determined the 2s orbital for Li using the Li$^+$ 1s orbital. Indeed, a numerical table we obtained for our best Li$^+$ orbital confirmed this. For Be, our orbitals differed from Hartree's[9] by a few units in the last figure he gave.

Generally speaking, we are confident that our SCF orbitals are equivalent to the solutions of the integro-differential Hartree-Fock equations to four decimal places. This is confirmed by the behavior of the fifth figure in the 1s orbitals; their tails cross the r axis, decrease to -1×10^{-5}, and then die out as they should. Further confirmation of this accuracy will be obtained when a program for the computation and tabulation of $F\phi_i-\epsilon_i\phi_i$ and $F\phi_i/\epsilon_i\phi_i$, now under construction, is completed. The accuracy of our orbital energies should be at least 4 figures, our total energies 7–8 figures.

APPENDIX

We put in Eq. (22) $e^{-v}=-(d/dv)e^{-v}$ and perform a partial integration with respect to v; the result is

$$C_{\alpha\beta}(t)=C_{\alpha,\beta-1}(t)-(\alpha!\beta!)^{-1}t^{\alpha+1}\int_0^\infty du\cdot u^{\alpha+\beta}e^{-(1+t)u}+\delta_{\beta0},$$

where the term $C_{\alpha,\beta-1}(t)$ is absent if $\beta=0$. Next, we multiply Eq. (22) by t, put the $te^{-ut}=-(d/du)e^{-ut}$, and perform a partial integration with respect to u; the result is

$$tC_{\alpha\beta}(t)=tC_{\alpha-1,\beta}(t)+(\alpha!\beta!)^{-1}t^{\alpha+1}\int_0^\infty du\cdot u^{\alpha+\beta}e^{-(1+t)u},$$

where the term $tC_{\alpha-1,\beta}(t)$ is absent if $\alpha=0$. Addition of these two equations and division by $1+t$ yields Eq. (23).

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[9] D. R. Hartree, Proc. Roy. Soc. (London) **A150**, 9 (1935).

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Correlated Orbitals for the Ground State of Heliumlike Systems[*]

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INTRODUCTION

FOR the ground state of atoms, molecules, and solids, the explicit solution of the Schrödinger equation to obtain an accurate wave function is virtually a hopeless task. Instead, one usually chooses a convenient function with adjustable parameters, and determines the best wave function within this class by minimizing the expectation value of the energy, computed from that wave function, with respect to these parameters. The form of the function chosen represents a certain restriction, and it is essential to use physical arguments in choosing such a form; in doing so, we essentially choose a model. The success of such a wave function can, to a certain extent, be judged by comparing the calculated energy with the experimental total energy.

One of the most successful models is the Hartree-Fock approximation,[1–4] in which there occur, instead of adjustable parameters, wholly adjustable undetermined one-electron functions or orbitals. The condition for minimizing the energy leads to nonlinear integro-differential equations for the orbitals, which can be solved by the iterative self-consistent field procedure.[1–4] The total energies obtained by this method are rather good, namely, about 99% of the experimental values or better; also, the lower ionization potentials and electron densities are calculated rather reliably. However, many other physical properties, calculated by the Hartree-Fock function, do not agree nearly as well with experimental data, notably dissociation (or cohesive) energies.

It is well known that the shortcomings of the Hartree-Fock method are due to neglect of the details of the electronic repulsions; the wave function for each individual electron is determined by the potential of the nuclei and that due to the probability density of the other electrons (we ignore the exchange potential, which does not alter this picture materially). On the whole, this allows electrons to come close together more often than is actually the case. The energy correction which would result if this effect is properly taken into account is commonly called the correlation energy.[5] The correlation energy is especially large be-

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[*] Work assisted by a grant from the National Science Foundation and by Wright Air Development Center, under contract with the University of Chicago.

[1] D. R. Hartree, Repts. Progr. Phys. **11**, 113 (1948).

[2] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, New York, 1957).

[3] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[4] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960), this issue.

[5] More precisely, the correlation energy is defined as the difference between the expectation value of the energy of the Hartree-Fock approximation and the correct eigenvalue of the nonrelativistic spin-independent infinite nuclear mass Hamiltonian.

tween two electrons in the same spatial orbital with opposite spins; therefore, a logical next step after the Hartree-Fock approximation is to construct a wave function in which the paired electrons avoid each other more strongly. Obviously the helium atom and its isoelectronic series is the simplest testing ground for such a model. The purpose of this paper is *not* to construct wave functions for heliumlike systems better than have been obtained to date,[6–11] but to determine the validity and limitations of a new form of wave function which has a conceptual simplicity comparable to the Hartree-Fock method and which perhaps can be extended to many-electron cases.

CORRELATED WAVE FUNCTIONS FOR HELIUMLIKE SYSTEMS

We investigated two types of wave functions, namely,

$$\Phi_C=\varphi(r_1)\varphi(r_2)\chi(r_{12}), \tag{1}$$

$$\Phi_O=[\varphi(r_1)\psi(r_2)+\psi(r_1)\varphi(r_2)]\chi(r_{12}); \tag{2}$$

Φ_C and Φ_O are not required to be normalized.

We call Φ_C the *correlated closed shell* and Φ_O the *correlated open shell.* The functions φ and ψ we call orbitals, and χ the correlation function. In Φ_O, we make *no* assumption about orthogonality between φ and ψ; obviously then, the correlated closed shell is a special case of the correlated open shell in which the two orbitals are identical.

In the past, a number of correlated closed-shell calculations have been carried out for He with various analytical choices for the orbital and correlation function. The first one was by Hylleraas,[12] who took $\varphi(r)=\exp(-\zeta r)$, $\chi(r_{12})=\exp(\gamma r_{12})$, with ζ and γ as variational parameters. Hartree and Ingman[13] rejected Hylleraas' choice for the correlation function as physically unreasonable. They argued that $\chi(r_{12})$ should approach a constant value for $r_{12}\rightarrow\infty$, expressing the separability of the wave function when the electrons are far apart, and should decrease to a smaller value for $r_{12}\rightarrow 0$, keeping the electrons apart. They specifically showed that the correlation function should reduce to a *finite* value for $r_{12}=0$. This fact, together with their assumption for $r_{12}\rightarrow\infty$, led them to choose $\chi(r_{12})=1-c\cdot\exp(-\eta r_{12})$; for the orbital they kept $\varphi(r)=\exp(-\zeta r)$.

Hartree and Ingman realized that their assumption about the asymptotic behavior of the correlation function is not strictly correct. However, the actual asymptotic behavior has very little influence on the total energy, and their assumption still might be a permissible and useful one. Our investigation was partially directed toward clarifying this point; our final conclusions are contained in the section Discussion of Results.

If complete flexibility is allowed for the orbital and correlation function, the condition of minimim energy leads, just as in the derivation of the Hartree-Fock equations, to coupled integro-differential equations for φ and χ. These equations were derived by Baber and Hassé,[14] who also attempted to solve them by numerical integration. This, however, led into difficulties for the equation for χ for r_{12} large. They then adopted $\chi(r_{12})=1+cr_{12}$, and solved the differential equation for φ numerically for various values of c. In the process they also determined the best ζ and c for $\varphi(r)=\exp(-\zeta r)$, $\chi(r_{12})=1+cr_{12}$, which had also been done before by Hylleraas.[12] The final energy for their best orbital is certainly in error, however. The calculation was recently repeated and corrected by Green et al.[15] The latter authors also carried out the determination of the best variational $\chi(r_{12})$ if the orbital is assumed in simple analytical form $\varphi(r)=\exp(-\zeta r)$.

Correlated open-shell calculations have been carried out for H^- by Chandrasekhar,[16] and for He and Li^+ by Green et al.[17] In these calculations, the best ζ, ζ', and c were determined for $\varphi(r)=\exp(-\zeta r)$, $\psi(r)=\exp(-\zeta' r)$, and $\chi(r_{12})=1+cr_{12}$.

The investigations reported here started from the same question as Baber and Hassé's original approach, namely, the determination of the best orbital and correlation function for the correlated closed shell. When it was found that the energies thus obtained were still inferior to those achieved with the *extremely simple* functions of Chandrasekhar and Green et al. for the correlated open shell, we also determined the best orbitals and correlation function for the open shell.

In order to circumvent the difficulty encountered by Baber and Hassé using the numerical integration process, we put forth the following *finite* analytical expressions for φ, ψ, and χ:

$$\begin{aligned}\varphi(r)&=\sum_{i=0}^{m}a_iu_i(r),\\ \psi(r)&=\sum_{i=0}^{m}b_iu_i(r),\\ \chi(r_{12})&=\sum_{\mu=0}^{n}c_\mu v_\mu(r_{12});\end{aligned}\tag{3}$$

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

[7] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

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[9] E. A. Hylleraas and J. Midtdal, Phys. Rev. **109**, 1013 (1958).

[10] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[11] W. Kolos, C. C. J. Roothaan, and R. A. Sack, Revs. Modern Phys. **32**, 178 (1960), this issue.

