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Atomic Many-Body Problem. III. The Calculation of Hylleraas-Type Correlated Wave Functions for the Beryllium Atom*

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By applying the theory of correlated wave functions, Hylleraas-type functions are computed for the beryllium atom. The theory is applied in a form in which only two-electron correlations are considered. Several different correlation factors as well as several different combinations of orbital functions are considered. It is shown that the Hylleraas method gives better results for the energy than the superposition of configurations in the 1s shell as well as in the 2s shell. The problem of the additivity of the correlation energy in pairs is analyzed and it is shown that the sum of pair-correlation energies is different from the correlation energy computed taking into account correlation in both shells simultaneously. The difference can be positive or negative depending on the wave functions, and it is not negligible if accurate values are required for the correlation energy. Comparing the computed values for the correlation energy resulting from two-electron correlations with the experimental value of the correlation energy, the size of the many-electron (more than two-electron) correlation effects is estimated. It is shown that these effects can not be neglected if accurate values are required for the correlation energy.

1. FORMULATION OF THE PROBLEM

IN a set of previous publications[1] a new method for the approximate solution of the many-electron Schrödinger equation had been developed by one of us (L. S.). In this method, which we called the theory of correlated wave function, the wave function of an atom is written as a linear combination of variational trial functions. According to the choice of the trial functions we obtain the following special cases of the theory:

(1) If the trial functions are linear combinations of central-field wave functions, the method is identical with the conventional method of superposition of configurations.

(2) The theory is formulated in such a way that the trial functions can depend explicitly on the distances between the electrons. Choosing the trial functions in this way we obtain a generalization of the Hylleraas method[2] originally developed for the He-like atoms.

(3) The trial functions can be chosen as the combination of the two possibilities mentioned above.

In the present paper we apply the theory to the calculation of correlated wave functions for the beryllium atom. The calculated wave functions are of the Hylleraas-type, i.e., we followed the choice mentioned under (2) above. The purposes of the calculations are:

(1) To show that the Hylleraas method gives better results than the superposition of configurations;

(2) To test which particular type of one-electron orbitals give the best results in a Hylleraas-type calculation;

(3) To try to find the best numerical methods for carrying out a Hylleraas-type calculation for atoms with arbitrary number of electrons.

The calculations are carried out for the beryllium atom because calculations had been done for this atom with other methods,[3] so we are able to compare our results with the results of other calculations. Also, the mathematical difficulties occurring in Hylleraas-type calculations for atoms with arbitrary number of electrons, are already occurring in a calculation for the beryllium atom (which is not true for the calculations for the He- or Li-like atoms). In other words, the theory of correlated wave functions which is developed for atoms with any number of electrons can be fully tested in the case of the beryllium atom.

2. THE THEORY OF CORRELATED WAVE FUNCTIONS

The theory has been described in detail before[4,5]; therefore in this section we restrict ourselves to the essential formulas. Let us consider an atom with N electrons. Let $\varphi_1(q)$, $\varphi_2(q)$, $\varphi_3(q),\cdots$, $\varphi_N(q)$ be a set of orthonormal spin orbitals which characterize the atom in the Hartree-Fock approximation.[6] Let us denote the spatial and spin coordinates of the jth electron by $q_j\equiv(x_j,y_j,z_j,\sigma_j)$. In the Hartree-Fock (H-F) approximation the wave function of the atom is given by

$$\psi_F=\frac{1}{\surd(N!)}\det[\varphi_1\varphi_2\cdots\varphi_N]=\frac{1}{\surd(N!)}\begin{vmatrix}\varphi_1(1)\cdots\varphi_1(N)\\ \varphi_2(1)\cdots\varphi_2(N)\\ \varphi_N(1)\cdots\varphi_N(N)\end{vmatrix}. \qquad (2.1)$$

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[1] L. Szasz, Z. Naturforsch. **14a**, 1014, (1959), **15a**, 909 (1960), J. Chem. Phys. **35**, 1072 (1961); Phys. Rev. **126**, 169 (1962) (Part I of the series); **132**, 936 (1963); J. Math. Phys. **3**, 1147 (1962) (Part II of the series).

[2] E. Hylleraas, Z. Physik **54**, 347 (1929); **60**, 624 (1930); **63**, 291 (1930); **65**, 209 (1930).

[3] See the discussion in Sec. V.

[4] The theory was first developed to describe only 2-electron correlations: L. Szasz, Z. Naturforsch. **15a**, 909 (1960).

[5] The general theory describing correlations of any order is developed in the first part of this series: L. Szasz, Phys. Rev. **126**, 169 (1962).

[6] In other words these are the orbitals which characterize the atom in the single-determinantal approximation. The φ's are not necessarily the H-F orbitals.

We now introduce correlated wave functions. First, let us expand (2.1) in terms of the orbitals φ_i and φ_k:

$$\begin{aligned}\psi_F&=\frac{1}{\sqrt{(N!)}}\sum_{s=1}^{N}\sum_{t=s+1}^{N}(-1)^{i+k+s+t}\begin{vmatrix}\varphi_i(s)&\varphi_i(t)\\ \varphi_k(s)&\varphi_k(t)\end{vmatrix}D^{(N-2)}(ik|st)\\ &=\frac{1}{\sqrt{(N!)}}\tilde{A}_p\left\{\begin{vmatrix}\varphi_i(1)&\varphi_i(2)\\ \varphi_k(1)&\varphi_k(2)\end{vmatrix}D^{(N-2)}(ik|12)\right\}.\end{aligned}\tag{2.2}$$

In this formula the first line is the ordinary Laplace expansion of the Slater determinant; $D^{(N-2)}(ik|st)$ is an $(N-2)\times(N-2)$ determinant which is obtained from (2.1) by striking out the rows containing the functions φ_i and φ_k and the columns containing q_s and q_t:

$$D^{(N-2)}(ik|st)=\begin{vmatrix}\varphi_1(1)\cdots\varphi_1(s-1)\varphi_1(s+1)\cdots\varphi_1(t-1)\varphi_1(t+1)\cdots\varphi_1(N)\\ \vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots\\ \varphi_{i-1}(1)\\ \varphi_{i+1}(1)\\ \vdots\\ \varphi_{k-1}(1)\\ \varphi_{k+1}(1)\\ \vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots\\ \varphi_N(1)\cdots \qquad\qquad\qquad\qquad \cdots\varphi_N(N)\end{vmatrix}.\tag{2.3}$$

In the second line of (2.2) $\tilde{A}_p$ is a partial antisymmetrizer operator[7] which generates the totally antisymmetric ψ_F from the expression in the curly bracket.

Let us introduce now the antisymmetric but otherwise completely arbitrary function $\Phi(ij|q_1q_2)\equiv\Phi(ij|12)$. The letters (i,j) indicate that this function will replace the antisymmetric product of the spin-orbitals φ_i and φ_j. To the right of the vertical bar in the Φ we indicate that this function depends on the coordinates q_1, q_2. Let us replace now the (2×2) determinant in (2.2) by the function Φ, and then we get *a correlated wave function*:

$$f(ik)=\frac{1}{\sqrt{(N!)}}\tilde{A}_p\{\Phi(ik|12)D^{(N-2)}(ik|12)\}.\tag{2.4}$$

In this function the correlation between the electron states i and k can be taken into account by writing Φ in the appropriate form. The wave function in which all 2-electron correlations are taken into account will be written in the form[8]

$$\Psi=\psi_F+\sum_{i,j}f(ij),\tag{2.5}$$

where ψ_F is given by (2.1) and $f(ij)$ by (2.4); the summation in (2.5) is taken for all electron pairs.

