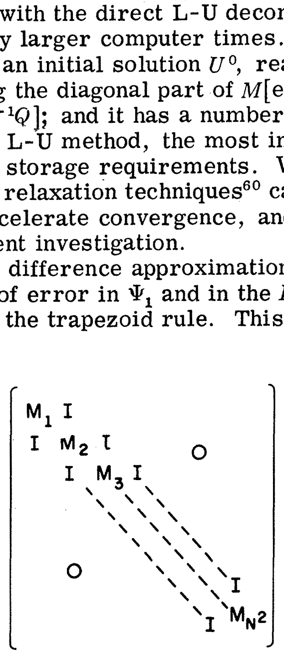

FIG. 1. The block-tridiagonal matrix ($N^2 \times N^2$) of matrices M and I, each $N \times N$.

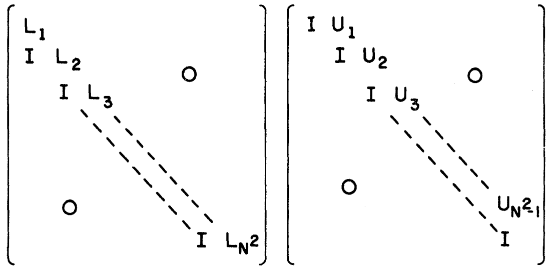

FIG. 2. The product of a lower block-tridiagonal matrix L and an upper tridiagonal matrix U, where LU =M of Fig. 1.

very greatly reduced using an extrapolation technique known as Richardson's differed approach to the limit,[61] for which an expectation value of interest is expanded in a power series in h

$$\langle A\rangle_h = A_c + A_2h^2 + A_4h^4 + O(h^6), \tag{60}$$

where the A's are constant. Since (60) contains three unknown A's, the desired "zero-mesh" quantity may be found by computing $\langle A\rangle h$ at three different mesh sizes and solving simultaneous equations. The error in $\langle A\rangle$ obtained by this extrapolation method is on the order of h_{max}^6, where h_{max} is the largest of the three meshes so that it is desirable to keep h_{max} as small as possible.

Our intent in applying numerical methods is to obtain energies in error by only chemically insignificant amounts, and we do not intend to compete with calculations as in Refs. 1–3. The actual accuracy of our numerical procedure is limited by the choice of a finite boundary and by inaccuracies in the finite difference-extrapolation sequences. These errors should in general be balanced against each other for a fixed number of mesh points: decreasing the upper limit n of the domain reduces the boundary error but increases the corresponding mesh size. A way to get some measure of the boundary error is to run several trial computations with the mesh size held fixed and n moved sucessively further out. When this was done for the hydrogenic helium expansion it was found that increasing n from $5.0a_0$ to $7.0a_0$ decreased $E_2(l=0)$ by 1×10^{-5} a.u., while changes in $E_2(l>0)$ were even smaller. A further extension for $7.0a_0$ to $8.0a_0$ changed $E_2(l=0)$ by 1×10^{-7} a.u. For the single calculation with $\alpha=\sigma=0$, n was taken as 5.0 a.u. and the chemically acceptable error was assumed in order to get the advantage of smaller mesh size. For the other calculations (discussed in the next section), the orbitals were more diffuse because of nuclear screening, and for these cases the boundary was arbitrarily taken as 7.0 a.u.

An interesting method of avoiding both boundary and mesh size problems might be the change of variables $\rho=cr/(1+cr)$, with c an appropriately chosen constant discussed below. The domain of the pair function is reduced to a unit square (since $\rho\rightarrow1$ as $r\rightarrow\infty$) on whose perimeter the pair function vanishes identically. Moreover, choosing $N=40$ makes $h=1/40$, which the present work suggests is a sufficiently small mesh size. Finally, the constant c may be chosen to adjust the number of intervals of ρ space to correspond to some desired length in r space; for example with $c=0.1$ and 1.0, half the intervals in ρ space correspond respectively to $r=1.0$ and 10.0 a.u. A disadvantage of this change in variables is that first derivatives are introduced into the pair equations; however, this problem is easily resolved in the iterative method of solution.