[12] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[13] D. R. Hartree and A. L. Ingman, Mem. Proc. Manchester Lit. & Phil. Soc. **77**, 79 (1933).

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

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[16] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

[17] L. C. Green, M. N. Lewis, M. M. Mulder, C. W. Wyeth, and J. W. Woll, Jr., Phys. Rev. **93**, 273 (1954).

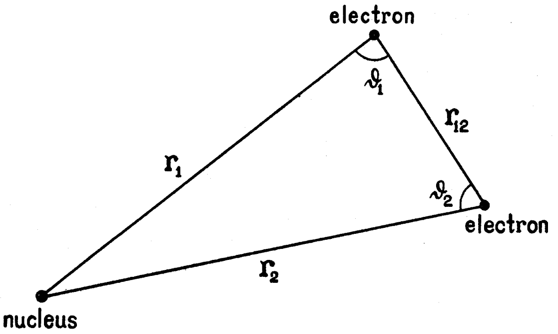

FIG. 1. Coordinate system.

for the basis function u_i and v_μ, we took

$$\begin{aligned} u_i(r) &= (\zeta r)^i e^{-\zeta r}, \\ v_\mu(r_{12}) &= (\zeta r_{12})^\mu. \end{aligned} \tag{4}$$

The coefficients a_i, b_i, c_μ, and the *orbital exponent* ζ are the variational parameters of our problem. The expansions (3) become equivalent to *completely flexible* functions φ, ψ, and χ if $m \to \infty$, $n \to \infty$. The results of our computations show that for a determination of the energy to about 10^{-5} a.u., or 0.0003 ev, this equivalence is achieved in practice with $m=n=4$.

SINGULARITIES IN THE WAVE FUNCTION AND THE HAMILTONIAN

For wave functions which depend only on r_1, r_2, r_{12}, and not on the spatial orientation of the triangle determined by the nucleus and the two electrons, the Hamiltonian is (see Fig. 1)

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12} + \mathcal{H}_{12}', \tag{5}$$

where

$$\begin{aligned} \mathcal{H}_i &= -\frac{1}{2}\left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i}\right) - \frac{Z}{r_i}, \quad i=1,2, \\ \mathcal{H}_{12} &= -\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right) + r_{12}^{-1}, \\ \mathcal{H}_{12}' &= -\frac{1}{2}\left(\cos\vartheta_1 \frac{\partial}{\partial r_1} + \cos\vartheta_2 \frac{\partial}{\partial r_2}\right)\frac{\partial}{\partial r_{12}}. \end{aligned} \tag{6}$$

The operators $\mathcal{H}_i$ and $\mathcal{H}_{12}$ have a singularity for $r_i=0$ and $r_{12}=0$, respectively. But $\mathcal{H}_{12}'$ also has a singularity, namely, for $r_1=r_2=r_{12}=0$, since the values of $\cos\theta_1$ and $\cos\theta_2$ depend on *how* the triangle of Fig. 1 is contracted to a point.

For the exact wave function, $\mathcal{H}\Phi/\Phi = E$ has a constant value. The singularities of $\mathcal{H}_i$ and $\mathcal{H}_{12}$ permit this only if

$$\left(\frac{1}{\Phi}\frac{\partial\Phi}{\partial r_1}\right)_{r_1=0} = \left(\frac{1}{\Phi}\frac{\partial\Phi}{\partial r_2}\right)_{r_2=0} = -Z, \tag{7}$$

$$\left(\frac{1}{\Phi}\frac{\partial\Phi}{\partial r_{12}}\right)_{r_{12}=0} = \tfrac{1}{2}. \tag{8}$$

With a conventional orbital product wave function, the condition (7) can be satisfied, but (8) is *always* violated. However, the wave functions (1) and (2) satisfy *both* conditions (7) and (8) if

$$\left(\frac{1}{\varphi}\frac{d\varphi}{dr}\right)_{r=0} = \left(\frac{1}{\psi}\frac{\partial\psi}{\partial r}\right)_{r=0} = -Z, \tag{9}$$

$$\left(\frac{1}{\chi}\frac{\partial\chi}{\partial r}\right)_{r=0} = \tfrac{1}{2}. \tag{10}$$

Hence, viewed in Cartesian three-dimensional space, the functions φ, ψ, and χ have *cusps* for $r \to 0$. Each cusp refers to a pair of Coulombic particles; the sign of the cusp is positive for a repulsion, negative for an attraction, and the magnitude is equal to the product of the two charges and the reduced mass of the two particles.

Unfortunately, the wave functions (1) and (2) lead to a singularity in $\mathcal{H}\Phi/\Phi$ due to $\mathcal{H}_{12}'$. We expect this to be much less harmful to the wave function than the singularities due to $\mathcal{H}_i$ and $\mathcal{H}_{12}$, if those are present, for two reasons. First, the latter lead to infinities in $\mathcal{H}\Phi/\Phi$, whereas the former leads to a bounded singularity. Secondly, the domains in which the latter occur are surfaces in the three-dimensional space framed by r_1, r_2, r_{12}, whereas the former occurs only at the single point $r_1=r_2=r_{12}=0$.

One can interpret this last fact by saying that the wave function forms (1) and (2) permit a correct account of two-body correlation but not of three-body correlation.

The importance of the correct cusp values was stressed by Pluvinage,[18] who carried out a correlated closed-shell calculation using a perturbation method. For the zeroth approximation he neglected $\mathcal{H}_{12}'$, so that the problem becomes strictly separable. The equation for φ is obviously the He$^+$ equation, yielding $\varphi = \exp(-2r)$. The equation for χ is also hydrogenic, but with a repulsive Coulomb potential, which has a continuous spectrum of eigenfunctions $\chi(\epsilon, r_{12})$, where ϵ is continuous. The best value of ϵ was determined by Pluvinage by minimizing the energy calculated with the *full* Hamiltonian. The resulting χ becomes exponentially large for $r_{12} \to \infty$; this is offset by the stronger exponential decrease of $\varphi(r)$.[19] Obviously, the wave function thus constructed satisfies both cusp conditions (8) and (9). However, first neglecting $\mathcal{H}_{12}'$ altogether leads to a rather bad zeroth approximation, and hence to a bad energy.

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[18] P. Pluvinage, Ann. Phys. **5**, 145 (1950).

[19] Our choice of basis set for χ, Eq. (4), also makes χ blow up for $r_{12} \to \infty$, although not exponentially. Baber and Hassé,[14] and Green et al.[15] showed that the correct asymptotic bahavior of χ is indeed exponential.

ITERATIVE EQUATIONS FOR THE EXPANSION COEFFICIENTS

In order to apply the variational principle to the wave functions (1) or (2) constructed from the orbital(s) and correlation function given by Eqs. (4) and (5), we first need a manageable expression for the expectation value of the total energy. For the present, we consider ζ as fixed so that for the correlated closed shell a_i and c_μ, and for the correlated open shell a_i, b_i, and c_μ, are the adjustable parameters.

The total Hamiltonian is

$$\mathcal{H}=-\tfrac{1}{2}(\Delta_1+\Delta_2)-Z[(1/r_1)+(1/r_2)]+(1/r_{12}); \qquad (11)$$

for the functions Φ_C and Φ_O given by Eqs. (1) and (2), we obtain

$$\begin{aligned}\langle\Phi_C|\mathcal{H}|\Phi_C\rangle=&\int\int dV_1dV_2\\ &\times\{[\nabla_1\varphi(1)]^2[\varphi(2)\chi(12)]^2\\ &-[\varphi(1)\varphi(2)]^2\chi(12)\Delta_{12}\chi(12)]\}\\ &+\int\int dV_1dV_2\{-Z[(1/r_1)+(1/r_2)]\\ &+(1/r_{12})\}[\varphi(1)\varphi(2)\chi(12)]^2, \qquad (12)\\ \langle\Phi_C|\Phi_C\rangle=&\int\int dV_1dV_2[\varphi(1)\varphi(2)\chi(12)]^2,\end{aligned}$$

$$\begin{aligned}\langle\Phi_O|\mathcal{H}|\Phi_O\rangle=&\int\int dV_1dV_2\\ &\times\{[\nabla_1\varphi(1)\psi(2)+\nabla_1\psi(1)\varphi(2)]^2[\chi(12)]^2\\ &-[\varphi(1)\psi(2)+\psi(1)\varphi(2)]^2\chi(12)\Delta_{12}\chi(12)\}\\ &+\int\int dV_1dV_2\\ &\times\{-Z[(1/r_1)+(1/r_2)]+(1/r_{12})\}\\ &\times[\varphi(1)\psi(2)+\psi(1)\varphi(2)]^2[\chi(12)]^2, \qquad (13)\\ \langle\Phi_O|\Phi_O\rangle=&\int\int dV_1dV_2\\ &\times[\varphi(1)\psi(2)+\psi(1)\varphi(2)]^2[\chi(12)]^2,\end{aligned}$$

where we have replaced the arguments r_1, r_2, r_{12} of φ, ψ, χ by the subscripts 1, 2, 12. It is to be noted that in Eqs. (12) and (13) the kinetic-energy terms contain no cross terms involving gradients of φ (or ψ) and χ. We show in the following how these terms were transformed in the case of Φ_C[20]; the corresponding transformation for Φ_O is similar.