In the *ansatz* (2.5) only the 2-electron correlations are taken into account. Higher-order correlations are introduced similarly. We define correlation functions[9] representing the higher-order correlations. Let us denote these by

$$\begin{aligned}&\Phi(i,j,l|1,2,3)\\ &\Phi(i,j,l,k|1,2,3,4)\\ &\vdots\\ &\Phi(1,2,\cdots,N|1,2,\cdots N).\end{aligned}\tag{2.6}$$

Similarly to (2.4) we introduce higher-order *correlated functions* by the following definitions:

$$\begin{aligned}f(i,j,l)&\equiv\frac{1}{\sqrt{(N!)}}\tilde{A}_p\{\Phi(ijl|123)D^{(N-3)}(ijl|123)\},\\ f(i,j,l,k)&\equiv\frac{1}{\sqrt{(N!)}}\tilde{A}_p\{\Phi(ijlk|1234)D^{(N-4)}(ijlk|1234)\},\\ &\vdots\\ f(1,2,\cdots,N)&\equiv\frac{1}{\sqrt{(N!)}}\Phi(1,2,3,\cdots N|1,2,3,\cdots N),\end{aligned}\tag{2.7}$$

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[7] In the present paper we use the symbol $\tilde{A}_p$ rather freely in various expressions. It always means an operator which antisymmetrizes the expression on which it operates, although its specific meaning may be different in the different expressions.

[8] First suggested in Ref. 4, Eq. (10).

[9] The nomenclature was developed in Ref. 5, Sec. 2.

where the $\tilde{A}_p$ are partial antisymmetrizer operators. The wave function in which all correlations are taken into account is written in the form[10]

$$\Psi=\psi_F+\sum_{i,j} f(ij)+\sum_{ij,l} f(ijl)+\cdots+f(1,2,\cdots,N), \quad (2.8)$$

where the summations are for all spin-orbital pairs in the second term, for all spin-orbital triplets in the third term, etc. The properties of the functions (2.5) and (2.8) had been discussed in detail before.[4,5] Here we mention only that if the correlation functions are expanded in terms of determinants built from central-field wave functions, then (2.5) and (2.8) are identical with the superposition of configurations. In this case (2.5) represents a function with only the single- and double-substitution configurations; in (2.8) configurations of all orders can be included. The function (2.8) has the form of the exact solution of the many-electron Schrödinger equation. The generalization of the Hylleraas method[2] on the other hand, is obtained by introducing the interelectronic distance r_{12} into $\Phi(ik|12)$ in (2.5) and by introducing the interelectronic distances r_{12}, $r_{13},\cdots$, in the higher-order correlation functions (2.6).

In the present paper we use only the *ansatz* (2.5). The actual calculations are done as follows. Let us introduce a set of variational trial functions for the electron pair (i,k) denoted by $\Phi_A(ik|12)$ where $A=1, 2,\cdots M$. Introducing the variational parameters $C_A(ik)$, we write

$$\Phi(ik|12)=\sum_{A=1}^{M} C_A(ik)\{\Phi_A(ik|12)\}. \quad (2.9)$$

Introducing the notation

$$f_A(ik)\equiv\frac{1}{\sqrt{(N!)}}\tilde{A}_p\{\phi_A(ik|12)D^{(N-2)}(ik|12)\}, \quad (2.9')$$

we get for the correlated wave function (2.4) by putting Φ in the form given by (2.9):

$$f(ik)=\sum_{A=1}^{M} C_A(ik)f_A(ik). \quad (2.10)$$

Let us introduce the Hamiltonian of the N-electron atom:

$$H=\sum_{i=1}^{N}(T_i+U_i)+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\(i\neq j)}}^{N} W_{ij}, \quad (2.11)$$

where

$$T_i=-\tfrac{1}{2}\Delta_i,\qquad U_i=-\frac{Z}{r_i},\qquad W_{ij}=\frac{1}{r_{ij}}, \quad (2.12)$$

the terms having their usual meaning (in atomic units). Also let

$$T=\sum_{i=1}^{N} T_i,\quad U=\sum_{i=1}^{N} U_i,\quad W=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\(i\neq j)}}^{N} W_{ij}. \quad (2.13)$$

Let us simplify the notation in (2.10) by condensing the indices (ik) into the single index α, and put

$$f(\alpha)=\sum_{A=1}^{M} C_A(\alpha)f_A(\alpha). \quad (2.14)$$

Let us assume that the values $A=0$, $\alpha=0$ characterize the H-F function, i.e., we put

$$C_0(0)=1,\qquad f_0(0)\equiv\psi_F. \quad (2.15)$$

With this notation (2.5) becomes

$$\Psi=\sum_{\alpha=0}^{L}\sum_{A=0}^{M} C_A(\alpha)f_A(\alpha)=\psi_F+\sum_{\alpha=1}^{L}\sum_{A=1}^{M} C_A(\alpha)f_A(\alpha). \quad (2.17)$$

The energy of the atom is given by

$$E=\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\frac{\sum_{\alpha,A}\sum_{\beta,B} C_A^*(\alpha)C_B(\beta)\langle f_A(\alpha)|H|f_B(\beta)\rangle}{\sum_{\alpha,A}\sum_{\beta,B} C_A^*(\alpha)C_B(\beta)\langle f_A(\alpha)|f_B(\beta)\rangle}. \quad (2.18)$$

Applying the energy-minimum principle we get the equation

$$\sum_{\beta,B} C_B(\beta)\{\langle f_A(\alpha)|H|f_B(\beta)\rangle-E\langle f_A(\alpha)|f_B(\beta)\rangle\}=0,$$
$$(\alpha=0, 1, 2,\cdots L;\ A=0, 1, 2,\cdots M), \quad (2.19)$$

from which the secular equation is obtained:

$$\det[\langle f_A(\alpha)|H|f_B(\beta)\rangle-E\langle f_A(\alpha)|f_B(\beta)\rangle]=0,$$
$$(\alpha, \beta=0, 1,\cdots L;\ A, B=0, 1,\cdots M). \quad (2.20)$$

The calculations are carried out as follows. We choose a set of correlated functions $\phi_A(ik|12)$ for each electron pair (i,k). Forming with ϕ_A the correlated function f_A according to formula (2.9′) we calculate the matrix elements occurring in (2.20), and solve the equation for the lowest E. The difficult part of the calculation is the calculation of the matrix components.

General formulas for the matrix components have been derived in the previous papers[4,5,11] and it has been shown that the calculation of these matrix components can be reduced to the calculation of six relatively simple

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[10] Suggested in Ref. 5, Eq. (2.11).

[11] Besides Refs. 4 and 5 a detailed presentation of these matrix components is given in the paper by L. Szasz, J. Math. Phys. 3, 1147 (1962).

basic integrals.[11] (For an atom with an arbitrary number of electrons.) The method for the numerical calculation of the six basic integrals is outlined in the Appendix.

