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Combined Use of the Methods of Superposition of Configurations and Correlation Factor on the Ground States of the Helium-Like Ions*

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The accurate solution of the Schrödinger equation by means of a combination of the method of correlation factor and the method using superposition of configurations is discussed. For a many-electron system, the total wave function divided by the nodeless function $g=g(r_{12},r_{13},r_{23}\cdots)$ may be expanded in a series of Slater determinants built up from a complete one-electron set. For a two-electron system, this expansion becomes very simple and, by going over to principal orbitals, it may be "diagonalized" and brought to a particularly rapidly convergent form.

The method is applied to the He-like ions (H^-, He, Li^+, and Be^{2+}) by choosing $g=1+\alpha r_{12}$ and by using a basis consisting of only three s-orbitals. The energies obtained differ from the exact values only by about 0.001–0.002 atomic units. Even the simpler wave functions $(u)^2(1+\alpha r_{12})$ and $(u,v)(1+\alpha r_{12})$ are discussed, and the forms obtained by truncating the expansion of Ψ in principal orbitals are studied in greater detail.

I. INTRODUCTION

In the independent-particle model of a many-electron system, the interaction of the electrons is taken into account by an average potential field. Although this method gives a comparatively small relative error in the energy, the difference between the experimental and theoretical value is of the same order of magnitude as the energy change in a normal chemical reaction. Therefore, it is of great importance to refine the wave function by treating the "correlation effect" in a correct way, i.e., to take into account the fact that the electrons, because of their mutual Coulomb repulsion, try to avoid each other.

In studying the correlation problem in the He atom, the method of "superposition of configurations" was first used practically by Hylleraas.[1] The slow convergence of the Legendre expansion, however, induced Hylleraas to include explicitly the interelectronic distance[2,3] r_{12} in the wave function, and his successful results have had a very strong influence on the later computations. Hylleraas' work on helium has been continued along several different lines.

The method using a power-series expansion in the three variables $s=r_1+r_2$, $u=r_{12}$, $t=r_2-r_1$, has been extended to a high degree of accuracy in the energy eigenvalue.[4] Recently Kinoshita[5] has pointed out that one could just as well use a power series expansion in s, (u/s), and (t/u), which implies a generalization to include negative powers of s and u. By means of a 39-term function, he obtained the energy value $E=2.903\,7225$ a.u.$_{\text{He}}$, which is in very good agreement with the latest experimental results with the necessary relativistic corrections.

It was early found[6] that Hylleraas' expansion could not be a formal solution to the helium wave equation, but the inclusion of the negative powers has changed the situation.[7] Even the inclusion of logarithmic terms in the wave function has been discussed.[8] The discussion of the existence and analytical character of the exact eigenfunction for the ground state of helium is still going on.[9]

With respect to the energy, the method using "correlated" basic variables described and discussed in references 2–9 shows an excellent accuracy for helium, but unfortunately this method cannot easily be generalized to systems containing more than two electrons. In connection with the general theory of many-particle systems, the helium atom is otherwise of particular interest, since it provides a simple example on which various approaches may be tested before they are applied to more complicated systems.

Considering generalizations to molecules and crystals the above-mentioned method[1] using "superposition of configurations" seems actually much more promising, since it is easily shown that every normalizable antisymmetric wave function may be expanded in a series of Slater determinants built up from a complete set of one-electron functions.[10] Because of the revived

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[1] E. A. Hylleraas, Z. Physik **48**, 469 (1928).

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

[3] E. A. Hylleraas, Z. Physik **65**, 209 (1930).

[4] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955); L. Wilets and I. J. Cherry, Phys. Rev. **103**, 112 (1956).

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

[6] Bartlett, Gibbons, and Dunn, Phys. Rev. **47**, 679 (1935); A. S. Coolidge and A. M. James, Phys. Rev. **51**, 855 (1937).

[7] P. Pluvinage, J. phys. radium **16**, 675 (1955); G. Munschy and P. Pluvinage, J. phys. radium **18**, 157 (1957); T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[8] T. H. Gronwall, Phys. Rev. **51**, 655 (1937); J. H. Bartlett, Phys. Rev. **88**, 525 (1952); **98**, 1067 (1955); V. A. Fock, Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **18**, 161 (1954); E. A. Hylleraas, Svensk Kem. Tidskr. **67**, 372 (1955); E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).