C. Energies for Ground-State Helium in Several Perturbation Expansions

Table I summarizes much of the perturbation literature for atom energies. The results of Kelly[11] are not included as he does not separate various orders of perturbation. It can be seen for the three atoms for which comparison is possible, the hydrogenic expansion is not necessarily much more slowly convergent than Hartree-Fock and, in fact, for helium it is even better through third order.

For the helium-atom ground state, we have used five perturbation expansions: (1) hydrogenic [$\sigma=0$, also exchangeless, $\alpha=0$]; (2) and (3) screened hydrogenic with $\sigma=\frac{1}{2}$ and $\frac{11}{16}$, respectively; (4) exchangeless with $\alpha=\frac{1}{2}$ from (38) and fully-iterated orbitals, which corresponds to the Hartree procedure; and (5) exchangeless with $\alpha=\frac{1}{4}$ from (39) with the orbitals a^0 being first iterates starting from a 1s Slater orbital of exponent 1.6875 as the zeroth iterate. Energy values for the expansions (1) and (4) have been obtained in previous calculations, while the energies from (2) and (3) are useful in providing checks on the numerical techniques, and the energy from (5) can be compared with that from the somewhat UHF-like expansion (4). The different rate of convergence of expansions of (1), (2), and (3) is of no significance, since the various E_n are related to each other. However, the difference between the convergence of the corresponding expansions in molecules may be important.[21]

In order to illustrate the rate of convergence of the l expansion of E_2 and the numerical errors involved in the computation, we compare in Table II our results for hydrogenic helium with the variational results of Byron and Joachain[15] and Knight and Scherr.[4] The components, $E_2(l)$ of the second-order energy differ from the more accurate variational values by at most 7×10^{-5} a.u. for $E_2(0)$ and, in fact, the total error through $l=7$ is only 8.6×10^{-5} a.u. higher than the variational value through $l=7$. The error in these terms is probably due to limitations of the extrapolation procedure. For example, the extrapolated value, $E_2(0)=-0.125\,262$, was obtained from the three values $-0.126\,0377$, $-0.126\,2027$, and $-0.126\,4127$, at mesh sizes h corresponding to $\frac{1}{9}$, $\frac{1}{8}$, and $\frac{1}{7}a_0$, respectively. Thus the extrapolation has succeeded in reducing the error by one order of magnitude. As anticipated, this error is roughly h_{max}^6, and explicitly $9h_{\text{max}}^6$.

Terms in higher l such as $E_2(5)$ and $E_2(7)$ have larger relative (although smaller absolute) errors than the $l=0$ term because the peakedness of the pair functions increases with l in the manner discussed by Schwartz.[3] In fact, Byron and Joachain[15] have suggested the largest source of error in their calculations arises from E_2's of higher l. The for-

TABLE I. Literature values for atomic perturbation energies (a.u.). The numbers in parentheses are the errors in parts per thousand, referred to E_{exact}.

$$E^{(n)}=\sum_{k=0}^{n}E_k$$

Helium: $E_{\text{exact}}=-2.903\,72$[2-5]

	Hydrogenic[4,5]	Hartree[15]	Hartree-Fock[15; a]
$E^{(0)}$	−4.000 00 (−3800)	−1.835 92 (3700)	−1.835 92 (3700)
$E^{(1)}$	−2.750 00 (530)	−2.861 67 (140)	−2.861 67 (140)
$E^{(2)}$	−2.907 66 (−14)	−2.909 84 (−21)	−2.898 92 (16)
$E^{(3)}$	−2.903 32 (1.4)	−2.902 67 (3.6)	−2.902 69 (3.5)
$E^{(4)}$	−2.903 53 (0.65)	−2.903 96 (−0.83)	−2.903 54 (0.62)
$E^{(5)}$	−2.903 66 (0.21)	−2.903 70 (0.069)	−2.903 70 (0.069)
$E^{(6)}$	−2.903 70 (0.069)		

Lithium: $E_{\text{exact}}=-7.478\,07$[b]