The convergence of the calculations can be improved by introducing an over-all scale factor k. We replace the original function $\Psi(q)$ by the normalized, scaled function

$$\Psi' = k^{(3N/2)}\Psi(kq), \tag{2.21}$$

where q stands for all particle coordinates $q_1, q_2, \cdots q_N$. The only change in the formalism is that the secular equation becomes

$$\begin{aligned}\det[k^2\langle f_A(\alpha)|T|f_B(\beta)\rangle + k\{\langle f_A(\alpha)|U|f_B(\beta)\rangle \\ +\langle f_A(\alpha)|W|f_B(\beta)\rangle\} - E\langle f_A(\alpha)|f_B(\beta)\rangle] = 0, \\ (\alpha, \beta = 0, 1, \cdots L; A, B = 0, 1, \cdots M).\end{aligned} \tag{2.22}$$

In this case the solution E of Eq. (2.22) is computed for different values of k and from the curve $E(k)$, the deepest value being selected.

One word about the general character of the matrix components. Let us reintroduce the indices (i,k) instead of α. We call "diagonal" the matrix components of the type

$$\langle f_A(ik)|H|f_B(ik)\rangle \tag{2.23}$$

in which, on either side of the operator H, the indices refer to the same spin-orbital pair (i,k). We call this a diagonal matrix component in spite of the fact that $f_A(ik)$ and $f_B(ik)$ contains the functions $\phi_A(ik)$ and $\phi_B(ik)$ which may be different functions of $\mathbf{r}_1$ and $\mathbf{r}_2$, as indicated by the different indices A and B. On the other hand, matrix components of the type

$$\langle f_A(ik)|H|f_B(kl)\rangle, \tag{2.24a}$$

$$\langle f_A(ik)|H|f_B(jl)\rangle \tag{2.24b}$$

are called off-diagonal matrix components.

The normalization and orthogonality conditions to which the wave functions are subjected are as follows: The one-electron orbitals are orthonormal:

$$\int \varphi_i^* \varphi_k dq = \delta_{ik}, \quad (i, k = 1, 2, \cdots N). \tag{2.25}$$

The two-electron functions are orthogonal to the one-electron functions in the following way:

$$\int \phi_A(ik|12)\varphi_s^*(1)dq_1 = 0, \qquad (i, k = 1, 2, \cdots N; s \neq i, k). \tag{2.26}$$

[The $\phi_A(ik|12)$ is *not* orthogonal to φ_i and φ_k.] The orthogonality (2.26) can be accomplished as follows. Let $\phi_A{}^0(ik|12)$ be an arbitrary two-electron function which does not satisfy (2.26). Then we put

$$\phi_A(ik|12) = [1 - \Omega(1) - \Omega(2) + \Omega(1)\Omega(2)]\phi_A{}^0(ik|12), \tag{2.27}$$

where $\Omega(1)$ is the following projection operator:

$$\Omega(1)f(1) = \sum_{\substack{j=1 \\ (j\neq i,k)}}^{N} \varphi_j(1)\int \varphi_j(2)f(2)dq_2. \tag{2.28}$$

It had been shown[4,5] that this type of orthogonalization does not change the total wave function, i.e., we have

$$\begin{aligned} f_A(ik) &= \frac{1}{\sqrt{(N!)}}\tilde{A}_p\{\phi_A{}^0(ik|12)D^{(N-2)}(ik|12)\} \\ &= \frac{1}{\sqrt{(N!)}}\tilde{A}_p\{\phi_A(ik|12)D^{(N-2)}(ik|12)\}. \end{aligned} \tag{2.29}$$

The normalization of the $\phi_A(ik|12)$ is not necessary if we work with the energy expression as given by (2.18).

3. THE CALCULATION

The electron configuration of the Be atom is $(1s)^2(2s)^2$. Therefore, the total correlated wave function is of the form

$$\begin{aligned}\Psi = \psi_F + f(1s,1s) + 4f(1s,2s) + f(2s,2s) \\ + 2f(1s,1s,2s) + 2f(1s,2s,2s) + f(1s,1s,2s,2s).\end{aligned} \tag{3.1}$$

In the present paper we neglect the 3- and 4-particle correlations and the $(1s\text{-}2s)$ correlation, i.e., we put

$$\Psi = \psi_F + f(1s,1s) + f(2s,2s). \tag{3.2}$$

For ψ_F we put

$$\psi_F = \frac{1}{\sqrt{(4!)}}\tilde{A}_p[\varphi_1(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)], \tag{3.3}$$

where

$$\begin{aligned} \varphi_1 = \psi_{1s}(\mathbf{r})\alpha, \quad \varphi_3 = \psi_{2s}(\mathbf{r})\alpha, \\ \varphi_2 = \psi_{1s}(\mathbf{r})\beta, \quad \varphi_4 = \psi_{2s}(\mathbf{r})\beta, \end{aligned} \tag{3.4}$$

(α and β are the spin functions). The ψ_{1s} and ψ_{2s} are orthonormal, i.e.,

$$\int \psi_i^* \psi_k dv = \delta_{ik}, \quad (i, k = 1s, 2s). \tag{3.5}$$

We simplify the notation by writing

$$\psi_{1s} \equiv \psi_1, \quad \psi_{2s} \equiv \psi_2. \tag{3.5'}$$

For $f(1s,1s)$ and $f(2s,2s)$ we put

$$\begin{aligned} f(1s,1s) &= \frac{1}{\sqrt{(4!)}}\tilde{A}_p\{\phi^0(1s,1s|12) \\ &\qquad \times D^{(N-2)}(1s,1s|1,2)\}, \\ f(2s,2s) &= \frac{1}{\sqrt{(4!)}}\tilde{A}_p\{\phi^0(2s,2s|12)D^{(N-2)}(2s,2s|12)\}, \end{aligned} \tag{3.6}$$

where $\phi^0(1s,1s)$ and $\phi^0(2s,2s)$ are not satisfying any orthogonality conditions. We put now

$$\phi^0(1s,1s|12)=\sum_i a_i\phi_i^0(1s,1s|12) \tag{3.7}$$

and

$$\phi^0(2s,2s|1,2)=\sum_i b_i\phi_i^0(2s,2s|1,2)\,, \tag{3.8}$$

where the a_i and b_i are variational parameters. We put the 2-electron functions in the form

$$\begin{aligned}\phi_i^0(1s,1s|1,2)&=\psi_3(r_1)\psi_3(r_2)g_i(r_1r_2r_{12})\\&\quad\times[\alpha(1)\beta(2)-\alpha(2)\beta(1)]\,, \qquad (3.9)\\ \phi_i^0(2s,2s|1,2)&=\psi_4(r_1)\psi_4(r_2)g_i(r_1r_2r_{12})\\&\quad\times[\alpha(1)\beta(2)-\alpha(2)\beta(1)]\,,\end{aligned}$$

where ψ_3 and ψ_4 are radial functions which depend only on r, g_i is a correlation factor depending on r_1, r_2, r_{12}, and we assume that g_i is symmetric. The spin function in the bracket is the (unnormalized) singlet spin function for 2 particles. The $\phi_i^0(1s,1s)$ and $\phi_i^0(2s,2s)$ are antisymmetric, due to the spin part. They are not normalized. In the following discussion we use the notation $\eta(1,2)=\alpha(1)\beta(2)-\alpha(2)\beta(1)$.