[9] See also T. Kato, Trans. Am. Math. Soc. **70**, 212 (1951); Research Report No. CX-25, New York University, 1956 (unpublished).

[10] For a simple proof, see, e.g., P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

interest in this approach, the helium case has recently been reexamined in greater detail,[11] and the results have confirmed the fairly slow convergence of the Legendre expansion.[12] The problem is to improve this situation.

The independent-particle model has the advantage of having a high degree of physical visuality, and Hylleraas[2] showed that it was possible to introduce a great deal of correlation in this scheme by means of a "correlation factor" $g=g(r_{12})$ in the wave function

$$\Psi=u(r_1)u(r_2)g(r_{12}). \tag{1}$$

Choosing u as a single exponential and $g=1+\alpha r_{12}$, Hylleraas obtained the surprisingly good energy[13] $E=-2.8912$ a.u.$_{\mathrm{He}}$. Later even more general forms of u and g in (1) have been investigated.[14]

In this paper, we shall try to combine the method with correlation factor g with the more systematic approach using superposition of configurations. If $g=g(r_{12},r_{13},r_{23},\cdots)$ is a nodeless and symmetric function of all the interelectronic distances, we can expand the antisymmetric function obtained by dividing the total wave function by g in a series of Slater determinants built up from a complete one-electron set, and the problem is then to choose the factor g so that the expansion converges as fast as possible. Hylleraas' numerical result indicates that, by using a conveniently chosen correlation factor g, one can essentially improve the convergence of the configurational expansion. In principle, the method is applicable to any many-electron system, but here we shall first test it on the series of He-like ions: H$^-$, He, Li$^+$, and Be^{2+}.

II. GENERAL DESCRIPTION OF THE METHOD TRANSFORMATION TO PRINCIPAL ORBITALS

The nonrelativistic Schrödinger equation for the He-like ions has the form $H_{\mathrm{op}}\Psi=E\Psi$, where $H_{\mathrm{op}}=T_{\mathrm{op}}+V_{\mathrm{op}}$ and

$$T_{\mathrm{op}}=-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2, \quad V_{\mathrm{op}}=-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}. \tag{2}$$

All quantities are expressed in modified atomic units, (a.u.$_Z$). For a two-electron system, the wave function may be factorized into a space part and a spin part. Concentrating our interest on the space function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$, we note that, for the ground state, it is symmetric in the two coordinates.

We introduce the correlation factor $g=1+\alpha r_{12}$ proposed by Hylleraas,[2] and we expand the symmetric function $\Psi(\mathbf{r}_1,\mathbf{r}_2)/(1+\alpha r_{12})$ for $\alpha\geq 0$ in a discrete, complete, and orthonormal set of real one-electron functions $\psi_k(\mathbf{r})$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)/(1+\alpha r_{12})=\sum_{k,l} C_{kl}\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2). \tag{3}$$

By multiplying with $(1+\alpha r_{12})$ we obtain the wave function

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(1+\alpha r_{12})\sum C_{kl}\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2). \tag{4}$$

The real coefficients C_{kl} $(=C_{lk})$ form a Hermitean matrix $\mathbf{C}$ which can be diagonalized by a unitary matrix $\mathbf{U}$:

$$\mathbf{U}^\dagger\mathbf{C}\mathbf{U}=\boldsymbol{\lambda}. \tag{5}$$

Introducing a complete orthonormal set of principal orbitals χ_k by the relation

$$\chi_k=\textstyle\sum_\alpha \psi_\alpha U_{\alpha k}, \tag{6}$$

we obtain

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(1+\alpha r_{12})\textstyle\sum_k \lambda_k\chi_k(\mathbf{r}_1)\chi_k(r_2). \tag{7}$$

The principal orbitals are identical with the natural orbitals[10,15] only in the special case $\alpha=0$.