	Hydrogenic[17]	Hartree-Fock[a]
$E^{(0)}$	−10.1250 (−3500)	−5.006 21 (3300)
$E^{(1)}$	−7.0566 (560)	−7.432 73 (61)
$E^{(2)}$	−7.4649 (18)	
$E^{(3)}$	−7.4726 (7.3)	

Beryllium: $E_{\text{exact}}=-14.6674$[b]

	Hydrogenic[18]	Hartree-Fock[15; a]
$E^{(0)}$	−20.0000 (−3900)	−10.083 88 (3100)
$E^{(1)}$	−13.7628 (620)	−14.573 02 (64)
$E^{(2)}$	−14.6404 (18)	−14.6482 (13)
$E^{(3)}$		~−14.6585 (6.1)[c]
$E^{(4)}$		~−14.6635 (2.6)
$E^{(5)}$		~−14.6655 (1.3)

[a] E_0 and E_1 were obtained by C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).
[b] A. W. Weiss, Phys. Rev. 122, 1826 (1961).
[c] The tilde is a reminder that these calculations omitted three-particle terms in Ψ_2 and in the evaluation of E_3.

mation of cusps can readily be seen from Fig. 3, in which the amplitudes of the radial pair functions $U_l(r_1, r_2)$ of Eq. (54) are plotted for $l=0$, 1, 3, 5, and 7 along the line $r_1+r_2=\text{constant}$—a perpendicular to the diagonal $r_1=r_2$—which passes through the maximum or minimum of the function. Because of the small magnitudes of the U's of higher l, the presence of cusps does not greatly affect the energy to the accuracy sought here and the slow

TABLE II. Numerical and variational perturbation energies for hydrogenic helium.

	Numerical	Variational[15]
$E_2(l=0)$	−0.125 262	−0.125 334
$(l=1)$	−0.026 495	−0.026 495
$(l=2)$	−0.003 900	−0.003 906
$(l=3)$	−0.001 072	−0.001 077
$(l=4)$	−0.000 402	−0.000 405
$(l=5)$	−0.000 182	−0.000 183
$(l=6)$	−0.000 094	−0.000 094
$(l=7)$	−0.000 053	−0.000 053
E_2 (through $l=7$)	−0.157 461	−0.157 547[15]
E_2 (all l)		−0.157 656,[15] −0.157 666[4]
E_3 (through $l=7$)	+0.004 165	
E_3 (all l)		−0.004 349[4]
E_2+E_3	−0.053 296	−0.153 317
$E^{(3)}$	−2.903 296	−2.903 316

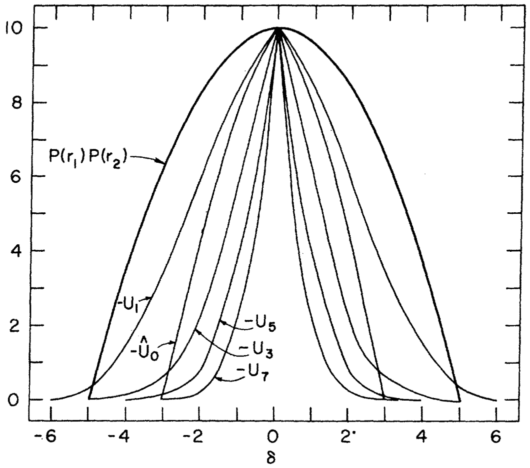

FIG. 3. Amplitudes of $P(r_1)P(r_2)$, $\hat{U}_0(r_1,r_2)$ and $U_l(r_1, r_2)$ for $l=1$, 3, 5, and 7 plotted against δ, the displacement from the diagonal along the line $r_1=-r_2+\text{constant}$ which passes through the function's minimum [maximum for $P(r_1)P(r_2)$]. $P(r_1)P(r_2)$ and $\hat{U}_0$ are the radial parts of $1s(1)1s(2)$ and the radial part of U_0 orthogonal to $P(r_1)P(r_2)$. A δ unit = 0.15 a.u. The functions are all symmetrical with respect to $r_1=r_2$, and they have been normalized on an arbitrary scale from 0 to 10 to show the relative peakedness. These results were obtained at mesh size $=\frac{1}{9}$. The scale factors can be obtained from Fig. 4.

convergence[3] is not a problem.