Having determined the general form of the trial functions we must choose specific functions for ψ_1, ψ_2, ψ_3, ψ_4 and for g_i.

A. The Choice of the One-Electron Orbitals for $\psi_1-\psi_4$

We would like to choose these orbitals in such a way as to get the best results with the minimum amount of mathematical difficulties in the calculations. The most obvious choices for ψ_1-ψ_4 are either the H-F functions or analytic Slater type functions. The arguments in favor of the H-F functions are the following: First, since these are the best orbitals in a single determinantal *ansatz*, the starting energy from which we try to approach the exact eigenvalue of the Schrödinger equation is the best possible which can be obtained with a single determinant; secondly, the analytic H-F functions are becoming available for many atoms,[12] and can be used conveniently in calculations of this type. On the other hand, as we have pointed out before,[13] in an ansatz of the form of (2.5) the H-F functions do not make the energy an absolute minimum. In other words, if we derive the equations for the best one-electron orbitals of the ansatz (2.5), these equations will be different from the H-F equations, which means that the *best orbitals* in an ansatz of the type (2.5) are not the (H-F) orbitals. In our opinion at the present time there is no clear-cut evidence which would show whether the H-F orbitals or the analytic Slater orbitals (or some other possibility) should be used in an ansatz with correlated wave functions.

In the absence of a clear-cut method for the choice of the one-electron orbitals we decided to test various types of orbital combinations for ψ_1-ψ_4 and check which combination gives the best energy. This is presented below. Fortunately we were able to develop a completely numerical method for the calculation of the necessary integrals for the secular equation. This numerical method works in the same way regardless of the form of the orbitals ψ_1-ψ_4, i.e., it does not matter whether the orbitals are simple analytic expressions like the Slater orbitals or more complicated analytic expressions like the Roothaan-type H-F orbitals (or functions given in the form of tables). The numerical method is described in the Appendix.

B. The Choice of the Correlation Factors

Here we follow the method of Hylleraas.[2] In the original calculations for He, Hylleraas suggested to put the correlation factor in the form of a power series in s, t, u, where $s=r_1+r_2$, $t=r_2-r_1$, $u=r_{12}$. These combinations are convenient for He but *not* convenient for atoms with more than 2 electrons. For machine calculations the best form is what was suggested by James and Coolidge and used successfully for the Li atom.[14] We put

$$g_i\equiv g_{\alpha\beta\gamma}\equiv(r_1{}^\alpha r_2{}^\beta+r_1{}^\beta r_2{}^\alpha)r_{12}{}^\gamma\,. \tag{3.10}$$

Here α, β, γ are positive integers or zero; g_i is put in symmetric form. The calculation was done in such a way that a general program has been written for the matrix components with an arbitrary combination of the parameters α, β, γ and for arbitrary one-electron functions ψ_1-ψ_4. In each case we have first calculated the ($1s$-$1s$) and ($2s$-$2s$) correlations separately, and after that we have calculated the combined total correlation energy.

C. $(1s-1s)$ Correlation

In the case of the He atom a six-parameter wave function gave good results. Therefore we first tried the ansatz:

$$\begin{aligned}\Psi=\frac{1}{\surd(4!)}\tilde{A}\{(\psi_1(1)\psi_1(2)&\\+\psi_3(1)\psi_3(2)[a_1r_{12}+a_2(r_1+r_2)&+a_3(r_1{}^2+r_2{}^2)\\&+a_4r_{12}{}^2+a_5r_1r_2])\psi_2(3)\psi_2(4)w\}\,,\end{aligned} \tag{3.11}$$

where $\tilde{A}$ is again the antisymmetrizer operator, w is the spin function,

$$w=\alpha(1)\beta(2)\alpha(3)\beta(4)\,, \tag{3.12}$$

and the variational parameters for the K shell are denoted by a_i ($i=1, 2,\cdots$). The coordinates of the two $1s$ electrons are denoted by 1, 2, the coordinates of the two $2s$ electrons by 3, 4. For ψ_1-ψ_4 we have first tried Slater type orbitals, which are

$$\psi_1=A_1e^{-Z_1r}\,,\quad \psi_2=A_2[re^{-Z_2r}-Be^{-Z_1r}]\,, \tag{3.13}$$

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[12] See, for instance, the recent calculations by E. Clementi [IBM J. Res. Develop. **9**, 2 (1965)] and "Tables of Atomic Functions," which is a supplement to the paper above.

[13] L. Szasz, Phys. Rev. **132**, 936 (1963).

[14] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

TABLE I. The correlation energy in the (1s) shell (all energies in a.u.).

Wave function	ψ_1 and ψ_2	ψ_3	Number of Hylleraas-type terms	Energy	Correlation energy	Percentage of total correlation
(3.11)	Slater orbitals	$\psi_3=\psi_1$	6	-14.6118	-0.0388	41.1
(3.11)	H-F functions	$\psi_3=\psi_1$	6	-14.6140	-0.0410	43.4
(3.11)	H-F functions	$\psi_3=$S.T.O.[a] $Z_3=3.7$	6	-14.6145	-0.0415	43.9
(3.21)	H-F functions	$\psi_3=$S.T.O. $Z_3=3.7$	11	-14.6153	-0.0423	44.8

[a] Slater type orbital.

where A_1 and A_2 are normalization constants, B is determined in such a way that ψ_2 is orthogonal to ψ_1 and Z_1 and Z_2 are variational parameters. These are determined by minimizing the energy with a single determinantal wave function built from the functions (3.13). We have

$$Z_1=3.6847\,,\quad A_1=3.9905\,,\quad B=2.5883\,,\qquad Z_2=0.9562\,,\quad A_2=0.2966\,. \tag{3.14}$$

For ψ_3 we put

$$\psi_3=\psi_1. \tag{3.15}$$

Minimizing the energy with respect to the parameters a_1-a_5 and an over-all scale factor k we obtain

$$E=-14.6118\text{ a.u.}\,,\quad (k=0.991)\,. \tag{3.16}$$

The Hartree-Fock energy is $E=-14.5730$ a.u. and the exact eigenvalue of the total Hamiltonian is estimated to be $E=-14.6674$ a.u.[12] The results are collected in Table I.