For convenience we introduce a few new notations: $\varphi_{kk}=\psi_k(\mathbf{r}_1)\psi_k(\mathbf{r}_2)$,

$$\varphi_{kl}=(1/\sqrt{2})\{\psi_k(r_1)\psi_l(r_2)+\psi_l(r_1)\psi_k(r_2)\}, \quad k\neq l, \tag{8}$$

and

$$\bar{C}_{kk}=C_{kk}, \quad \bar{C}_{kl}=\sqrt{2}C_{kl}, \quad k\neq l. \tag{9}$$

Correspondingly (4) takes the form:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(1+\alpha r_{12})\sum_{l\leq k}\bar{C}_{kl}\varphi_{kl}(\mathbf{r}_1,\mathbf{r}_2). \tag{10}$$

Writing the functions φ_{kl} with $l\leq k$ in lexicographic order, φ_{11}, φ_{21}, φ_{22}, φ_{31}, $\cdots$, we can introduce a single index i [instead of the double index (k,l)] indicating the place in this order:

$$\varphi_1=\varphi_{11}, \quad \varphi_2=\varphi_{21}, \quad \varphi_3=\varphi_{22}, \quad \cdots, \tag{11}$$

and correspondingly $a_i=\bar{C}_{kl}$. This enables us to write Ψ as a single sum:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=(1+\alpha r_{12})\textstyle\sum_i a_i\varphi_i(\mathbf{r}_1,\mathbf{r}_2). \tag{12}$$

To approximate the solution of the Schrödinger equation by means of Ritz's method, we shall use the nonorthogonal set $\Phi_i=(1+\alpha r_{12})\varphi_i$ having an overlap matrix $\boldsymbol{\Delta}$ with the elements

$$\Delta_{ij}=\Delta_{ij}^{(0)}+2\alpha\Delta_{ij}^{(1)}+\alpha^2\Delta_{ij}^{(2)}, \tag{13}$$

where $\Delta_{ij}^{(n)}=\int\varphi_i\varphi_j r_{12}^n dv_1dv_2$. The energy is represented by the matrix

$$H_{ij}=H_{ij}^{(0)}+\alpha H_{ij}^{(1)}+\alpha^2 H_{ij}^{(2)},$$

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[11] P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); R. E. Watson, Quarterly Progress Report of the Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1956 (unpublished), p. 38; Tycko, Thomas, and King, Phys. Rev. **109**, 369 (1958); H. Shull and P. O. Löwdin, Technical Note from Uppsala Quantum Chemistry Group, June 15, 1958 (unpublished), J. Chem. Phys. (to be published).

[12] Compare also Green, Lewis, Mulder, Wyeth, and Woll, Phys. Rev. **93**, 273 (1954).

[13] Reference 2, p. 356.

[14] T. D. H. Baber and H. R. Hassé, Proc. Cambridge Phil. Soc. **33**, 253 (1937); P. Pluvinage, Ann. phys. **5**, 145 (1950).

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

TABLE I. Ground-state energy of the He-like ions.

	Z	E	"E_{exact}"	$E-E_{\text{exact}}$
H^-	1	−0.526 37	−0.527 56[a]	+0.001 19
He	2	−2.902 28	−2.903 76[b]	+0.001 48
Li^+	3	−7.278 07	−7.279 93[c]±12	+0.001 86
Be^{2+}	4	−13.653 48	−13.655 43[c]±46	+0.001 95

[a] L. R. Heinrich, Astrophys. J. **99**, 59 (1944).
[b] See reference 5.
[c] Semiempirical, reference 19.

where

$$H_{ij}^{(0)}=\int \varphi_i H_{\text{op}} \varphi_j dv_1 dv_2,$$

$$H_{ij}^{(1)}=\int r_{12}(\varphi_i H_{\text{op}}\varphi_j+\varphi_j H_{\text{op}}\varphi_i)dv_1 dv_2, \tag{15}$$

$$H_{ij}^{(2)}=\int r_{12}\varphi_i(H_{\text{op}}r_{12}\varphi_j)dv_1 dv_2.$$

The coefficients a_i in (12) are found by solving the system of linear equations

$$\textstyle\sum_j (H_{ij}-E\Delta_{ij})a_j=0, \tag{16}$$

and the eigenvalues E are determined by the determinantal equation

$$\det\{H_{ij}-E\Delta_{ij}\}=0. \tag{17}$$

III. TRUNCATED BASIS: SCALING PROBLEM AND CHOICE OF PARAMETER

In the numerical computation, it is not possible to use an infinite set $\{\psi_k\}$, so we are forced to truncate the one-electron basis to finite order M. This implies that the series (12) will contain only $M(M+1)/2$ terms. This procedure can be dangerous, since the truncated set may not be appropriate for the physical problem under consideration. It may be "out of scale" with respect to the dimension of the system, and many fundamental relations, as for instance the virial theorem, are then no longer fulfilled. Following Hylleraas,[2] we shall adjust the truncated set by introducing a scale factor η, so that