Another interesting feature of Ψ_1 is that U's for $l > 0$ are entirely negative while $\hat{U}_0$, that part of our U_0 orthogonal to Ψ_0, is negative near the nucleus and positive further out. (Ψ_0 is, of course, positive throughout the domain.) When viewed along the diagonal $r_1 = r_2$, as shown in Fig. 4, along with $U_l(l > 0)$, $\hat{U}_0$ has a negative minimum at about $0.33a_0$ and in the region near the nucleus looks very much like $r^2 R_{2s}{}^2(r)$, where R_{2s} is the radial part of a 2*s* orbital.

The sum of $E_2(l)$ through $l = 7$ is −0.157 474 a.u. compared with the value −0.157 666 obtained by Knight and Scherr[4] and claimed to be good to better than six decimal places. Our value of E_2 through $l = 7$ is in error by about −0.0002 a.u.; however, since our E_2 is quite close to the variational E_2 through $l = 7$, our error is due almost entirely to neglect of higher l values. Although an extrapolation in l reduces the error in E_2, it turns out to be unnecessary since the error in E_2 and E_3 appear to cancel. It is hoped that this cancellation will hold in atoms other than helium.

Our value of $E^{(3)}$, the energy through third order, is −2.903 296, differing from Knight and Scherr's value (−2.903 316) by less than 2×10^{-5} a.u. Similar good agreement was obtained for the Hartree expansion, where the numerical method gives −2.902 59 a.u., and Byron and Joachain[15] obtained −2.902 67 a.u.

Table III contains the results through $E^{(3)}$ for all five perturbation expansions we considered. The screened-nucleus expansions give a check on the internal consistency of our method, since the terms in the various expansions can be seen to be related to each other—as has been observed previously,[62,63] although it has not been generally recognized. Thus $E^{(2)}$ is actually the same in all expansions and is independent of σ, and furthermore, the E_3's of any two expansions are related by

$$E_3(\sigma_1)/E_3(\sigma_2) = (2-\sigma_2)/(2-\sigma_1).$$

From Table III it can be seen that our $E^{(2)}$ is constant to 6 ppm, and for the ratios of E_3's we obtained 0.744, 0.649, and 0.873 quite close to the exact ratios of 0.75, 0.656, and 0.875. Notice that the energy $E^{(3)}(\sigma)$ can be given approximately as

$$E^{(3)}(\sigma) = E^{(3)}(\sigma = 0) + 0.0028\sigma$$

which, if set equal to the exact nonrelativistic energy, such that

$$\sum_{n=4}^{\infty} E_n = 0$$

would find the "optimum" $\sigma \sim -\frac{1}{7}$ for a third-order calculation, or negative screening. This, of couse, does not imply that E_4, E_5, etc., themselves are zero or even small, which should illustrate the completely arbitrary nature of finding "optimum" screening parameters. The same type of argument applies to the calculation of electromagnetic properties of atoms in hydrogenic and screened hydrogenic expansions.[62]

The two exchangeless energy results as given in the last two columns of Table III show reasonably rapid convergence, both oscillating about the exact solution rather than approaching it monotonically as does the Hartree-Fock expansion.[15] Through third order the $\alpha = \frac{1}{2}$ expansion appears to converge more rapidly than the $\alpha = \frac{1}{4}$ expansion.