Next we tried H-F functions for ψ_1-ψ_3. We have used the analytic functions computed by Roothaan, Sachs, and Weiss.[15] These are of the form:

$$\begin{aligned}\psi_1=&[0.088737(6.5^3/\pi)^{1/2}+0.004895(6.5^5/3\pi)^{1/2}r]\exp(-6.5r)\\&+[0.935313(3.4^3/\pi)^{1/2}-0.022712(3.4^5/3\pi)^{1/2}r]\exp(-3.4r)\\&+[0.004590(0.9^3/\pi)^{1/2}-0.002201(0.9^5/3\pi)^{1/2}r]\exp(-0.9r)\,,\\\psi_2=&[0.075841(6.5^3/\pi)^{1/2}+0.028953(6.5^5/3\pi)^{1/2}r]\exp(-6.5r)\\&+[0.064546(3.4^3/\pi)^{1/2}+0.208057(3.4^5/3\pi)^{1/2}r]\exp(-3.4r)\\&-[0.386020(0.9^3/\pi)^{1/2}+0.740733(0.9^5/3\pi)^{1/2}r]\exp(-0.9r)\,.\end{aligned} \tag{3.17}$$

Minimizing again with respect to a_1-a_5 and k we get

$$E=-14.6140\text{ a.u.}\,,\quad (k=1.000)\,. \tag{3.18}$$

Next we have tried a combination of H-F and Slater orbitals. For ψ_1 and ψ_2 we put the H-F functions (3.17) and for ψ_3 we put the Slater-type functions

$$\psi_3=A_3e^{-Z_3r}, \tag{3.19}$$

where A_3 is again a normalization constant. This choice enables us to test whether the energy can be improved by varying Z_3. We have computed the energy for various values of Z_3, minimizing the parameters a_1-a_5 and k with each value of Z_3. We obtained the following results:

Z_3	E (a.u.)
4.33	-14.6133
4.00	-14.6142
3.85	-14.61445
3.70	-14.6145
3.60	-14.6143

(3.20)

It is clear that the minimum is at about $Z_3=3.7$. In the remaining part of the calculations we have used this value for Z_3. (For this Z_3 we get $k=1.000$.)

Comparing the first three entries of Table I, we see that the combination which gives the best results is H-F functions for ψ_1-ψ_2 and Slater type functions for ψ_3. We note that the value of $Z_3=3.7$ is very close to the original value of $Z_3=3.6847$ computed without correlation factors.

Our next goal was to compute the best wave functions for (1s-1s) correlation. It is clear that from the 6-term wave functions listed in Table I we have tried to improve that one which gave the best energy, i.e., the third combination. The procedure is as follows. We have added to the 6-term wave function those terms of the Hylleraas expansion which have the next higher powers of r_1, r_2, and r_{12}. First we have added one term at a time observing the improvement in energy. Then we selected those terms which gave the best improvement and extended the wave functions by adding them to the 6-term expression. In addition to the higher-order terms we have added also the term $\psi_3(1)\psi_3(2)$ without any correlation factor.

The best wave function for the (1s-1s) correlation

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[15] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

TABLE II. The correlation energy in the (2*s*) shell (all energies in a.u.).

Wave function	ψ_1 and ψ_2	ψ_4	Number of Hylleraas-type terms	Energy	Correlation energy	Percentage of total correlation
(3.23)	Slater orbitals	$\psi_4=\psi_2$	6	−14.58895	−0.0159	16.8
(3.23)	H-F functions	$\psi_4=\psi_2$	6	−14.60585	−0.03285	34.7
(3.23)	H-F functions	$\psi_4=$S.T.O $Z_4=0.9$	6	−14.61565	−0.04265	45.1
(3.28)	H-F functions	$\psi_4=$S.T.O $Z_4=0.9$	17	−14.61750	−0.0445	47.1

then becomes

$$\Psi=\frac{1}{\surd(4!)}\tilde{A}\{(\psi_1(1)\psi_1(2)+\psi_3(1)\psi_3(2)[a_1+a_2r_{12}+a_3(r_1+r_2)+a_4(r_1^2+r_2^2)+a_5r_{12}^2+a_6r_1r_2+a_7(r_1+r_2)r_{12}+a_8r_{12}^3+a_9(r_1+r_2)r_{12}^2+a_{10}(r_1+r_2)r_{12}^3])\times\psi_2(3)\psi_2(4)w\}. \qquad (3.21)$$

In this function ψ_1-ψ_2 are the H-F functions (3.18), ψ_3 is the Slater function (3.19) with $Z_3=3.7$, and the energy obtained is

$$E=-14.61535 \text{ a.u.}, \quad (k=0.999) \qquad (3.22)$$

(listed as No. 4 in Table I).

We have established that *with the given set of one-electron orbitals* ψ_1, ψ_2, ψ_3, the convergence limit for the (1*s*-1*s*) correlated wave function is reached with the value (3.22). This was established in such a way that we have tried to add additional terms to (3.21) and improve the energy (3.22); it became clear that the addition of further terms does not have any effect on the energy (3.22). Therefore the correlation energy of the 1*s* electrons is

$$E_{\text{corr}}(1s\text{-}1s)=-0.04235 \text{ a.u.}=-1.152 \text{ eV}.$$

D. The (2*s*−2*s*) Correlation

In the case of the (2*s*-2*s*) correlation we do not have the guideline of the He calculations. In the absence of such guidelines we have tried first the same 6-parameter wave functions as in the case of the 1*s* electrons. We have put

$$\Psi=\frac{1}{\surd(4!)}\tilde{A}\{(\psi_2(3)\psi_2(4)+\psi_4(3)\psi_4(4)\times[b_1r_{34}+b_2(r_3+r_4)+b_3(r_3^2+r_4^2)+b_4r_{34}^2+b_5r_3r_4])\psi_1(1)\psi_1(2)w\}. \qquad (3.23)$$

For the one-electron orbitals we have put first the Slater functions given by (3.13). For ψ_4 we put $\psi_4=\psi_2$ and obtained

$$E=-14.58895 \text{ a.u.}, \quad (k=1.004). \qquad (3.24)$$

Next we have put H-F functions for the one-electron orbitals, i.e., we put for ψ_1 and ψ_2 the functions given in (3.17) and for ψ_4 we again put $\psi_4=\psi_2$. The result is

$$E=-14.60585 \text{ a.u.}, \quad (k=1.000), \qquad (3.25)$$

which is a considerable improvement over (3.24).

Next we have tried a combination of H-F and Slater functions, similarly as we have done in the case of 1*s* electrons. For ψ_1 and ψ_2 we put the H-F functions (3.17). For ψ_4 we should put the 2*s* Slater function given by (3.13). This can be simplified, however, remembering that the 2-electron functions are orthogonalized to ψ_1 in Eq. (2.27). Therefore the second term in the Slater function (3.13) is not necessary. Also the 2*s* Slater function is of the form re^{-Z_4r}; in our case however, we can drop the r because we have the option of selecting any power of r in the correlation factor. Therefore we put for ψ_4,

$$\psi_4=A_4e^{-Z_4r}, \qquad (3.26)$$

where A_4 is a normalization constant. Then we calculated the energy with this combination and with the 6 terms given in (3.23). The calculations were done for different values of Z_4 to see which value gives the best energy. The results are

$$\begin{array}{cc} Z_4 & E \text{ (a.u.)} \\ 0.95 & -14.61525 \\ 0.90 & -14.61565 \\ 0.85 & -14.61555 \\ 0.80 & -14.61505 \end{array} \qquad (3.27)$$

from which it is clear that the best energy is at about $Z_4=0.9$. In the remaining part of the calculations we have used the value 0.9 for Z_4 ($k=1.001$). The results of the first three trials are given in Table II.