$$\Phi_i(\eta_1\mathbf{r}_1,\mathbf{r}_2)=\eta^3\Phi_i(\eta\mathbf{r}_1,\eta\mathbf{r}_2)=\eta^3(1+\alpha\eta r_{12})\varphi_i(\eta\mathbf{r}_1,\eta\mathbf{r}_2). \tag{18}$$

It is easily shown that $\Delta_{ij}(\eta)=\Delta_{ij}(1)$ and further

$$T_{ij}(\eta)=\eta^2T_{ij}(1),\quad V_{ij}(\eta)=\eta V_{ij}(1). \tag{19}$$

The characteristic roots of the truncated secular equation (17) will be functions of both of the parameters η and α. Equation (16) may be written in matrix form:

$$\mathbf{Ha}=E\mathbf{\Delta a}, \tag{20}$$

where $\mathbf{a}$ is a column vector formed by the coefficients a_i. Multiplying by the row vector $\mathbf{a}^\dagger$, we obtain

$$E=\frac{\mathbf{a}^\dagger\mathbf{Ha}}{\mathbf{a}^\dagger\mathbf{\Delta a}}=\langle\mathbf{H}\rangle_{\text{a}}. \tag{21}$$

Differentiation with respect to any parameter κ leads to the relation[16]:

$$\frac{\partial E}{\partial\kappa}=\left\langle\frac{\partial\mathbf{H}}{\partial\kappa}-E\frac{\partial\mathbf{\Delta}}{\partial\kappa}\right\rangle_{\text{a}}. \tag{22}$$

Choosing $\kappa=\eta$ and $\kappa=\alpha$ respectively, we obtain

$$\partial E/\partial\eta=2\eta\langle\mathbf{T}\rangle_{\text{a}}+\langle\mathbf{V}\rangle_{\text{a}}, \tag{23}$$

$$\partial E/\partial\alpha=2\alpha\langle\mathbf{H}^{(2)}-E\mathbf{\Delta}^{(2)}\rangle_{\text{a}}+\langle\mathbf{H}^{(1)}-E\mathbf{\Delta}^{(1)}\rangle_{\text{a}}. \tag{24}$$

These relations are useful in the evaluation of E_{min}.

IV. CHOICE OF BASIS AND EVALUATION OF THE MATRIX ELEMENTS

As one-electron basis $\{\psi_k\}$, we have chosen the discrete, complete, and orthogonal set, recently suggested by Shull and Löwdin[17]:

$$[nlm]=\{(n+l+1)!\}^{-\frac{3}{2}}\{(n-l-1)!\}^{\frac{1}{2}}\times r^le^{-r/2}L_{n+l+1}{}^{2l+2}(r)Y_{lm}(\theta,\varphi), \tag{25}$$

where $L_{n+l+1}{}^{2l+2}$ are the Laguerre polynomials of order $(2l+2)$ and Y_{lm} are normalized spherical harmonics.

The evaluation of the matrix elements was carried out by means of a theorem[2] that, if f is a function of only the variables r_1, r_2, and r_{12}, then

$$\int f(r_1,r_2,r_{12})dv_1dv_2=8\pi^2\int_0^\infty\int_0^\infty\int_{|r_1-r_2|}^{r_1+r_2} f(r_1,r_2,r_{12})r_1r_2r_{12}dr_1dr_2dr_{12}. \tag{26}$$

It is easily shown that, in using the basis (25), all the matrix elements involved may be expressed in terms of the quantities

$$A(p,q,n)=\int_0^\infty\int_0^\infty\int_{|r_1-r_2|}^{r_1+r_2} e^{-2(r_1+r_2)}\times r_1{}^pr_2{}^qr_{12}{}^ndr_1dr_2dr_{12}, \tag{27}$$

which can be calculated by elementary methods. For details we refer to the Appendix. Since the energy depends on the two parameters, η and α, it is convenient to evaluate the matrices $\Delta_{ij}{}^{(n)}$, $T_{ij}{}^{(n)}$, and $V_{ij}{}^{(n)}$ for $n=0$, 1, 2 separately.