The kinetic energy contributions from Δ_1 and Δ_2 are equal, so that the total kinetic energy part is

$$\begin{aligned}-\int\int dV_1dV_2\Phi_C\Delta_1\Phi_C=&\int\int dV_1dV_2(\nabla_1\Phi_C)^2\\ =&\int dV_2[\varphi(2)]^2\int dV_1[\nabla_1\varphi(1)\chi(12)]^2\\ =&\int dV_2[\varphi(2)]^2\int dV_1\\ &\times\{[\nabla_1\varphi(1)]^2[\chi(12)]^2+[\varphi(1)]^2[\nabla_1\chi(12)]^2\\ &+2\varphi(1)\chi(12)[\nabla_1\varphi(1)]\cdot[\nabla_1\chi(12)]\}\\ =&\int dV_2[\varphi(2)]^2\int dV_1\\ &\times\{[\nabla_1\varphi(1)]^2[\chi(12)]^2+[\varphi(1)]^2[\nabla_1\chi(12)]^2\\ &+\chi(12)[\nabla_1\chi(12)]\cdot\nabla_1[\varphi(1)]^2\}\\ =&\int dV_2[\varphi(2)]^2\int dV_1\\ &\times\{[\nabla_1\varphi(1)]^2[\chi(12)]^2-[\varphi(1)]^2\chi(12)\Delta_1\chi(12)\};\end{aligned}$$

this is just the kinetic-energy part of Eq. (12) since $\Delta_1\chi(12)=\Delta_{12}\chi(12)$.

We now substitute the expansions for the orbitals and correlation function, Eqs. (3), into the expressions (12) and (13); the results are

$$\begin{aligned}\langle\Phi_C|\mathcal{H}|\Phi_C\rangle=&\sum_{ijkl\mu\nu}H_{ijkl\mu\nu}a_ia_ja_ka_lc_\mu c_\nu,\\ \langle\Phi_C|\Phi_C\rangle=&\sum_{ijkl\mu\nu}S_{ijkl\mu\nu}a_ia_ja_ka_lc_\mu c_\nu,\end{aligned}\qquad (14)$$

$$\begin{aligned}\langle\Phi_O|\mathcal{H}|\Phi_O\rangle=&\sum_{ijkl\mu\nu}\tilde{H}_{ijkl\mu\nu}a_ia_jb_kb_lc_\mu c_\nu,\\ \langle\Phi_O|\Phi_O\rangle=&\sum_{ijkl\mu\nu}\tilde{S}_{ijkl\mu\nu}a_ia_jb_kb_lc_\mu c_\nu,\end{aligned}\qquad (15)$$

where

$$\begin{aligned}H_{ijkl\mu\nu}=&\tfrac{1}{2}\int\int dV_1dV_2\{[\nabla_1u_i(1)]\cdot[\nabla_1u_j(1)]u_k(2)u_l(2)\\ &+[\nabla_1u_k(1)]\cdot[\nabla_1u_l(1)]u_i(2)u_j(2)\}v_\mu(12)v_\nu(12)\\ &-\tfrac{1}{2}\int\int dV_1dV_2u_i(1)u_j(1)u_k(2)u_l(2)\\ &\times[v_\mu(12)\Delta_{12}v_\nu(12)+v_\nu(12)\Delta_{12}v_\mu(12)]\\ &+\int\int dV_1dV_2\{-Z[(1/r_1)+(1/r_2)]+(1/r_{12})\}\\ &\times u_i(1)u_j(1)u_k(2)u_l(2)v_\mu(12)v_\nu(12),\\ S_{ijkl\mu\nu}=&\int\int dV_1dV_2u_i(1)u_j(1)\\ &\times u_k(2)u_l(2)v_\mu(12)v_\nu(12), \qquad (16)\end{aligned}$$

$$\begin{aligned}\tilde{H}_{ijkl\mu\nu}=&2H_{ijkl\mu\nu}+H_{ikjl\mu\nu}+H_{ilkj\mu\nu},\\ \tilde{S}_{ijkl\mu\nu}=&2S_{ijkl\mu\nu}+S_{ikjl\mu\nu}+S_{ilkj\mu\nu}.\end{aligned}\qquad (17)$$

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[20] We are indebted to Dr. W. Kolos for pointing out this transformation.

The *supermatrices* $H, S, \tilde{H}, \tilde{S}$ defined by Eqs. (16) and (17) are all symmetrical in each of the three index pairs ij, kl, $\mu\nu$, and also symmetrical for the exchange $ij \rightarrow kl$. As a matter of fact, the symmetrical definition of these quantities was chosen to facilitate the efficient use of storage in the machine computations.

The condition of minimum energy, $\delta E=0$, where $E=\langle\Phi|\mathcal{H}|\Phi\rangle/\langle\Phi|\Phi\rangle$, readily leads to the following pseudo-eigenvalue equations for the correlated closed shell:

$$\begin{aligned} \mathbf{H}^a\mathbf{a}&=E\mathbf{S}^a\mathbf{a},\\ \mathbf{H}^c\mathbf{c}&=E\mathbf{S}^c\mathbf{c}, \end{aligned} \tag{18}$$

where $\mathbf{a}$ and $\mathbf{c}$ are the column vectors of the coefficients a_i and c_μ, respectively, and the matrices $\mathbf{H}^a$, etc. are obtained by contractions of the supermatrices (16) with the vectors $\mathbf{a}$ and $\mathbf{c}$, namely,

$$\begin{aligned} H_{ij}{}^a&=\sum_{kl\mu\nu} H_{ijkl\mu\nu}a_ka_lc_\mu c_\nu,\\ S_{ij}{}^a&=\sum_{kl\mu\nu} S_{ijkl\mu\nu}a_ka_lc_\mu c_\nu,\\ H_{\mu\nu}{}^c&=\sum_{ijkl} H_{ijkl\mu\nu}a_ia_ja_ka_l,\\ S_{\mu\nu}{}^c&=\sum_{ijkl} S_{ijkl\mu\nu}a_ia_ja_ka_l. \end{aligned} \tag{19}$$

Hence $\mathbf{a}$ and $\mathbf{c}$ are eigenvectors of two simultaneous pseudo-eigenvalue problems, with the same eigenvalue. The solution of the problem is achieved in a manner analogous to the self-consistent field method. A set of vectors $\mathbf{a}$, $\mathbf{c}$ is assumed, the matrices $\mathbf{H}^a$, etc. are computed from these by Eqs. (19), and the eigenvalue problems (18) are solved to give new vectors $\mathbf{a}$, $\mathbf{c}$. The whole process is then repeated until assumed and calculated vectors agree. When that has been accomplished, the eigenvalues of the two Eqs. (18) are automatically equal.

For the correlated open shell the procedure is analogous. The pseudo-eigenvalue equations are now

$$\begin{aligned} \tilde{\mathbf{H}}^a\mathbf{a}&=E\tilde{\mathbf{S}}^a\mathbf{a},\\ \tilde{\mathbf{H}}^b\mathbf{b}&=E\tilde{\mathbf{S}}^b\mathbf{b},\\ \tilde{\mathbf{H}}^c\mathbf{c}&=E\tilde{\mathbf{S}}^c\mathbf{c}, \end{aligned} \tag{20}$$

where

$$\begin{aligned} \tilde{H}_{ij}{}^a&=\sum_{kl\mu\nu} \tilde{H}_{ijkl\mu\nu}b_kb_lc_\mu c_\nu,\\ \tilde{S}_{ij}{}^a&=\sum_{kl\mu\nu} \tilde{S}_{ijkl\mu\nu}b_kb_lc_\mu c_\nu,\\ \tilde{H}_{ij}{}^b&=\sum_{kl\mu\nu} \tilde{H}_{ijkl\mu\nu}a_ka_lc_\mu c_\nu,\\ \tilde{S}_{ij}{}^b&=\sum_{kl\mu\nu} \tilde{S}_{ijkl\mu\nu}a_ka_lc_\mu c_\nu,\\ \tilde{H}_{\mu\nu}{}^c&=\sum_{ijkl} \tilde{H}_{ijkl\mu\nu}a_ia_jb_kb_l,\\ \tilde{S}_{\mu\nu}{}^c&=\sum_{ijkl} \tilde{S}_{ijkl\mu\nu}a_ia_jb_kb_l. \end{aligned} \tag{21}$$

TABLE I.[a] Total energies and expectation values of $r_1^2+r_2^2$ for different expansion lengths for the He correlated closed-shell wave function.