The conclusions to be drawn from Table III are that all five expansions converge very rapidly, and

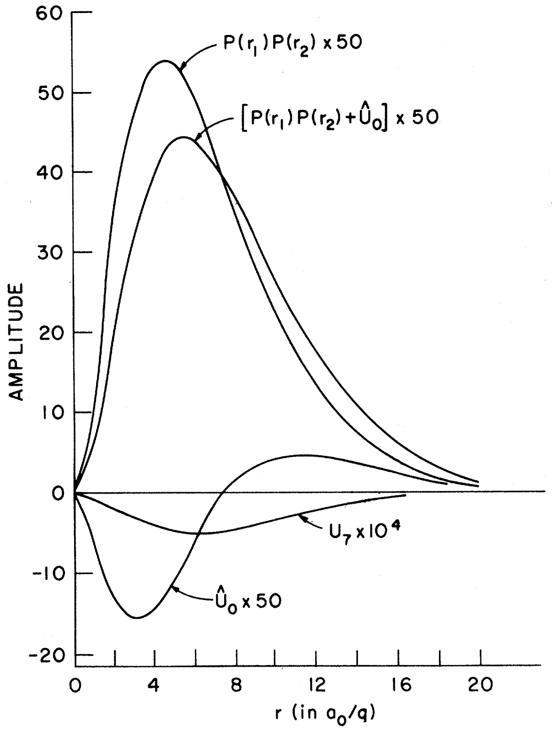

FIG. 4. Amplitudes of $P(r_1)P(r_2)$, $\hat{U}_0$, $[P(r_1)P(r_2) + \hat{U}_0]$, and U_7 are plotted along the diagonal $r = r_1 = r_2$. U_7 typifies U_l, $l > 0$ all of which are negative with minima at about $(6/9)a_0$.

TABLE III. Energies for various expansions.

	Hydrogenic	Screened nucleus		Exchangeless	
	$\sigma = 0$, $\alpha = 0$	$\sigma = \frac{1}{2}$	$\sigma = \frac{11}{16}$	$\alpha = \frac{1}{2}$ (Hartree)	$\alpha = \frac{1}{4}$
$E^{(0)}$	−4.000 000	−2.250 000	−1.722 654	−1.835 891	−2.828 048
$E^{(1)}$	−2.750 000	−2.812 500	−2.707 027	−2.861 649	−2.834 202
$E^{(2)}$	−2.907 461	−2.907 473	−2.907 479	−2.909 710	−2.911 688
$E^{(3)}$	−2.903 296	−2.901 878	−2.901 067	−2.902 586	−2.901 772
Error[a]	−0.000 428	−0.001 846	−0.002 657	−0.001 138	−0.001 952

[a] Referred to $E_{\text{exact}} = -2.903\,724$.

surprisingly enough, the most accurate $E^{(3)}$ is obtained from the unscreened hydrogenic procedure, which has the worst $E^{(0)}$ and might have been thought the least likely to converge rapidly. Since the present calculations are virtually insensitive to the choice of H_0, it remains for further studies to determine which possible expansions will converge most rapidly. We have succeeded in demonstrating once again that one need not use the Hartree-Fock procedure with its computational disadvantages in order to obtain accurate energy values, at least for the special case of helium atom. There seems no reason, however, to imagine that the convergence of the exchangeless procedure will be drastically different for large atoms than it is for helium. Further studies on larger atoms using these methods and the procedure of Musher and Silbey[64] are being undertaken in our laboratory in order to further clarify these points.

V. SUMMARY

The important points made in this paper can be summarized as follows: A new derivation has been presented for the explicit form of the first-order perturbation correction Ψ_1 for a separable many-electron H_0. The pair problem occurring for Ψ_1 has been examined in detail, and it has been shown that the number of interorbital pairs can be reduced by foregoing spin symmetry. This simplification may be of some practical utility when used in conjunction with the numerical methods discussed here. When partial-wave expansions are used, the number of pairs that need be calculated for atoms is reduced still further. An explicit derivation of the contribution to Ψ_2 has also been given.

The choice of H_0 has been discussed and it was suggested that exchange operators be removed. For atoms, H_0 should retain spherical symmetry, and for molecules, a realistic H_0 should be expanded in partial waves. A numerical procedure for solving the pair equations has been given and shown to be an accurate alternative to the Hylleraas variational procedure. The study of various H_0's for the helium ground state led to no significant improvement in energy convergence, at least through third order. None the less, the absence of exchange should be an important computational simplification.

We are presently employing these pair equations, radial expansions, and numerical methods on larger atoms and examining related problems in finite nuclei.