In the actual calculations, we have chosen a truncated

TABLE II. Optimum values of the parameters η and α.

	α	η	$\alpha\eta$
H^-	0.458	0.7648	0.3503
He	0.146	1.9729	0.2880
Li^+	0.0855	3.1456	0.2689
Be^{2+}	0.0607	4.29746	0.2609

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[16] For a detailed treatment of the scaling problem, see P. O. Löwdin, Technical Note from Uppsala Quantum Chemistry Group, January 20, 1958; J. Mol. Spectroscopy (to be published).

[17] H. Shull and P. O. Löwdin, J. Chem. Phys. **23**, 1362, 1565 (1955); Phys. Rev. **101**, 1730 (1956).

TABLE III. Coefficients a_i in the expansion (12). Note that these functions are chosen so that $a_1 = 1$; $N = \int |\Psi|^2 dv_1 dv_2$.

	a_1	a_2	a_3	a_4	a_5	a_6	N
H^-	+1.000000	−0.055653	−0.099281	+0.154719	+0.006903	+0.002494	4.999788
He	+1.000000	−0.128136	−0.023678	+0.051264	+0.000082	−0.003645	1.917904
Li^+	+1.000000	−0.148801	−0.008957	+0.036321	−0.000594	−0.002768	1.517154
Be^{2+}	+1.000000	−0.153931	−0.002832	+0.029888	−0.000876	−0.002161	1.364091

basis consisting of only three functions: $[1s]$, $[2s]$, $[3s]$, where $Y_{00} = (4\pi)^{-\frac{1}{2}}$. This corresponds to an expansion (12) of six terms, and a secular determinant (17) of order six.

The calculation of the lowest eigenvalue E and the associated eigenvector a_i, was carried out by an iteration-variation procedure.[18] The parameters η and α were varied independently until the optimum energy was found.

V. RESULTS OF THE CALCULATIONS

The results of the calculations are condensed in Tables I–V. Table I gives the lowest energy E in comparison to the exact value E_{exact} associated with the nonrelativistic Hamiltonian (1). The latter is obtained either from accurate calculations (H^-, He) or from spectroscopic data[19] corrected for relativistic effects. All the results are expressed in modified atomic units.

The parameters η and α corresponding to minimum energy are listed in Table II, and the associated coefficients a_i are condensed in Table III. The transformation to principal orbitals according to (6) is straightforward and the λ values are listed in Table IV.

We notice how λ_1 becomes more dominating in comparison to λ_2 and λ_3 as Z increases. This indicates that the radial correlation looses some of its importance as we go to higher nuclear charges.

Finally in Table V we have given the unitary matrix $\mathbf{U}$ which transforms the set $(1s)$, $(2s)$, $(3s)$, into the set χ_1, χ_2, and χ_3 of principal orbitals. The high diagonal coefficients in the $\mathbf{U}$ matrices indicate that the original basis chosen does not differ very much from the principal orbitals in this case.

TABLE IV. The values of the coefficients λ_k in expansion (7) of a normalized wave function.

	Z	λ_1	λ_2	λ_3
H^-	1	+0.4532	−0.0454	−0.0038
He	2	+0.7888	−0.0231	−0.0033
Li^+	3	+0.8212	−0.0163	−0.0025
Be^{2+}	4	+0.8666	−0.0126	−0.0020

VI. SIMPLER WAVE FUNCTIONS. TRUNCATION OF THE EXPANSION (7)

In this section we would like to discuss the energy values obtained by interrupting the expansion (7) at different values of k.[20] Truncating the sum to contain only a single term, we have

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = (1+\alpha r_{12})\lambda_1\chi_1(r_1)\chi_1(r_2). \tag{28}$$

Using the first principal orbital χ_1 and the α value given in Sec. V, we obtain the energies listed in Table VI.