$m \diagdown n$	0	1	2	3	4
0	−2.84765 2.10700 ($\zeta=1.6875$)	−2.89112 2.15310 ($\zeta=1.85$)	−2.89112 2.15230 ($\zeta=1.848$)	−2.89123 2.15888 ($\zeta=1.848$)	−2.89125 2.15830 ($\zeta=1.848$)
2	−2.86159 2.36076 ($\zeta=1.921$)	−2.89805 2.36086 ($\zeta=1.935$)	−2.90034 2.36332 ($\zeta=1.8335$)	−2.90034 2.36322 ($\zeta=1.83$)	−2.90036 2.36406 ($\zeta=1.826$)
4	−2.86168 2.36954 ($\zeta=1.97$)	−2.89806 2.36294 ($\zeta=1.80$)	−2.90037 2.36776 ($\zeta=1.64$)	−2.90037 2.36762 ($\zeta=1.64$)	−2.90039 2.36824 ($\zeta=1.65$)

[a] For some reason, as yet not fully understood, the best results for $m=1$ and $m=3$ are identical with those for $m=0$ and $m=2$, respectively.

EVALUATION OF THE SUPERMATRIX ELEMENTS

In order to evaluate explicitly the supermatrix elements $H_{ijkl\mu\nu}$ and $S_{ijkl\mu\nu}$, we have to substitute into the right-hand sides of Eqs. (14) and (15) the specific expressions for the basis functions, Eqs. (4). This immediately yields the general supermatrix elements in terms of one family of primitive integrals, namely,

$$\begin{aligned} \lambda H_{ijkl\mu\nu}=\tfrac{1}{2}\zeta^2\{&ijI_{i+j-1,k+l+1,\mu+\nu+1}+klI_{i+j+1,k+l-1,\mu+\nu+1}\\ &-(i+j)I_{i+j,k+l+1,\mu+\nu+1}-(k+l)I_{i+j+1,k+l,\mu+\nu+1}\\ &+2I_{i+j+1,k+l+1,\mu+\nu+1}-[\mu(\mu+1)+\nu(\nu+1)]\\ &\times I_{i+j+1,k+l+1,\mu+\nu-1}\}-Z\zeta[I_{i+j,k+l+1,\mu+\nu+1}\\ &+I_{i+j+1,k+l,\mu+\nu+1}]+\zeta I_{i+j+1,k+l+1,\mu+\nu},\\ \lambda S_{ijkl\mu\nu}=I&_{i+j+1,k+l+1,\mu+\nu+1}, \end{aligned} \tag{22}$$

with

$$I_{\alpha\beta\gamma}=\lambda\int\int dV_1dV_2e^{-2\zeta(r_1+r_2)} \times(\zeta r_1)^{\alpha-1}(\zeta r_2)^{\beta-1}(\zeta r_{12})^{\gamma-1}; \tag{23}$$

λ is an arbitrary numerical factor which we pick to our convenience.

The double-volume integration can be carried out over the three internal coordinates r_1, r_2, r_{12} and the three Eulerian angles which define the spatial orientation of the triangle of Fig. 1.[21] Since the integrand does not depend on the latter, those integrations can be carried out immediately; introducing scaled coordinates $\rho_i=\zeta r_i$, $\rho_{12}=\zeta r_{12}$, and choosing $\lambda=\zeta^3/8\pi^2$, we obtain

$$I_{\alpha\beta\gamma}=\int_0^\infty d\rho_1\int_0^\infty d\rho_2 \int_{|\rho_1-\rho_2|}^{\rho_1+\rho_2} d\rho_{12}e^{-2(\rho_1+\rho_2)}\rho_1{}^\alpha\rho_2{}^\beta\rho_{12}{}^\gamma. \tag{24}$$

Equation (24) shows that $I_{\alpha\beta\gamma}$ is a pure number depending on the integers α, β, γ only.

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[21] The method of integration used here was introduced by E. Hylleraas.[12]

TABLE II. Total energies and expectation values of $r_1^2+r_2^2$ for different expansion lengths for the He correlated open-shell wave function.

$m \backslash n$	0	1	2	3	4
0	−2.84765 2.10700 ($\zeta=1.6875$)	−2.89112 2.15310 ($\zeta=1.85$)	−2.89112 2.15230 ($\zeta=1.848$)	−2.89123 2.15888 ($\zeta=1.848$)	−2.89125 2.15830 ($\zeta=1.848$)
1	−2.86049 2.12156 ($\zeta=1.713$)	−2.89450 2.16674 ($\zeta=1.84$)	−2.89465 2.18116 ($\zeta=1.848$)	−2.89529 2.20322 ($\zeta=1.844$)	−2.89531 2.20224 ($\zeta=1.844$)
2	−2.87752 2.41156 ($\zeta=1.899$)	−2.90193 2.37980 ($\zeta=1.94$)	−2.90289 2.38054 ($\zeta=1.86$)	−2.90305 2.38316 ($\zeta=1.914$)	−2.90306 2.38272 ($\zeta=1.915$)
3	−2.87774 2.40378 ($\zeta=2.01$)	−2.90205 2.37624 ($\zeta=2.065$)	−2.90297 2.37854 ($\zeta=1.935$)	−2.90312 2.38126 ($\zeta=2.017$)	−2.90315 2.38000 ($\zeta=1.999$)
4	−2.87798 2.41606 ($\zeta=2.082$)	−2.90213 2.38150 ($\zeta=2.13$)	−2.90304 2.38402 ($\zeta=1.948$)	−2.90316 2.38432 ($\zeta=2.04$)	−2.90319 2.38424 ($\zeta=1.916$)

In order to derive recurrence relations between the $I_{\alpha\beta\gamma}$, we introduce the transformation $x=\rho_1+\rho_2$, $y=\rho_1-\rho_2$, $z=\rho_{12}$, yielding

$$I_{\alpha\beta\gamma}=\int_0^\infty dx\int_0^x dz\int_0^z dy e^{-2x}F_{\alpha\beta}(x,y)z^\gamma, \tag{25}$$

where

$$F_{\alpha\beta}(x,y)=\tfrac{1}{2}\{[\tfrac{1}{2}(x+y)]^\alpha[\tfrac{1}{2}(x-y)]^\beta +[\tfrac{1}{2}(x+y)]^\beta[\tfrac{1}{2}(x-y)]^\alpha\}. \tag{26}$$

In Eq. (25) we write $e^{-2x}=-\frac{1}{2}(d/dx)e^{-2x}$, and perform a partial integration with respect to x; the result is

$$I_{\alpha\beta\gamma}=\tfrac{1}{4}(\alpha I_{\alpha-1,\beta\gamma}+\beta I_{\alpha,\beta-1,\gamma}+2J_{\alpha\beta\gamma}), \tag{27}$$

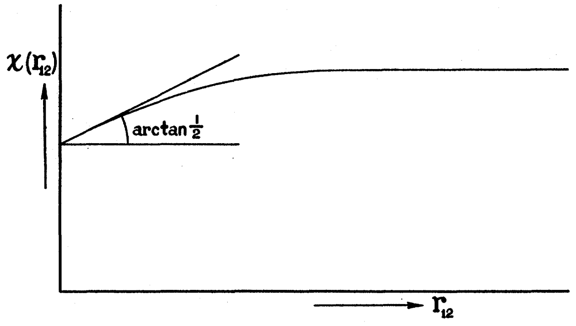

FIG. 2. Correlation function, schematic.

where

$$J_{\alpha\beta\gamma}=\int_0^\infty dx\int_0^x dy e^{-2x}F_{\alpha\beta}(x,y)x^\gamma; \tag{28}$$

applying the same process to Eq. (28), we obtain

$$J_{\alpha\beta\gamma}=\tfrac{1}{4}(\alpha J_{\alpha-1,\beta\gamma}+\beta J_{\alpha,\beta-1,\gamma}+2\gamma J_{\alpha\beta,\gamma-1}) +2^{-\alpha-\beta-\gamma-3}[\delta_{\alpha 0}(\beta+\gamma)!+\delta_{\beta 0}(\alpha+\gamma)!]. \tag{29}$$

The recurrence relations (27) and (29) allow us to calculate $J_{\alpha\beta\gamma}$ and $I_{\alpha\beta\gamma}$. No serious loss of significant figures can occur in this process, since all quantities are positive and additive.

RESULTS AND DISCUSSION

A digital computer program was written for the Remington Rand Univac Scientific 1103 at Wright-Patterson Air Force Base. Input data are the nuclear charge Z, the expansion lengths m and n (limited to $\leqslant 4$, due to the size of the memory), the orbital exponent ζ, and a tag, 0 or 1, which distinguishes between closed

TABLE III. Various wave functions of correlated closed-shell type for He.