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Appendix A: Some Details

The explicit form of the second-order energy is obtained from the Ψ_1 of (11) as

$$E_2=\sum_{a<b}\Big[\langle P^{(2)}a(1)b(2)\,|g(12)\,|u_{ab}(12)\rangle+\sum_{c\neq a,b}\langle P^{(3)}a(1)b(2)c(3)\,|g(13)+g(23)\,|u_{ab}(12)c(3)\rangle$$

$$+\sum_{c<d\neq a,b}\langle P^{(4)}a(1)b(2)c(3)d(4)\,|g(34)\,|u_{ab}(12)c(3)d(4)\rangle-\sum_{c<d}\langle P^{(2)}c(1)d(2)\,|g(12)\,|c(1)d(2)\rangle$$

$$\times\langle P^{(2)}a(1)b(2)\,|u_{ab}(12)\rangle\Big], \qquad \text{(A.1)}$$

where

$$P^{(n)}=\sum_{q=0}^{n!}(-1)^q P_q$$

is the projector onto the antisymmetric representation of the symmetric group of n particles, e.g., $P^{(2)}=(1-P_{12})$. The first three terms in the bracket arise from $\langle 0\,|H_1\,|1\rangle$ while the last term arises from $-E_1\langle 0\,|1\rangle$.

This expression can, however, be simplified further by examining the third set of terms in detail. They can be divided into the following three types, containing two, one, and zero "coincidences," respectively, in the overlap integrals,

$$\langle P^{(2)}ab\,|u_{ab}\rangle\langle P^{(2)}cd\,|g\,|cd\rangle, \qquad \text{(A.2a)}$$

$$\langle P^{(2)}ac\,|u_{ab}\rangle\langle P^{(2)}bd\,|g\,|cd\rangle, \qquad \text{(A.2b)}$$

$$\langle P^{(2)}cd\,|u_{ab}\rangle\langle P^{(2)}ab\,|g\,|cd\rangle. \qquad \text{(A.2c)}$$

The terms in (A.2c) can be seen to cancel all the terms of the last sum of (A.1) except those in which $c=a$ and/or $d=b$ in the double sum. In addition, the terms of (A.2b) and (A.2c) sum to zero by an argument analogous to one given previously.[65] Thus, for example, the substitution of the formal solution

$$u_{ab}=[\epsilon_a+\epsilon_b-h_0(1)-h_0(2)]^{-1}$$

$$\times[g(12)a(1)b(2)+\text{b.c. terms}]$$

into (A.2c) leads to the vanishing double sum

$$\sum_{a<b}\ \sum_{\substack{c<d\\(c,d)\neq(a,b)}}(\epsilon_a+\epsilon_b-\epsilon_c-\epsilon_d)^{-1}$$

$$\times|\langle P^{(2)}cd\,|g\,|ab\rangle\,|^2=0 \qquad \text{(A.3)}$$

since for every choice of a, b, c, and d the same squared matrix element will appear twice in the summation once multiplied by $(\epsilon_a + \epsilon_b - \epsilon_c - \epsilon_d)^{-1}$ and the other time by $(\epsilon_c + \epsilon_d - \epsilon_a - \epsilon_b)^{-1}$ with any singularities properly taken care of by the boundary condition terms. The same argument provides for the vanishing of the sum of (A.2b).

Thus E_2 can be written as

$$E_2 = \sum_{a<b} \Big\{ \langle P^{(2)}ab | g | u_{ab} \rangle + \sum_{c \neq a,b} \langle P^{(3)}a(1)b(2)c(3) | g(13) + g(23) | u_{ab}(12)c(3) \rangle - \sum_{c<d}{}' \langle P^{(2)}cd | g | cd \rangle \langle P^{(2)}ab | u_{ab} \rangle \Big\}, \tag{A.4}$$

in which the primed sum indicates at least one coincidence between the sets $\{c, d\}$ and $\{a, b\}$. This expression cannot be further simplified in a practical sense, and there appears to be no way to decrease further the amount of labor necessary to calculate E_2.