The wave function (28) is of the general form $(1+\alpha r_{12})u(r_1)u(r_2)$. From the point of view of comparison and generalization to more complicated systems, it is interesting to study the simplest possible functions u, namely $1s$ orbitals (simple exponentials) and SCF (self-consistent field) functions.[21]

The results of such calculation using unscaled functions u and varying α, are condensed in Table VII. We note the improvement in the energy as we vary α. Much better results are obtained by introducing a scale factor η according to Sec. III. The energy values are given in Table VIII.

We also investigated the case when u is a sum of two exponentials:

$$u(r) = A_1 e^{-a_1 r} + A_2 e^{-a_2 r}, \tag{29}$$

where in addition to the normalization constant and the scale factor, we have two variational parameters. The corresponding energies are given in Table IX.

Let us now consider the expansion (7) truncated to contain the first two principal orbitals χ_1 and χ_2. Since λ_1 and λ_2 have opposite signs, we can write $\lambda_1 = a^2$, $\lambda_2 = -b^2$ and we obtain

$$\begin{aligned}\Psi = (1+\alpha r_{12})\{a^2\chi_1(r_1)\chi_1(r_2) - b^2\chi_2(r_1)\chi_2(r_2)\}\\ = (1+\alpha r_{12})(u,v),\end{aligned} \tag{30}$$

where

$$(u,v) = u(r_1)v(r_2) + u(r_2)v(r_1), \tag{31}$$

and

$$\begin{aligned} u(r) &= a\chi_1(r) - b\chi_2(r), \\ v(r) &= a\chi_1(r) + b\chi_2(r). \end{aligned} \tag{32}$$

Wave functions of the type $(1+\alpha r_{12})(u,v)$ have been previously investigated by Chandrasakher[22] who pointed out that excellent results are obtained for H^-, if u and

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[18] P. O. Löwdin, Technical Note from the Uppsala Quantum Chemistry Group, April 23, 1958 (unpublished).

[19] *Atomic Energy Levels*, National Bureau of Standards Circular No. 467, edited by C. E. Moore (U. S. Government Printing Office, Washington, D. C., 1948), Vol. I.

[20] Compare the corresponding treatment of the expansion in natural orbitals. See reference 15.

[21] For the He-like ions, we have used analytic SCF functions. P. O. Löwdin, Phys. Rev. **90**, 120 (1953); Green, Lewis, and Woll, Phys. Rev. **93**, 757 (1954).

[22] S. Chandrasakher, Astrophys. J. **100**, 176 (1944).

TABLE V. The unitary matrices **U** defined in (5).

	H^-			He	
+0.993613	−0.034676	+0.107382	+0.995542	−0.038326	+0.035624
+0.044852	+0.994576	−0.093843	+0.090966	+0.988809	−0.118254
−0.103546	+0.098060	+0.989779	+0.024899	−0.120967	−0.992344
	Li^+			Be^{2+}	
+0.994409	−0.102543	+0.025222	+0.994083	−0.106621	+0.020778
+0.104985	+0.985725	−0.131619	+0.108449	+0.985057	−0.133800
−0.011366	+0.133531	+0.990980	−0.006202	+0.135261	+0.990791

TABLE VI. Energy corresponding to wave function (7) containing only the first principal orbital.

	$E^{(1)}$
H^-	−0.5174
He	−2.8973
Li^+	−7.2733
Be^{2+}	−13.6488

TABLE VII. Ground-state energies corresponding to the wave function (28) with u given by unscaled $1s$ orbital or SCF function.

		$u=1s$-orbital, $\eta=Z-\frac{5}{16}$			$u=$SCF function		
	Z	$E_{\alpha=0}$	E_α opt.	α	$E_{\alpha=0}$	E_α opt.	α
H^-	1	−0.4727	−0.4964	0.246	−0.4878	−0.5022	0.152
He	2	−2.8477	−2.8748	0.199	−2.8617	−2.8807	0.156
Li^+	3	−7.2227	−7.2507	0.188	−7.2364	−7.2566	0.154
Be^{2+}	4	−13.5977	−13.6261	0.184	−13.6113	−13.6320	0.153

v are approximated by single exponentials having different exponents. The case of He and Li^+ has been treated similarly by Green *et al.*[12]

In Table X are listed the energies corresponding to the first two principal orbitals. For comparison we have included also the results obtained by using single exponentials for u and v. The values for $\alpha=0$ are taken from Shull and Löwdin.[23]

We note that the two-term principal orbital result in the last column of Table X is better than the best corresponding exponential wave function with optimized α. This is so even though the α used in the truncated function is optimized with respect to the complete wave function and not with respect to the energy of the truncated basis. This seems to imply that, in the method using correlation factor, the principal orbitals play an important role similar to that of the natural orbitals in the case $\alpha=0$.