It is clear from Table II that the combination H-F/Slater orbitals gives the best results for this particular set of parameters. The next step was to take this combination which gave the best results and try to improve it by adding more terms. This was done in such a way that we took those terms of the Hylleraas expansion which have the next higher powers beyond the terms given in (3.23), and added these terms one by one to (3.23). Observing the improvement in the energy, we selected those terms which gave the best results separately and then added them simultaneously to the functions (3.23). Repeating this procedure several times, we arrived at the following function:

$$\Psi=\frac{1}{\surd(4!)}\tilde{A}\{(\psi_2(3)\psi_2(4)+\psi_4(3)\psi_4(4)[b_1+b_2r_{34}+b_3(r_3+r_4)+b_4(r_3^2+r_4^2)+b_5r_{34}^2$$
$$+b_6r_3r_4+b_7(r_3+r_4)r_{34}+b_8(r_3+r_4)r_{34}^2+b_9(r_3^2r_4+r_3r_4^2)+b_{10}r_3^2r_4^2+b_{11}r_{34}^3+b_{12}(r_3^4+r_4^4)$$
$$+b_{13}r_3^3r_4^3+b_{14}r_{34}^4+b_{15}(r_3+r_4)r_{34}^3+b_{16}(r_3^3r_4+r_3r_4^3)])\psi_1(1)\psi_1(2)w\}, \qquad (3.28)$$

which gives the energy

$$E=-14.61750\text{ a.u.};\quad (k=0.999). \qquad (3.29)$$

Here we have established similarly, as in the case of the ($1s$-$1s$) correlation, that (3.29) is the convergence limit for the energy with the given set of one-electron orbitals. In other words we have established that the addition of further terms to (3.28) does not have any effect on the energy (3.29). Therefore for the given set of one-electron orbitals the best value of energy for the $2s$-$2s$ correlation which can be computed with a simple Hylleraas type power series is given by (3.29). The correlation energy for the $2s$ electron is therefore

$$E_{\text{corr}}(2s\text{-}2s)=-0.04450\text{ a.u.}=-1.210\text{ eV}.$$

E. Total Correlation

Our next task is to compute the total correlation energy. This is done in such a way that we include correlation in the wave functions simultaneously in the ($1s$) and in the ($2s$) subshell. Naturally we expect to obtain the best value by combining those wave functions which gave the best value for the $1s$-$1s$ and $2s$-$2s$ correlations separately. Besides this, we have tried also other combinations.

Let us consider Tables I and II. In each of the tables the first entry is the correlated function with Slater-type orbitals. Since this combination does not give a good result in the $2s$-$2s$ case we started with the second entry which is the correlated orbital with the H-F functions. We set up the wave functions as a combination of the functions (3.11) and (3.23), i.e., we put

$$\Psi=\frac{1}{\surd(4!)}\tilde{A}\{(\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)$$
$$+\psi_3(1)\psi_3(2)[a_1r_{12}+a_2(r_1+r_2)+a_3(r_1^2+r_2^2)+a_4r_{12}^2+a_5r_1r_2]\psi_2(3)\psi_2(4)$$
$$+\psi_4(3)\psi_4(4)[b_1r_{34}+b_2(r_3+r_4)+b_3(r_3^2+r_4^2)+b_4r_{34}^2+b_5r_3r_4]\psi_1(1)\psi_1(2))w\}. \qquad (3.30)$$

In this function ψ_1 and ψ_2 are the H-F functions given by (3.17) and $\psi_3=\psi_1$, $\psi_4=\psi_2$. We obtained the energy

$$E=-14.6455\text{ a.u.},\quad (k=1.02). \qquad (3.31)$$

At this point we checked whether the energy value (3.31) gives a correlation energy which is approximately the sum of the ($1s$-$1s$) and ($2s$-$2s$) correlation energies computed separately with the corresponding wave functions. In Tables I and II the corresponding entries (the second line) give the following correlation energies:

$$E_c(1s\text{-}1s)=-0.0410\text{ a.u.},$$
$$E_c(2s\text{-}2s)=-0.03285\text{ a.u.},$$
$$E_c(1s\text{-}1s)+E_c(2s\text{-}2s)=-0.07385\text{ a.u.}$$

The total correlation energy, denoted by E_{Tc}, as given by (3.31), is

$$E_{Tc}=-0.0725\text{ a.u.}$$

Therefore we see that $E_c(1s\text{-}1s)+E_c(2s\text{-}2s)\neq E_{Tc}$ and the difference is

$$E_\Delta=E_{Tc}-[E_c(1s\text{-}1s)+E_c(2s\text{-}2s)]=+0.00135\text{ a.u.}$$

If the correlation energy would be additive in electron pairs, E_Δ would be zero. The size of E_Δ shows to what extent the correlation energy is *not* additive.

Next we have combined the functions given in the third row of the Tables I and II. We considered again the functions (3.30) but now ψ_1 and ψ_2 are the HF functions and ψ_3 and ψ_4 are Slater functions given by (3.19) and (3.26) with $Z_3=3.7$ and $Z_4=0.9$. We have the energy

$$E=-14.6542\text{ a.u.},\quad (k=1.012) \qquad (3.32)$$

considerably better than (3.31). Again we calculated E_Δ and we got $E_\Delta=+0.0034$ a.u.

At this point we wanted to check how good the results would be if we replaced the H-F orbitals in this ansatz by Slater functions. Therefore we considered again (3.30), but now ψ_1 and ψ_2 are the Slater functions (3.13) whereas ψ_3 and ψ_4 are again given by (3.19) and (3.26). We obtained

$$E=-14.6525 \text{ a.u.}, \quad (k=1.012), \tag{3.33}$$

and for E_Δ we get $E_\Delta=-0.0115$ a.u. It is interesting to note that E_Δ is negative with this combination.

Finally we combined the functions in the fourth rows of Tables I and II. We considered the function

$$\begin{aligned}\Psi=\frac{1}{\sqrt{(4!)}}\tilde{A}\{(\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)+\psi_3(1)\psi_3(2)[a_1+a_2r_{12}+a_3(r_1+r_2)+a_4(r_1^2+r_2^2)+a_5r_{12}^2+a_6r_1r_2\\ +a_7(r_1+r_2)r_{12}+a_8r_{12}^3+a_9(r_1+r_2)r_{12}^2+a_{10}(r_1+r_2)r_{12}^3]\psi_2(3)\psi_2(4)+\psi_4(3)\psi_4(4)[b_1+b_2r_{34}+b_3(r_3+r_4)\\ +b_4(r_3^2+r_4^2)+b_5r_{34}^2+b_6r_3r_4+b_7(r_3+r_4)r_{34}+b_8(r_3+r_4)r_{34}^2+b_9(r_4^2r_3+r_4r_3^2)+b_{10}r_3^2r_4^2+b_{11}r_{34}^3\\ +b_{12}(r_3^4+r_4^4)+b_{13}r_3^3r_4^3+b_{14}r_{34}^4+b_{15}(r_3+r_4)r_{34}^3+b_{16}(r_3^3r_4+r_3r_4^3)]\psi_1(1)\psi_1(2))w\},\end{aligned} \tag{3.34}$$

and we obtained

$$E=-14.6565 \text{ a.u.}, \quad (k=1.015) \tag{3.35}$$

and

$$E_\Delta=+0.0033 \text{ a.u.}$$

The best result for the correlation energy is therefore obtained with (3.34) and we have

$$E_{Tc}=-0.0835 \text{ a.u.}=-2.2719 \text{ eV}. \tag{3.36}$$

The results of the calculation of the total correlation are given in Table III.