Wave function	Comments	Energy	Energy discrepancy	Orbital cusp	Corr. cusp	Reference
$e^{-\zeta(r_1+r_2)}$	Best ζ	−2.84766	−0.05606	−1.6875	...	b
$\varphi(r_1)\varphi(r_2)$	Best φ, Hartree-Fock	−2.86168	−0.04204	−2.000	...	c
$e^{-2(r_1+r_2)}\chi(r_{12})$	χ from repulsive hydrogenic differential equation	−2.878	−0.026	−2.000	0.500	d
$e^{-\zeta(r_1+r_2)}e^{\gamma r_{12}}$	Best ζ and γ	−2.8896	−0.0141	−1.860	0.260	e
$e^{-\zeta(r_1+r_2)}(1+cr_{12})$	Best ζ and c	−2.89112	−0.01260	−1.8497	0.364	e, f, g
$e^{-\zeta(r_1+r_2)}(1-ce^{-\eta r_{12}})$	Best ζ, η, and c	−2.89115	−0.01257	−1.8395	0.379	h
$e^{-\zeta(r_1+r_2)}\chi(r_{12})$	Best ζ; χ by numerical integration	−2.89126[a]	−0.01246	−1.849	0.50	g
$\varphi(r_1)\varphi(r_1)(1+cr_{12})$	Best c; φ by numerical integration	−2.89806[a]	−0.00566	−1.999	0.35	f, g
$\varphi(r_1)\varphi(r_2)\chi(r_{12})$	Best φ and χ, expanded in basis set	−2.90039	−0.00333	−2.021	0.465	i
Exact wave function	Neglecting relativistic, etc. effects, infinite nuclear mass	−2.90372	...	...	...	j

[a] In agreement with our expansion results, Table I, $m=0$, $n=4$, and $m=4$, $n=1$, respectively.
[b] See any textbook.
[c] See reference 25.
[d] See reference 18.
[e] See reference 12.
[f] See reference 14.
[g] See reference 15.
[h] See reference 13.
[i] See this paper.
[j] See references 6–11.

TABLE IV. Wave functions and energies for the correlated open shell.

Atom	Orbitals		Correlation function	E	Reference
	$e^{-0.478r}$	$e^{-1.075r}$	$1+0.3121r_{12}$	-0.52592	[a]
H$^-$	$\varphi(r)$	$\psi(r)$	$\chi(r_{12})$	-0.52718	[b]
	Exact wave function			-0.52780	[c]
	$e^{-1.436r}$	$e^{-2.208r}$	$1+0.2924r_{12}$	-2.90142	[d]
He	$\varphi(r)$	$\psi(r)$	$\chi(r_{12})$	-2.90320	[b]
	Exact wave function			-2.90372	[e]
	$e^{-2.362r}$	$e^{-3.299r}$	$1+0.2770r_{12}$	-7.27718	[d]
Li$^+$	$\varphi(r)$	$\psi(r)$	$\chi(r_{12})$	-7.27939	[b]
	Exact wave function			-7.27991	[c]

[a] See reference 16.
[b] See this paper.
[c] See reference 10.
[d] See reference 17.
[e] See references 6–11.

and open shell. After the program has been executed, the total energy and the expansion coefficients are printed out. A maximal run, $m=n=4$, requires about two minutes per iteration for the open-shell case and somewhat less for the closed-shell case. Closed-shell runs converge in about 10 iterations or less, starting from $\varphi=\exp(-\zeta r)$, $\chi=1$ as the initial approximation. The open-shell runs converge very slowly, requiring up to 60 iterations when starting from $\varphi=\psi=\exp(-\zeta r)$, $\chi=1$. In all cases, ζ was varied until a minimum had been obtained. For open-shell runs the results obtained with one ζ were used as input for a neighboring ζ to speed up the convergence.

In addition to the total energies, we computed the diamagnetic susceptibilities for various wave functions. For any atomic system this quantity is given by[22]

$$\chi=\tfrac{1}{6}N\alpha^2a^3\langle\Phi|\sum_i r_i^2|\Phi\rangle, \tag{30}$$

where χ is the molar susceptibility, N is Avogadro's number, α the fine structure constant, and a the Bohr radius. The most recent values for the elementary constants[23] yield, for the proportionality factor $\frac{1}{6}N\alpha^2a^3$, the numerical value 0.74336×10^{-6}. The evaluation of the integral $\langle\Phi|r_1^2+r_2^2|\Phi\rangle$ in terms of the primitive integrals $I_{\alpha\beta\gamma}$ defined by Eq. (24) is analogous to the

TABLE V. Energies and expectation values of $r_1^2+r_2^2$ as a function of Z.[a]

Atom or ion	Energies				$\langle\Phi\|r_1^2+r_2^2\|\Phi\rangle$	
	Hartree-Fock	Correlated closed shell	Correlated open shell	Eigenvalue (Pekeris)	Correlated closed shell	Correlated open shell
H$^-$	-0.48793	-0.52190	-0.52718	-0.52775	19.40	23.46
	(0.03982)	(0.00585)	(0.00057)			
He	-2.86168	-2.90039	-2.90319	-2.90372	2.368	2.384
	(0.04204)	(0.00333)	(0.00053)			
Li^{1+}	-7.23641	-7.27692	-7.27939	-7.27991	0.8903	0.8922
	(0.04350)	(0.00299)	(0.00052)			
Be^{2+}	-13.61130	-13.65271	-13.65505	-13.65557	0.4636	0.4640
	(0.04427)	(0.00286)	(0.00052)			
B^{3+}	-21.98623			-22.03097		
	(0.04474)					
C^{4+}	-32.36119	-32.40351	-32.40574	-32.40625	0.1914	0.1915
	(0.04506)	(0.00274)	(0.00051)			
N^{5+}	-44.73616			-44.78145		
	(0.04529)					
O^{6+}	-59.11114	-59.15392	-59.15609	-59.15660	0.1039	0.1039
	(0.04546)	(0.00268)	(0.00051)			
F^{7+}	-75.48613			-75.53171		
	(0.04558)					
Ne^{8+}	-93.86111	-93.90416	-93.90630	-93.90681	0.0651	0.0651
	(0.04570)	(0.00265)	(0.00051)			

[a] The numbers in parentheses are the deviations of the approximate energies from the exact eigenvalues.

TABLE VI. Closed-shell orbital functions.

Z	1	2	3	4	6	8	10
ζ	0.70	1.65	2.55	3.45	5.20	7.00	10.80
Cusp	-1.020	-2.021	-3.021	-4.022	-6.022	-8.022	-10.023
N_a	1.7464	5.2203	9.8416	15.355	28.601	44.336	62.212
a_0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
a_1	-0.45659	-0.22457	-0.18476	-0.16572	-0.15805	-0.14606	0.07198
a_2	0.16372	0.06344	0.04412	0.03462	0.02693	0.02161	0.00846
a_3	-0.02559	-0.00703	-0.00469	-0.00359	-0.00274	-0.00290	0.00045
a_4	0.00218	0.00041	0.00023	0.00017	0.00012	0.00009	0.00000

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[22] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).
[23] E. Richard Cohen and Jesse W. M. DuMond, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. XXXV.

TABLE VII. Closed-shell correlation functions.

Z	1	2	3	4	6	8	10
ζ	0.70	1.65	2.55	3.45	5.20	7.00	10.80
Cusp	0.458	0.465	0.464	0.464	0.463	0.462	0.460
N_c	2.3874	2.8916	3.2167	3.3814	3.6501	3.7083	2.0249
c_0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
c_1	0.65391	0.28162	0.18211	0.13437	0.08895	0.06598	0.04262
c_2	0.11445	−0.01422	−0.01742	−0.01547	−0.01194	−0.00939	−0.00504
c_3	−0.03016	−0.00238	0.00004	0.00056	0.00071	0.00064	0.00029
c_4	0.00139	0.00015	0.00002	−0.00002	−0.00003	−0.00003	−0.00001

TABLE VIII. Open-shell orbital functions.

Z	1	2	3	4	6	8	10
ζ	0.692	1.916	3.08	4.30	6.5995	8.70	10.80
Cusp	−1.011	−1.990	−2.963	−3.935	−5.906	−7.896	−9.894
N_a	2.0810	6.1233	11.262	17.286	31.558	48.330	67.295
a_0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
a_1	−0.46064	−0.03888	0.03790	0.08486	0.10514	0.09239	0.08388
a_2	0.08518	−0.05692	−0.06222	−0.05832	−0.05087	−0.04733	−0.04399
a_3	−0.00626	0.01473	0.01418	0.01239	0.01075	0.01026	0.00966
a_4	0.00016	−0.00087	−0.00078	−0.00061	−0.00052	−0.00053	−0.00052
Cusp	−0.989	−2.078	−3.114	−4.146	−6.176	−8.185	−10.185
N_b	0.98844	4.0350	8.1334	13.119	25.297	39.944	56.709
b_0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
b_1	−0.42869	−0.08430	−0.01088	0.03575	0.06413	0.05925	0.05694
b_2	0.38470	0.18957	0.14529	0.12165	0.09719	0.08328	0.07360
b_3	−0.07899	−0.02827	−0.02045	−0.01530	−0.01216	−0.01177	−0.01113
b_4	0.00789	0.00192	0.00127	0.00091	0.00069	0.00066	0.00062

TABLE IX. Open-shell correlation functions.