VII. CORRELATION EFFECTS. PROPERTIES OF THE WAVE FUNCTION

Let us now study how the correlation effects are implied in the wave function treated in this paper. The introduction of the correlation factor $g=(1+\alpha r_{12})$ means that, in the two-electron probability density,

$$|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2=(1+\alpha r_{12})^2\sum_k\lambda_k\chi_k(\mathbf{r}_1)\chi_k(\mathbf{r}_2), \qquad (33)$$

one will give pairs $(\mathbf{r}_1,\mathbf{r}_2)$ with large r_{12} a higher probability in comparison to pairs $(\mathbf{r}_1,\mathbf{r}_2)$ with small r_{12}. The importance of this "Coulomb hole" becomes clear, if we consider the special case $|\mathbf{r}_1|=|\mathbf{r}_2|$ and vary r_{12}. The factor $g=(1+\alpha r_{12})$ is therefore of main importance in treating the angular correlation.

In order to study the radial correlation, we place the two points $\mathbf{r}_1$ and $\mathbf{r}_2$ on the same straight line through the nucleus and keep one of them fixed. In this case, the variation of the factor $g=(1+\alpha r_{12})$ is very small around the point $r_{12}=0$ in comparison to the large change in the second factor in the right-hand member of (33); and one can conclude that the essential part of the radial correlation must be embedded in the second factor.

Let us now study the one-electron density defined by the relation

$$\gamma(\mathbf{r}_1)=\int|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2dv_2, \qquad (34)$$

for a wave function of the form (7) and compare it

TABLE VIII. Ground-state energies as in Table VII, but with scaling. $\eta=$scale factor. $\bar{\alpha}=\eta\alpha$ optimized.

		$u=$scaled $1s$-function			$u=$scaled SCF function		
	Z	E	η	$\bar{\alpha}$	E	η	$\bar{\alpha}$
H^-	1	−0.5088	1.2010	0.493	−0.5164	1.2400	0.477
He	2	−2.8911	1.0962	0.366	−2.8954	1.0958	0.322
Li^+	3	−7.2682	1.0631	0.337	−7.2712	1.0593	0.290
Be^{2+}	4	−13.6441	1.0467	0.322	−13.6465	1.0427	0.277

TABLE IX. Ground-state energy corresponding to $u=A_1e^{-a_1r}+A_2e^{-a_2r}$.

	a_1	a_2	A_1	A_2	E
H^-	0.51086	1.13717	0.34290	1.42201	−0.520500
He	1.56317	2.49720	2.70716	2.56910	−2.898063
Li^+	2.60065	3.92698	6.79381	3.11156	−7.273847
Be^{2+}	3.64318	5.64693	12.45402	2.98896	−13.64918

TABLE X. Ground-state energies corresponding to wave functions of the form $(u,v)(1+\alpha r_{12})$.

	Simple exponentials		Two principal orbitals
	$\alpha=0$	α optimized	
H^-	−0.5133	−0.5259	−0.5262
He	−2.8757	−2.9014	−2.9020
Li^+	−7.2490	−7.2772	−7.2778
Be^{2+}	−13.6230		−13.6531

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[23] H. Shull and P. O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).

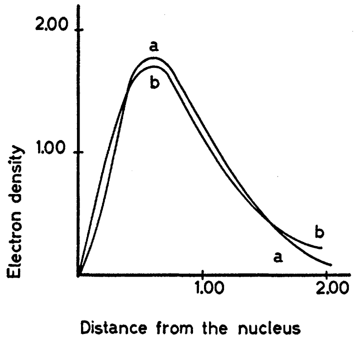

FIG. 1. Radial electron densities $(4\pi)^2\gamma(r)r^2$ for (a) a correlated wave function, and (b) the SCF function.

with the same quantity in the Hartree-Fock approximation. For this purpose, we have used an analytic self-consistent field function.[21] The quantity $\gamma(r_1)r_1^2$ for He has been plotted for both cases in Fig. 1. We note that the two curves have the same general shape. Their difference is everywhere less than 0.08 at every point. The "correlated" density is more contracted than the SCF curve, which shows a larger extension of the electronic cloud. This trend is also reflected in the quantities $\langle r^n\rangle_{\text{Av}}$ defined by

$$\langle r^n\rangle_{\text{Av}}=\int_0^\infty \gamma(r_1)r_1^{n+2}dr_1. \tag{35}$$

The results for He are condensed in Table XI.