Notice that Eq. (11) which defines the u_{ab} does not restrict these functions to be one-electron orthogonal to the remaining occupied orbitals c, d, $\cdots$. Thus u_{ab} can, and indeed will contain contributions of the form $\varphi(1)c(2)c(3)\cdots$ and $c(1)\varphi'(2) \times c(3)\cdots$ which give rise to terms in Ψ_1 such as $\mathfrak{A}\varphi(1)c(2)c(3)d(4)\cdots$, etc., which clearly vanish by the laws of determinants and make no contributions to the energy. Since, however, these terms are not subtracted out of the u_{ab} in the first sum of (A.1) or (A.4) they will occur, in the second sums as well, and thus appear to be exclusion-principle-violating (EPV) terms.[11] As is well-known, we could have replaced u_{ab} everywhere by[15]

$$\hat{u}_{ab}(12) = u_{ab}(12) - \sum_{c \neq a,b} \Big[c(1) \int c(j) u_{ab}(j2) dj + c(2) \int c(j) u_{ab}(1j) dj - c(1)c(2) \int c(i)c(j) u_{ab}(ij) di dj \Big] \tag{A.5}$$

without changing Ψ_1 and hence E_2, the only apparent change being that two of the six permutations in the second term of (A.4), the EPV terms, will give zero, the corresponding terms having been shifted into the first term. Notice that the u_{ab} will, however, contain contributions of the form u_{ab} will, however, contain contributions of the form $\varphi(1)b(2)c(3)\cdots$ and $a(1)\varphi'(2)c(3)\cdots$, etc., which are true single excitations, and whose corresponding parts of Ψ_1 do not vanish, so that the variety of other terms in (A.4) cannot be practically eliminated. Only in the special case of the Hartree-Fock self-consistent expansion, for which the net effect of such single excitations vanishes so that these two permutations vanish anyway, does this provide any actual simplification. There is a correspondingly greater number of terms in E_3 which cannot be eliminated by any orthogonalization procedure. In view of the great deal of algebra involved in obtaining E_3 for large atoms, it is perhaps better to use the procedure recently discussed by Musher and Silbey based on a Hartree-like nonsymmetric H_0 for which the algebra is considerably reduced.

We now make the observation that, by defining the $g(ij)$ as in Eq. (5) to be the *same* for all electrons i and j, we have derived a set of equations (12) which when symmetrized and applied to the Hartree-Fock expansion are actually different from those of Sinanoḡlu, e.g., Eq. (34) of Ref. 12. While both derivations are "correct" and the final results identical even though the actual pair functions differ, it is illustrative to indicate the differences in detail.

The procedure of Sinanoḡlu, also used by Byron and Joachain, defines a set of pair operators $h(ij)$ which are *different* depending on which orbitals are being operated on. Their definition is only applicable to the Hartree-Fock problem, but a slight generalization which includes the exchangeless procedure can serve to further clarify the situation.

Consider the class of H_1's which can be written as

$$H_1 = \sum_{\rho, i} V_\rho(i) + \sum_{i<j} \frac{1}{r_{ij}}, \tag{A.6}$$

where $V_\rho(i)$ is some effective potential due to orbital a_ρ, or some approximation, thereof, $a_\rho{}^0$, operating on electron i. Thus, for example,

$$-V_\rho(i) = [-a_\rho | -a_\rho] - [-a_\rho | a_\rho -] \tag{A.6a}$$

for the UHF expansion with the h_0 of (32), and

$$-V_\rho(i) = \alpha[-a_\rho{}^0 | -a_\rho{}^0] \tag{A.6b}$$

for the exchangeless expansion with the h_0 of (34). When the product $-H_1\Psi_0$ of (9) is expanded out as

$$-H_1\Phi + H_1 P_{12}\Phi - \cdots$$

with

$$\Psi_0 = (N!)^{1/2}\mathfrak{A}\Phi \equiv \mathfrak{A}a_1(1)a_2(2)\cdots,$$

the H_1 operating on Φ can be written as

$$H_1[\Phi] = \sum_{i<j} h_\Phi(ij), \tag{A.7}$$

where

$$h_\Phi(ij) = 1/r_{ij} + V_j(i) + V_i(j) + [1/(N-1)][V_i(i) + V_j(j)] \tag{A.8}$$