Z	1	2	3	4	6	8	10
ζ	0.692	1.916	3.08	4.30	6.5995	8.70	10.80
Cusp	0.523	0.487	0.476	0.471	0.467	0.465	0.464
N_c	1.4046	1.2512	1.2616	1.2159	1.2508	1.3566	1.4240
c_0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
c_1	0.75625	0.25399	0.15456	0.10958	0.07070	0.05343	0.04293
c_2	−0.06688	−0.03670	−0.02393	−0.01724	−0.01147	−0.00903	−0.00744
c_3	0.00280	0.00424	0.00279	0.00198	0.00133	0.00107	0.00090
c_4	−0.00001	−0.00020	−0.00013	−0.00009	−0.00006	−0.00005	−0.00004

evaluation of the total energy but simpler; we omit the details. For He, our best correlated closed- and open-shell wave functions yielded for χ 1.876×10^{-6} and 1.889×10^{-6}, which are in excellent agreement with the experimental value[24] 1.88×10^{-6}. The Hartree-Fock value is also in essentially complete agreement with experiment, namely, 1.877×10^{-6}.

In order to investigate the effect of the finite expansion lengths for the orbital(s) and correlation function, calculations were carried out for different values of m and n for $Z=2$; the results are shown in Tables I and II. As mentioned previously, it appears that $m=n=4$ is equivalent to a full variational treatment to an accuracy of about 10^{-5} a.u. in the energy. The accompanying relative accuracy in the wave function is about the square root of the accuracy in the energy, or about $10^{-2}-10^{-3}$ in the present case. This is confirmed by the cusp values obtained from our calculations; apparently our best finite expansion wave functions differ by about 10^{-2} from wave functions which would have the proper behavior at $r_1=0$, $r_2=0$, and $r_{12}=0$.

It is instructive to compare our best energies and wave functions with others of similar types[12–17]; this is shown in Tables III and IV. At this point we call attention to an earlier attempt to expand the correlation function for the closed shell, namely,

$$\chi(r_{12})=c-e^{-\eta r_{12}}\sum_{\lambda=0}^{l}c_\lambda(\zeta r_{12})^\lambda, \qquad (31)$$

which is an obvious generalization of Hartree and Ingman's form for the correlation function. Such a form would make sense if for optimum η and increasing l the correlation function would settle down to something like Fig. 2. In particular, we would expect a ratio

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[24] A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924); **24**, 418 (1924).

TABLE X. Numerical closed-shell orbital functions.

Zr	H^-	He	Li^{1+}	Be^{2+}	C^{4+}	O^{6+}	Ne^{8+}
0.	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
0.2	0.81652	0.81791	0.81822	0.81835	0.81849	0.81855	0.81858
0.4	0.66845	0.67044	0.67056	0.67054	0.67051	0.67047	0.67045
0.6	0.54882	0.55078	0.55044	0.55013	0.54977	0.54954	0.54941
0.8	0.45204	0.45353	0.45258	0.45192	0.45116	0.45073	0.45047
1.0	0.37361	0.37432	0.37274	0.37171	0.37056	0.36993	0.36954
1.2	0.30993	0.30969	0.30749	0.30612	0.30462	0.30380	0.30331
1.4	0.25810	0.25682	0.25408	0.25243	0.25062	0.24966	0.24907
1.6	0.21583	0.21350	0.21029	0.20841	0.20637	0.20529	0.20464
1.8	0.18124	0.17790	0.17433	0.17227	0.17007	0.16891	0.16821
2.0	0.15285	0.14859	0.14474	0.14257	0.14026	0.13906	0.13833
2.2	0.12947	0.12439	0.12036	0.11812	0.11577	0.11455	0.11381
2.4	0.11016	0.10437	0.10024	0.09798	0.09562	0.09442	0.09368
2.6	0.09413	0.08776	0.08360	0.08135	0.07904	0.07786	0.07715
2.8	0.08079	0.07394	0.06982	0.06763	0.06538	0.06424	0.06355
3.0	0.06963	0.06243	0.05839	0.05627	0.05411	0.05303	0.05238
3.2	0.06026	0.05282	0.04889	0.04686	0.04482	0.04380	0.04318
3.4	0.05235	0.04476	0.04099	0.03906	0.03714	0.03619	0.03562
3.6	0.04566	0.03800	0.03440	0.03259	0.03080	0.02991	0.02938
3.8	0.03997	0.03232	0.02891	0.02721	0.02555	0.02473	0.02425
4.0	0.03511	0.02753	0.02431	0.02274	0.02121	0.02046	0.02002
4.2	0.03094	0.02348	0.02047	0.01901	0.01761	0.01693	0.01653
4.4	0.02736	0.02006	0.01725	0.01591	0.01463	0.01402	0.01366
4.6	0.02426	0.01716	0.01455	0.01332	0.01216	0.01161	0.01128
4.8	0.02158	0.01470	0.01228	0.01116	0.01011	0.00961	0.00933
5.0	0.01925	0.01260	0.01037	0.00936	0.00841	0.00797	0.00771
5.2	0.01721	0.01082	0.00877	0.00785	0.00700	0.00660	0.00637
5.4	0.01543	0.00930	0.00742	0.00659	0.00583	0.00547	0.00527
5.6	0.01387	0.00800	0.00628	0.00553	0.00485	0.00454	0.00436
5.8	0.01250	0.00689	0.00532	0.00465	0.00404	0.00376	0.00361
6.0	0.01129	0.00594	0.00451	0.00391	0.00337	0.00312	0.00298
6.2	0.01021	0.00513	0.00383	0.00328	0.00281	0.00259	0.00247
6.4	0.00926	0.00443	0.00325	0.00276	0.00234	0.00215	0.00204
6.6	0.00842	0.00383	0.00276	0.00233	0.00195	0.00179	0.00169
6.8	0.00767	0.00332	0.00234	0.00196	0.00163	0.00148	0.00140
7.0	0.00700	0.00287	0.00199	0.00165	0.00136	0.00123	0.00116
7.2	0.00639	0.00249	0.00170	0.00139	0.00113	0.00102	0.00096
7.4	0.00585	0.00216	0.00144	0.00117	0.00095	0.00085	0.00079
7.6	0.00537	0.00188	0.00123	0.00099	0.00079	0.00071	0.00066
7.8	0.00493	0.00163	0.00105	0.00084	0.00066	0.00059	0.00054
8.0	0.00454	0.00142	0.00090	0.00071	0.00055	0.00049	0.00045
8.2	0.00418	0.00124	0.00077	0.00060	0.00046	0.00041	0.00037
8.4	0.00385	0.00108	0.00065	0.00050	0.00039	0.00034	0.00031
8.6	0.00356	0.00094	0.00056	0.00043	0.00032	0.00028	0.00026
8.8	0.00329	0.00082	0.00048	0.00036	0.00027	0.00024	0.00021
9.0	0.00304	0.00072	0.00041	0.00031	0.00023	0.00020	0.00018
9.2	0.00281	0.00063	0.00035	0.00026	0.00019	0.00016	0.00015
9.4	0.00261	0.00055	0.00030	0.00022	0.00016	0.00014	0.00012
9.6	0.00242	0.00049	0.00026	0.00019	0.00014	0.00011	0.00010
9.8	0.00224	0.00043	0.00022	0.00016	0.00011	0.00010	0.00008
10.0	0.00208	0.00037	0.00019	0.00014	0.00010	0.00008	0.00007

$c/(c-c_0)$ of order unity, and somewhat larger than one. We did find, however, upon varying η and optimizing the coefficients c_λ, a wildly varying ratio $c/(c-c_0)$ while the energy hardly changed; in some cases this ratio even became negative. Although we obtained a rather good energy with it (-2.90036 for He), we abandoned the expansion (31) in favor of that given by Eqs. (3) and (4).

In Table V are listed, as a function of Z, the energies obtained with the Hartree-Fock function,[25] the correlated closed shell, the correlated open shell, the accurate energies obtained by Pekeris,[10] and the diamagnetic susceptibility integrals $\langle\Phi|r_1^2+r_2^2|\Phi\rangle$. Whereas the Hartree-Fock energy deviates from the correct eigenvalues by about 1.2 ev (this is the correlation energy), the deviation is only about 0.15 ev for the correlated closed shell, and 0.015 for the correlated open shell.

In Tables VI–XIII are given the orbital exponents, expansion coefficients, and normalization constants of the various wave functions. The functions are all chosen to be unity at the origin. If they are multiplied by the normalization constants N_a, N_b, N_c, we obtain the orbitals φ_N and ψ_N, so that

$$\int_0^\infty drr^2\varphi_N^2=1,$$

$$\int_0^\infty drr^2\psi_N^2=1;$$

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[25] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960), this issue.