TABLE XI. Average values $\langle r^n\rangle_{\text{Av}}$ for He for a correlated wave function based on Table III in comparison with the SCF values.

	Correlated wave function	SCF function
$\langle r\rangle_{\text{Av}}$	0.897	0.930
$\langle r^2\rangle_{\text{Av}}$	1.141	1.193
$\langle r^3\rangle_{\text{Av}}$	1.901	1.944

An investigation of the influence of correlation on the atomic "form factor" for He is now also inprogress.

APPENDIX. CALCULATION OF MATRIX ELEMENTS

In calculating the matrix elements, we put $\eta=1$ in the functions $[nlm]$ defined by (25) for $l=0$. Each one of the products $\varphi_i\varphi_j$ may now be expressed in the form

$$\varphi_i\varphi_j=\frac{1}{(4\pi)^2}\sum_{p,q} b(pq;ij)r_1^p r_2^q e^{-2(r_1+r_2)}. \tag{A1}$$

Let L_{op} be the nuclear attraction operator and C_{op} the electronic Coulomb repulsion operator, so that

$$L=-Z/r_1-Z/r_2,\quad C=1/r_{12}, \tag{A2}$$

and $V=L+C$. Expressing the matrix elements in the quantity (27), one obtains

$$\begin{aligned}\Delta_{ij}^{(0)}&=\delta_{ij},\\ \Delta_{ij}^{(n)}&=\tfrac{1}{2}\sum b(pq;ij)\\ &\quad\times A(p+1,q+1,n+1),\quad n=1,2.\end{aligned} \tag{A3}$$

$$\begin{aligned}L_{ij}^{(0)}&=-Z\sum b(pq;ij)(p+2)!(q+1)!/(2^{p+q+4}),\\ L_{ij}^{(n)}&=-nZ\sum b(pq;ij)\\ &\quad\times A(p,q+1,n+1),\quad n=1,2.\end{aligned} \tag{A4}$$

$$\begin{aligned}C_{ij}^{(0)}&=\tfrac{1}{2}\sum b(pq;ij)A(p+1,q+1,0),\\ C_{ij}^{(1)}&=2\Delta_{ij}^{(0)}=2\delta_{ij},\\ C_{ij}^{(2)}&=\Delta_{ij}^{(1)}.\end{aligned} \tag{A5}$$

The matrix elements of T_{op} are slightly more complicated. It may be convenient to introduce also the expansion

$$\varphi_i T_{\text{op}}\varphi_j=\frac{-\frac{1}{2}}{(4\pi)^2}\sum_{p=-1}\sum_{q=-1}\bar{b}(pq;ij)r_1^p r_2^q e^{-2(r_1+r_2)}. \tag{A6}$$

The matrix $T_{ij}^{(2)}$ requires some consideration, but, by application of vector operator formulas, we obtain

$$T_{ij}^{(2)}=\delta_{ij}+\tfrac{1}{2}\int r_{12}^2[\varphi_i T_{\text{op}}\varphi_j+\varphi_j T_{\text{op}}\varphi_i]dv_1dv_2. \tag{A7}$$

This gives the result

$$\begin{aligned}T_{ij}^{(0)}&=-\sum \bar{b}(pq;ij)(p+2)!(q+2)!/(2^{p+q+7}),\\ T_{ij}^{(1)}&=-\tfrac{1}{4}\sum[\bar{b}(pq;ij)+b(pq;ji)]\\ &\quad\times A(p+1,q+1,2),\\ T_{ij}^{(2)}&=-\tfrac{1}{8}\sum[\bar{b}(pq;ij)+b(pq;ji)]\\ &\quad\times A(p+1,q+1,3)+\delta_{ij},\end{aligned} \tag{A8}$$

and the evaluation is straightforward.

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