and where the subscripts i and j of the V's refer to the orbital of an Φ which electrons i and j are in, respectively, and are *not* electron indices, being different, therefore from the subscripts in $1/r_{ij}$. The equation for the pair function v_{ab} corresponding to the u_{ab} of (12) thus becomes

$$[h_0(1) + h_0(2) - \epsilon_a - \epsilon_b] v_{ab}(12) = -\{r_{12}{}^{-1} + V_b(1) + V_a(2) + (N-1)^{-1}[V_a(1) + V_b(2)]\} a(1)b(2) + \text{b.c. terms.} \tag{A.9}$$

Notice that from the form of H_1 given by (A.5) there are $N^2 V_j(i)$'s of which $N(N-1)$ are for $i \neq j$ so that two of these can be associated as appropriate with each of the $N(N-1)/2$ terms r_{ij}^{-1}. The remaining N terms, $V_i(i)$, however must be somehow divided among these $N(N-1)/2$ terms and this is done symmetrically in the definition (A.8) of $h_\Phi(ij)$. Clearly, the breakup of H_1 into terms $h(ij)$ will be different for each permutation $P\Phi$ of Ψ_0 which makes the derivation somewhat cumbersome to present fully, although it is straightforward and has been given previously.[12] Notice that in the above notation our $g(ij)$ is defined as

$$g(ij) = 1/r_{ij} + [1/(N-1)] \textstyle\sum_k [V_k(i) + V_k(j)], \quad \text{(A.10)}$$

and thus distributes *all* the potentials symmetrically and not just the "self-potentials" $V_i(i)$.

For the UHF expansion the $h(ij)$ notation has the simplification that self-potential terms drop since

$$-V_\rho(i) a_\rho(i) = \{[-a_\rho \mid -a_\rho] - [-a_\rho \mid a_\rho -]\} \times a_\rho(i) = 0, \quad \text{(A.11)}$$

where now the $-V_\rho(i)$ correspond exactly to the $S_\rho(x_i) - R_\rho''(x_i)$ of Sinanoğlu.[12] The equation (A.9) thus reduces to

$$[h_0(1) + h_0(2) - \epsilon_a - \epsilon_b] v_{ab}(12) = -[r_{12}^{-1} + V_b(1) + V_a(2)] a(1) b(2) + \text{b.c. terms} \quad \text{(A.12)}$$

which relates to the Eqs. (27)[15] of Byron and Joachain's Be calculations for v_+ and v_- by an argument analogous to that of Eqs. (13)–(19) above.

The Sinanoğlu formulation based on the $h(ij)$ provides an important conceptual advantage over our $g(ij)$ formulation for this UHF case in that it enables a simple demonstration of the lack of single excitations in Ψ_1. The projection of the right-hand side of (A.12) onto either $a(1)$ or $b(2)$ is immediately seen to vanish,[15] so that $\chi_a(1)$ and $\chi_b(2)$ of

$$v_{ab}(12) = a(1)\chi_b(2) + \chi_a(1) b(2) + v_{ab}'(12)$$

must be taken as zero; and v_{ab} does not contain single excitations from a and b. The u_{ab} of (12) in the Hartree-Fock procedure actually contains such single excitations, although the net effect of the single excitations in all the pairs making up Ψ_1 can be shown to vanish.

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Magnetic Hyperfine Interaction Constants and Electronic *g* Factors for Eight Atomic States of Rh^{103} †

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Electronic *g* factors and magnetic hyperfine interaction constants have been measured for the eight lowest-lying atomic levels of Rh^{103}. The data are analyzed in terms of available wave functions.

INTRODUCTION

The low-lying levels of Rh I arise from the three even-parity configurations $4d^75s^2$, $4d^85s$, and $4d^9$. Since terms from each of these occur below 13 000 cm^{-1}, a considerable amount of configuration interaction can be expected. Moreover, a high degree of spin-orbit mixing occurs within each of the first two configurations. For these reasons, even the low-lying levels can have complex admixtures