TABLE XI. Numerical closed-shell correlation functions.

r	H^-	He	Li^{1+}	Be^{2+}	C^{4+}	O^{6+}	Ne^{8+}
0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
0.1	1.04632	1.04607	1.04531	1.04454	1.04312	1.04180	1.04050
0.2	1.09371	1.09130	1.08835	1.08553	1.08036	1.07562	1.07122
0.3	1.14209	1.13564	1.12915	1.12310	1.11223	1.10254	1.09383
0.4	1.19141	1.17902	1.16769	1.15738	1.13920	1.12347	1.10968
0.5	1.24162	1.22139	1.20401	1.18848	1.16169	1.13914	1.11978
0.6	1.29264	1.26269	1.23809	1.21652	1.18005	1.15013	1.12482
0.7	1.34443	1.30289	1.26997	1.24159	1.19461	1.15685	1.12517
0.8	1.39692	1.34192	1.29965	1.26381	1.20562	1.15953	1.12085
0.9	1.45006	1.37976	1.32716	1.28327	1.21328	1.15826	1.11158
1.0	1.50380	1.41634	1.35250	1.30005	1.21774	1.15293	1.09673
1.1	1.55808	1.45164	1.37569	1.31424	1.21911		
1.2	1.61285	1.48562	1.39677	1.32593	1.21742		
1.3	1.66805	1.51825	1.41574	1.33517	1.21267		
1.4	1.72364	1.54948	1.43264	1.34204	1.20480		
1.5	1.77955	1.57930	1.44750	1.34661	1.19369		
1.6	1.83575	1.60768	1.46033	1.34892			
1.7	1.89217	1.63459	1.47116	1.34903			
1.8	1.94878	1.66002	1.48003	1.34697			
1.9	2.00552	1.68394	1.48698	1.34280			
2.0	2.06235	1.70634	1.49202	1.33654			
2.1	2.11921	1.72720	1.49520				
2.2	2.17607	1.74652	1.49656				
2.3	2.23288	1.76429	1.49613				
2.4	2.28960	1.78050	1.49395				
2.5	2.34617	1.79515	1.49006				
2.6	2.40257	1.80824	1.48451				
2.7	2.45874	1.81978	1.47734				
2.8	2.51465	1.82976	1.46860				
2.9	2.57026	1.83820	1.45834				
3.0	2.62552	1.84510	1.44660				
3.1	2.68040	1.85049					
3.2	2.73487	1.85436					
3.3	2.78887	1.85676					
3.4	2.84239	1.85768					
3.5	2.89537	1.85717					
3.6	2.94780	1.85524					
3.7	2.99963	1.85192					
3.8	3.05083	1.84725					
3.9	3.10136	1.84126					
4.0	3.15121	1.83398					
4.1	3.20033						
4.2	3.24870						
4.3	3.29629						
4.4	3.34307						
4.5	3.38902						
4.6	3.43409						
4.7	3.47828						
4.8	3.52156						
4.9	3.56390						
5.0	3.60527						

TABLE XII. Numerical open-shell orbital functions.

Zr	H^-		He		Li^{1+}		Be^{2+}		C^{4+}		O^{6+}		Ne^{8+}	
0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
0.2	0.81644	1.82532	0.81785	0.81788	0.81868	0.81740	0.81918	0.81716	0.81921	0.81753	0.81898	0.81797	0.81876	0.81832
0.4	0.66638	0.68935	0.66638	0.67757	0.66721	0.67558	0.66786	0.67437	0.66809	0.67370	0.66802	0.67354	0.66790	0.67353
0.6	0.54334	0.58290	0.54118	0.56789	0.54169	0.56377	0.54233	0.56124	0.54284	0.55889	0.54308	0.55770	0.54319	0.55703
0.8	0.44268	0.49894	0.43824	0.48079	0.43838	0.47429	0.43897	0.47034	0.43976	0.46617	0.44032	0.46387	0.44068	0.46249
1.0	0.36041	0.43209	0.35402	0.41051	0.35383	0.40163	0.35437	0.39632	0.35542	0.39047	0.35625	0.38718	0.35683	0.38516
1.2	0.29322	0.37825	0.28539	0.35288	0.28500	0.34182	0.28549	0.33534	0.28675	0.32810	0.28777	0.32402	0.28850	0.32149
1.4	0.23840	0.33432	0.22968	0.30493	0.22918	0.29201	0.22965	0.28459	0.23105	0.27631	0.23219	0.27167	0.23302	0.26878
1.6	0.19371	0.29796	0.18461	0.26451	0.18410	0.25010	0.18453	0.24200	0.18603	0.23302	0.18721	0.22805	0.18808	0.22494
1.8	0.15731	0.26740	0.14825	0.23004	0.14779	0.21455	0.14819	0.20603	0.14973	0.19667	0.15090	0.19155	0.15177	0.18836
2.0	0.12769	0.24133	0.11900	0.20039	0.11862	0.18421	0.11898	0.17549	0.12052	0.16603	0.12164	0.16092	0.12247	0.15774
2.2	0.10361	0.21876	0.09553	0.17471	0.09524	0.15819	0.09555	0.14947	0.09705	0.14014	0.09809	0.13516	0.09887	0.13208
2.4	0.08405	0.19897	0.07671	0.15235	0.07652	0.13581	0.07678	0.12726	0.07821	0.11823	0.07915	0.11348	0.07986	0.11054
2.6	0.06817	0.18141	0.06166	0.13281	0.06156	0.11653	0.06175	0.10827	0.06310	0.09968	0.06393	0.09521	0.06456	0.09245
2.8	0.05530	0.16569	0.04963	0.11571	0.04960	0.09989	0.04973	0.09203	0.05098	0.08396	0.05170	0.07981	0.05225	0.07726
3.0	0.04486	0.15149	0.04002	0.10072	0.04004	0.08554	0.04010	0.07814	0.04125	0.07065	0.04187	0.06684	0.04235	0.06451
3.2	0.03641	0.13860	0.03235	0.08758	0.03240	0.07317	0.03240	0.06627	0.03344	0.05938	0.03396	0.05592	0.03437	0.05381
3.4	0.02957	0.12685	0.02622	0.07606	0.02629	0.06250	0.02622	0.05614	0.02716	0.04986	0.02760	0.04674	0.02793	0.04484
3.6	0.02403	0.11611	0.02132	0.06599	0.02139	0.05333	0.02127	0.04750	0.02211	0.04182	0.02246	0.03902	0.02274	0.03733
3.8	0.01956	0.10626	0.01739	0.05718	0.01746	0.04544	0.01729	0.04014	0.01803	0.03503	0.01832	0.03254	0.01855	0.03104
4.0	0.01594	0.09724	0.01424	0.04949	0.01429	0.03868	0.01408	0.03388	0.01474	0.02932	0.01497	0.02711	0.01515	0.02579
4.2	0.01301	0.08896	0.01171	0.04279	0.01174	0.03288	0.01150	0.02857	0.01207	0.02451	0.01225	0.02256	0.01240	0.02141
4.4	0.01065	0.08138	0.00967	0.03695	0.00968	0.02793	0.00940	0.02406	0.00991	0.02047	0.01005	0.01876	0.01016	0.01775
4.6	0.00873	0.07443	0.00802	0.03189	0.00800	0.02370	0.00771	0.02025	0.00815	0.01708	0.00825	0.01559	0.00834	0.01471
4.8	0.00718	0.06807	0.00667	0.02750	0.00663	0.02009	0.00633	0.01702	0.00672	0.01424	0.00679	0.01294	0.00685	0.01218