F. Simplified Wave Functions

We wanted to see how good the results could be when obtained by using just one r_{12} term in both shells. First we considered the two shells separately. We put for the 1s shell

$$\Psi=\frac{1}{\sqrt{(4!)}}\tilde{A}\{\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)[1+a_1r_{12}]w\}, \tag{3.37}$$

and for the (2s) shell

$$\Psi=\frac{1}{\sqrt{(4!)}}\tilde{A}\{\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)[1+b_1r_{34}]w\}; \tag{3.38}$$

and finally we combined the two functions above and put

$$\Psi=\frac{1}{\sqrt{(4!)}}\tilde{A}\{\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\times[1+a_1r_{12}+b_1r_{34}]w\}. \tag{3.39}$$

In these functions ψ_1 and ψ_2 are the H-F orbitals. The results are as follows[16]:

Function	Energy	Corr. energy	E_Δ	k
(3.37)	−14.60465	−0.03165	···	1.034
(3.38)	−14.59355	−0.02055	···	1.009
(3.39)	−14.6316	−0.05859	−0.0064	1.045

It is interesting to note that in this case the combined result computed with (3.39) is much better than the sum of the separate results calculated with (3.37) and (3.38) and therefore E_Δ is negative and fairly large. This can be easily explained by looking at the scale factors. The scale factor in the combined function (3.39) is larger than in the separate cases (3.37) and (3.38). Now a larger k means deeper energy, since the center of the charge distribution is shifted toward the nucleus with increasing k. In the wave function (3.37) and (3.38) one of the shells is uncorrelated. On the other hand, since the scale factor is common to both shells, if one of the shells is uncorrelated the scale factor tends to be closer to 1 since if both shells are uncorrelated its value is exactly 1. If both shells are correlated as in (3.39), the scale factor can be (and is) larger, resulting in the negative E_Δ and in the good energy obtained with the function (3.39).

4. EVALUATION OF RESULTS

The correct value of the total correlation energy is estimated to be[12] $E_c=-0.0944$ a.u. We obtained $E_{Tc}=-0.0835$ a.u. which gives 88.4% of the correlation energy. This can be considered a very good result since now the accuracy of the calculation is improved from 0.64% in the H-F calculation to 0.074% in the present calculation. The rest of the correlation energy is probably due to the (1s-2s) correlation which we have not considered and to the 3- and 4-electron correlations which are also neglected. The size of the (1s-2s) correlation is about −0.0050 a.u. (see next section). The size of the many-electron effects is not known; the calculations of Watson[17] indicate that the 3-electron correlations are negligible, but the 4-electron correlations are not. If the estimate −0.0050 a.u. is correct for the (1s-2s) correlation, then the size of the 4-electron effects is about −0.0060 a.u.

The main result of the calculations is that the Hylleraas-type expansion gives good results for the Be

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[16] All energies are in atomic units.

[17] R. E. Watson, Phys. Rev. **119**, 170 (1960).

TABLE III. The total correlation energy (all energies in a.u.).

Wave function	ψ_1 and ψ_2	ψ_3 and ψ_4	Number of terms $1s$	$2s$	Energy	E_c	E_Δ	% of total corr.
(3.30)	H-F functions	$\psi_3=\psi_1$, $\psi_4=\psi_2$	5	5	-14.6455	-0.0725	$+0.00135$	76.8
(3.30)	H-F functions	ψ_3 by (3.19); ψ_4 by (3.26)	5	5	-14.6542	-0.0812	$+0.0034$	86.0
(3.30)	ψ_1 and ψ_2 by (3.13)	ψ_3 by (3.19); ψ_4 by (3.26)	5	5	-14.6525	-0.0795	-0.0115	84.2
(3.34)	H-F functions	ψ_3 by (3.19); ψ_4 by (3.26)	10	16	-14.6565	-0.0835	$+0.0033$	88.4

atom. As we will show in the next section, the results are better than the results of the calculations with superposition of configurations, and this is true in the ($1s$) shell as well as in the ($2s$) shell. It is interesting that the correlation energy is *not additive* in pairs. The validity of this statement depends of course on the degree of accuracy we require. Example: The best results (indeed the convergence limits) for the ($1s$-$1s$) and ($2s$-$2s$) correlations are

$$E_c(1s\text{-}1s)=-0.04235 \text{ a.u.},$$
$$E_c(2s\text{-}2s)=-0.04450 \text{ a.u.},$$
$$E_c(1s\text{-}1s)+E_c(2s\text{-}2s)=-0.08685 \text{ a.u.}$$

On the other hand, the total correlation obtained with the function (3.34) gives $E_{Tc}=-0.08350$ a.u. The difference E_Δ is only -0.0033 a.u., which is about 4% of the total; therefore one could say that correlation energy is additive in a very good approximation. On the other hand, if E_Δ would indeed be zero, then the correlation energy obtained with (3.34) would be $E_c(1s\text{-}1s)+E_c(2s\text{-}2s)=-0.08685$ a.u., which would be a considerably better result than the result actually obtained. A byproduct of this consideration is the observation that the whole concept of "($1s$-$1s$) correlation" or "($2s$-$2s$) correlation" has limited validity only. It is not exactly clear what is meant by these concepts, since we get different results for these quantities if we compute them separately or if we compute them simultaneously.

5. COMPARISON WITH OTHER CALCULATIONS

For the Be atom there are two large-scale calculations with the superposition of configurations and one calculation with the perturbation method. (These are the only large scale *ab initio* calculations, i.e., calculations in which the exact Hamiltonian is used.) In the calculation of Watson[17] 37 configurations gave $E=-14.6574$ a.u. The breakdown according to contributions in the various shells is as follows[18]:

E_c ($1s$-$1s$) $=-0.0376$ a.u. (22 configurations)
E_c ($2s$-$2s$) $=-0.0417$ a.u. (5 configurations)
E_c ($1s$-$2s$) $=-0.0022$ a.u. (4 configurations)
E_c (4-electron effects) $=-0.0028$ a.u. (3 configurations).
E_{Tc} $=-0.0843$ a.u.

For comparison our results are

$$E_c(1s\text{-}1s)=-0.0423 \text{ a.u.} \quad \text{(10 parameters)},$$
$$E_c(2s\text{-}2s)=-0.0412 \text{ a.u.} \quad \text{(16 parameters)}.$$

There is an ambiguity in this presentation, since we cannot write here the *best* value for the $1s$-$1s$ and for the $2s$-$2s$ correlation but only their contributions to the final energy (3.35), and we get different values for $E_c(1s\text{-}1s)$ and $E_c(2s\text{-}2s)$ depending on which one is computed first (this is the result of $E_\Delta\neq 0$). There is no ambiguity, however, if we compare the sum $E_c(1s\text{-}1s)+E_c(2s\text{-}2s)$. Then we get

Watson:

$$E_c(1s\text{-}1s)+E_c(2s\text{-}2s)=-0.0793 \text{ a.u.} \quad \text{(27 configurations)};$$

Present calculation:

$$E_c(1s\text{-}1s)+E_c(2s\text{-}2s)=-0.0835 \text{ a.u.} \quad \text{(26 parameters)}.$$

The comparison is very favorable for the Hylleraas expansion since we have a better energy with the same size expansion. It is demonstrated clearly that in this case the Hylleraas method gives better results than the superposition of configurations. There is one feature of the calculations with superposition of configurations which we want to discuss here. It was pointed out by Watson[17] that in the ($2s$) shell the superposition of just 2 configurations, the $(2s)^2+(2p)^2$ gave an improvement in the energy $E_c=-0.04116$ a.u. The addition of the configuration d^2 to the above two configurations improved the energy only by -0.0004 a.u. From the total correlation energy in the ($2s$) shell, for which Watson obtained $E_c(2s\text{-}2s)=-0.0417$ a.u., 98.7% is supplied by the configuration p^2. The effectiveness of the p^2 configuration was also shown by Linderberg and Shull.[19] This fact had been interpreted in such a way that it was assumed that in the ($2s$) shell the electron correlation is entirely different from the electron correlation in the ($1s$) shell; it was assumed that whereas in the ($1s$) shell one r_{12} term gives the larger part of the correlation, in the ($2s$) shell the r_{12} term is not effective.