TABLE XII.—*Continued.*

Zr	H^-		He		Li^{1+}		Be^{2+}		C^{4+}		O^{6+}		Ne^{8+}	
5.0	0.00593	0.06225	0.00558	0.02369	0.00552	0.01702	0.00521	0.01430	0.00554	0.01187	0.00559	0.01073	0.00564	0.01008
5.2	0.00491	0.05694	0.00468	0.02040	0.00460	0.01441	0.00429	0.01201	0.00458	0.00988	0.00461	0.00890	0.00465	0.00833
5.4	0.00409	0.05210	0.00394	0.01756	0.00384	0.01219	0.00354	0.01008	0.00379	0.00822	0.00381	0.00737	0.00383	0.00689
5.6	0.00341	0.04768	0.00333	0.01511	0.00322	0.01031	0.00292	0.00845	0.00314	0.00684	0.00315	0.00611	0.00316	0.00569
5.8	0.00286	0.04366	0.00281	0.01300	0.00270	0.00872	0.00241	0.00708	0.00261	0.00569	0.00261	0.00506	0.00261	0.00470
6.0	0.00242	0.04000	0.00239	0.01118	0.00226	0.00737	0.00199	0.00594	0.00216	0.00473	0.00216	0.00419	0.00216	0.00388
6.2	0.00205	0.03667	0.00203	0.00962	0.00190	0.00623	0.00165	0.00498	0.00180	0.00393	0.00179	0.00347	0.00178	0.00320
6.4	0.00174	0.03364	0.00173	0.00828	0.00160	0.00527	0.00136	0.00417	0.00149	0.00326	0.00148	0.00287	0.00147	0.00264
6.6	0.00149	0.03089	0.00147	0.00713	0.00135	0.00446	0.00113	0.00349	0.00124	0.00271	0.00122	0.00238	0.00122	0.00218
6.8	0.00128	0.02838	0.00125	0.00614	0.00113	0.00377	0.00093	0.00293	0.00103	0.00225	0.00101	0.00197	0.00101	0.00180
7.0	0.00111	0.02611	0.00107	0.00529	0.00095	0.00319	0.00077	0.00245	0.00085	0.00187	0.00084	0.00163	0.00083	0.00149
7.2	0.00096	0.02404	0.00091	0.00456	0.00080	0.00270	0.00063	0.00206	0.00071	0.00156	0.00069	0.00135	0.00068	0.00123
7.4	0.00084	0.02215	0.00077	0.00393	0.00067	0.00229	0.00052	0.00173	0.00059	0.00130	0.00057	0.00112	0.00056	0.00102
7.6	0.00073	0.02043	0.00066	0.00339	0.00056	0.00194	0.00043	0.00145	0.00049	0.00108	0.00047	0.00093	0.00046	0.00084
7.8	0.00064	0.01887	0.00056	0.00293	0.00047	0.00164	0.00035	0.00121	0.00040	0.00090	0.00039	0.00077	0.00038	0.00070
8.0	0.00056	0.01744	0.00047	0.00253	0.00039	0.00139	0.00029	0.00102	0.00033	0.00075	0.00032	0.00064	0.00031	0.00058
8.2	0.00050	0.01613	0.00040	0.00219	0.00033	0.00118	0.00023	0.00086	0.00028	0.00062	0.00026	0.00053	0.00026	0.00048
8.4	0.00044	0.01494	0.00034	0.00190	0.00027	0.00101	0.00019	0.00072	0.00023	0.00052	0.00022	0.00044	0.00021	0.00040
8.6	0.00039	0.01384	0.00028	0.00164	0.00023	0.00086	0.00015	0.00061	0.00018	0.00043	0.00018	0.00037	0.00017	0.00033
8.8	0.00034	0.01284	0.00024	0.00142	0.00019	0.00073	0.00012	0.00051	0.00015	0.00036	0.00014	0.00031	0.00014	0.00028
9.0	0.00031	0.01191	0.00020	0.00124	0.00015	0.00062	0.00010	0.00043	0.00013	0.00030	0.00012	0.00026	0.00011	0.00023
9.2	0.00027	0.01106	0.00016	0.00107	0.00013	0.00053	0.00008	0.00036	0.00010	0.00025	0.00010	0.00021	0.00009	0.00019
9.4	0.00024	0.01028	0.00014	0.00093	0.00010	0.00045	0.00006	0.00031	0.00008	0.00021	0.00008	0.00018	0.00007	0.00016
9.6	0.00021	0.00956	0.00011	0.00081	0.00008	0.00039	0.00005	0.00026	0.00007	0.00018	0.00006	0.00015	0.00006	0.00013
9.8	0.00019	0.00889	0.00009	0.00071	0.00007	0.00033	0.00004	0.00022	0.00006	0.00015	0.00005	0.00013	0.00005	0.00011
10.0	0.00017	0.00827	0.00007	0.00062	0.00005	0.00028	0.00003	0.00018	0.00005	0.00012	0.00004	0.00011	0.00004	0.00009

TABLE XIII. Numerical open-shell correlation functions.

r	H^-	He	Li^{1+}	Be^{2+}	C^{4+}	O^{6+}	Ne^{8+}
0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
0.1	1.05201	1.04735	1.04542	1.04409	1.04203	1.04032	1.03875
0.2	1.10339	1.09217	1.08676	1.08270	1.07619	1.07081	1.06612
0.3	1.15414	1.13465	1.12449	1.11668	1.10435	1.09464	1.08679
0.4	1.20427	1.17494	1.15902	1.14677	1.12809	1.11432	1.10401
0.5	1.25377	1.21320	1.19073	1.17367	1.14873	1.13162	1.11964
0.6	1.30267	1.24957	1.22000	1.19798	1.16731	1.14765	1.13411
0.7	1.35095	1.28421	1.24715	1.22024	1.18456	1.16279	1.14642
0.8	1.39864	1.31725	1.27248	1.24090	1.20098	1.17675	1.15417
0.9	1.44573	1.34881	1.29629	1.26035	1.21675	1.18852	1.15354
1.0	1.49223	1.37903	1.31881	1.27891	1.23180	1.19639	1.13928
1.1	1.53814	1.40802	1.34026	1.29680	1.24576	1.19796	
1.2	1.58348	1.43589	1.36084	1.31418	1.25800	1.19014	
1.3	1.62824	1.46274	1.38071	1.33114	1.26759	1.16912	
1.4	1.67243	1.48868	1.40000	1.34770	1.27334	1.13041	
1.5	1.71606	1.51379	1.41883	1.36377	1.27377	1.06881	
1.6	1.75913	1.53817	1.43727	1.37923	1.26713		
1.7	1.80165	1.56188	1.45538	1.39386	1.25140		
1.8	1.84362	1.58500	1.47317	1.40737	1.22425		
1.9	1.88505	1.60761	1.49063	1.41940	1.18309		
2.0	1.92595	1.62974	1.50775	1.42950	1.12507		
2.1	1.96632	1.65147	1.52444	1.43717			
2.2	2.00616	1.67284	1.54063	1.44180			
2.3	2.04548	1.69387	1.55618	1.44275			
2.4	2.08429	1.71462	1.57096	1.43927			
2.5	2.12260	1.73511	1.58479	1.43054			
2.6	2.16040	1.75535	1.59747				
2.7	2.19770	1.77536	1.60875				
2.8	2.23451	1.79515	1.61839				
2.9	2.27084	1.81472	1.62609				
3.0	2.30668	1.83407	1.63153				
3.1	2.34205	1.85318	1.63437				
3.2	2.37695	1.87203	1.63424				
3.3	2.41139	1.89060	1.63073				
3.4	2.44537	1.90887	1.62342				
3.5	2.47889	1.92678	1.61183				
3.6	2.51197	1.94430					
3.7	2.54460	1.96138					
3.8	2.57680	1.97795					
3.9	2.60857	1.99397					
4.0	2.63991	2.00935					
4.1	2.67083						
4.2	2.70133						
4.3	2.73142						
4.4	2.76112						
4.5	2.79041						
4.6	2.81930						
4.7	2.84781						
4.8	2.87594						
4.9	2.90369						
5.0	2.93107						

the correlation function χ_N then achieves that the total wave function Φ_N given by Eq. (1) or (2) is normalized in the usual sense:

$$\int dV\Phi_N^2=1.$$

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Correlated Orbitals for the Ground State of the Hydrogen Molecule[*]

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INTRODUCTION

FOR the ground state of the helium atom and its isoelectronic series, wave functions constructed from a conventional orbital product, times a correlation function depending on the interelectronic distance only, have been relatively successful.[1] The best correlated closed shell, using the same orbital for both electrons, yields energies within 0.15 ev of experiment; the best correlated open shell, using a symmetrized product of two different orbitals, comes within 0.015 ev.

In this paper we give the results of similar calculations on the hydrogen molecule. The correlated closed shell for H_2 is represented by

$$\Phi_C=\varphi(1)\varphi(2)\chi(r_{12}), \tag{1}$$

where φ is a one-electron function or orbital, and $\chi(r_{12})$ is the correlation function. The orbital φ must be of species σ_g; expressing φ in terms of the usual elliptic coordinates,[2] this means that

$$\varphi(\xi,\eta)=\varphi(\xi,-\eta). \tag{2}$$

For the correlated open shell there are two different possibilities. They both have in common that the total wave function is given by

$$\Phi={}_0[\varphi(1)\psi(2)+\psi(1)\varphi(2)]\chi(r_{12}). \tag{3}$$

The difference between the two open shells is in the orbitals. One type, which we call the *in-out correlated open shell*, is built from a φ and ψ which both have σ_g symmetry and satisfy Eq. (2). For the other type, called the *left-right correlated open shell*, the orbitals φ and ψ have only cylindrical, or σ, symmetry, and they are each other's mirror image with respect to the center of the molecule.

The first correlated closed-shell calculation was done by Frost and Braunstein.[3] They used a simple LCAO for the orbital $\varphi=1s_a+1s_b$, and a two-term correlation function $\chi(r_{12})=1+cr_{12}$; the effective nuclear charge of the $1s$ orbitals and the constant c were the adjustable parameters. Their calculation yielded a binding energy which was still in error by 0.6 ev. Since we expect (from analogy with the helium series) only about 0.15 ev or less for well-adjusted orbital(s) and correlation function, Frost and Braunstein's choice for these was clearly too inflexible. We adopted the expressions

$$\begin{aligned}\varphi(\xi,\eta)&=\sum_{i=0}^{m}a_iu_i(\xi,\eta),\\ \psi(\xi,\eta)&=\sum_{i=0}^{m}b_iu_i(\xi,\eta),\\ \chi(r_{12})&=\sum_{\mu=0}^{n}c_\mu v_\mu(r_{12});\end{aligned} \tag{4}$$

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[1] C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. **32**, 194 (1960), this issue.

[2] If a and b refer to the two nuclei, and R is the internuclear distance, $\xi=(r_a+r_b)/R$, $\eta=(r_a-r_b)/R$.

[3] A. A. Frost and J. Braunstein, J. Chem. Phys. **19**, 1133 (1951).