Our calculations show that although the single r_{12} term is indeed not as effective as the p^2 configuration, the Hylleraas expansion if carried far enough, gives better results. Let us consider again the function (3.28).

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[18] Two configurations listed by Watson do not improve the energy given to six figures.

[19] J. Linderberg and H. Shull, J. Mol. Spectr. 5, 1 (1960).

TABLE IV. Improvement in the energy term by term. All energies are in atomic units.

Function	Energy	Corr. energy	Improv. in energy
H-F	-14.5730	...	...
$\psi_4(3)\psi_4(4)[b_1+b_2r_{34}]$	-14.5991	-0.0261	-0.0261
(r_3+r_4)	-14.6078	-0.0348	-0.0087
$(r_3^2+r_4^2)$	-14.6085	-0.0355	-0.0007
r_{34}^2	-14.6152	-0.0422	-0.0067
r_3r_4	-14.6157	-0.0427	-0.0005
(The remaining 10 terms)	-14.6175	-0.0445	-0.0018

We give in Table IV the improvement in the energy term-by-term.

As we see the r_{12} terms gives a large improvement in the energy; but also the contribution from some of the further terms is fairly large, and eventually the series gives a better result than the superposition of configurations.

In our opinion this result shows that one has to be very careful when attaching particular physical meaning to terms in a variational wave function. It is true that the p^2 configuration gives a very large part of the correlation energy; but an even better result can be obtained with a Hylleraas series, in which the dominant terms are r_{12}, (r_1+r_2), and r_{12}^2. Contrary to the expectations, the Hylleraas series is capable to describe the electron correlation not only in the $(1s)$ shell but in the $(2s)$ shell as well.

The other large-scale calculation with superposition of configurations was done by Weiss.[20] In that calculation the individual contributions from the various subshells are not given. Comparison with the present calculations is difficult since in our calculations the $1s$-$2s$ correlation is not considered while in Weiss's calculation it is included. If we accept for the $1s$-$2s$ correlation the value computed by Kelly[21] (see below) $E_c(1s\text{-}2s) = -0.0050$ a.u. then by adding this to our result we would get $E_{Tc}+E_c(1s\text{-}2s) = -0.0885$ a.u. The correlation energy computed by Weiss with 55 configurations is $E_c = -0.0879$ a.u. The comparison is again favorable for the Hylleraas-type expansion.

The correlation energy in the Be atom was computed with perturbation theory by Kelly.[21] In that calculation the correlation energies of the various subshells are computed separately. We can compare these results with the best results we have obtained, for each subshell, computing the correlation energies separately. The comparison gives

	Kelly	Present calculations
$E_c(1s\text{-}1s)$	$=-0.04212$ a.u.	-0.0423 a.u.
$E_c(2s\text{-}2s)$	$=-0.04387$ a.u.	-0.0445 a.u.
$E_c(1s\text{-}2s)$	$=-0.0050$ a.u.	Not computed

When we compare these two sets of data, we must be careful to remember the difference between the perturbation theory and the variation method. In the variation method the computed energy is always an upper limit to the energy; it is not clear whether this is the case in the perturbation theory used by Kelly. The agreement between the two sets of numbers is good.

Calculations for the Be atom were also done with the method of Sinanoğlu.[22] In this method the starting point is the function (2.5). After several simplifications in the energy expressions differential equations are derived for the two electron functions. The correlation energy of each electron pair is computed separately; the total correlation is assumed to be the sum of pair energies.

Calculations for the Be atom were carried out with this method by Sinanoğlu and Tuan (ST)[23] and by Geller, Taylor, and Levine (GTL).[24] We compare here the best results obtained by us for each pair with their results (all energies in atomic units):

	ST	GTL	Present paper
$E_c(1s\text{-}1s)$	-0.04395	-0.04208	-0.0423
$E_c(2s\text{-}2s)$	-0.04392	-0.04438	-0.0445

The comparison between our results and the other results is difficult because it is not clear what effects the approximations carried out in the energy expression in the Sinanoğlu theory have on the computed energy. The agreement between the results obtained by us and those obtained by ST and GTL is good.

There is one point in the calculations of Sinanoğlu which we want to discuss here. In the theory of correlated wave functions we have introduced the following orthogonality condition between the two-electron functions and the one-electron orbitals [Eq. (2.26)]:

$$\int \phi_A(ik|12)\varphi_s^*(1)dq_1 \equiv 0, \quad (s=1,2,\cdots,N;\ s\neq i,k). \tag{5.1}$$

In the calculations mentioned above the stronger condition is introduced[22]:

$$\int \phi_A(ik|12)\varphi_s^*(1)dq_1 \equiv 0, \quad (s=1,2,\cdots,N;\ i \text{ and } k \text{ included}). \tag{5.2}$$

It is worthwhile to analyze which of the above two conditions gives better results in the calculations. First let us investigate which of the two conditions involves more numerical work.

In order to see that let us denote the nonorthogonal two-electron function by $\phi_A{}^0(ik|12)$. Then the or-

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[20] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[21] H. P. Kelly, Phys. Rev. **131**, 684 (1963).

[22] O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962); **36**, 3198 (1962).

[23] D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. **41**, 2677 (1964).

[24] M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. **43**, 1727 (1965).

thogonalized function satisfying (5.1) is given by (2.27).

$$\phi_A(ik|12) = (1-\Omega(1)-\Omega(2)+\Omega(1)\Omega(2))\phi_A{}^0(ik|12), \quad (5.3)$$

where $\Omega(1)$ is given by (2.28). Let us consider the special case of the beryllium atom and let $i=2s\alpha$, $k=2s\beta$, where α and β indicate the spin directions. Straightforward calculations give the formula for $\phi_A(2s,2s|1,2)$:

$$\phi_A(2s,2s|1,2)=\psi_A(2s,2s|1,2)\eta(1,2), \quad (5.4)$$

where $\eta(1,2)=\alpha(1)\beta(2)-\alpha(2)\beta(1)$ is the spin function and ψ_A is given by

$$\psi_A(2s,2s|1,2)=\psi_A{}^0(2s,2s|1,2)-\psi_{1s}(1)\int\psi_{1s}(3)\psi_A{}^0(2s,2s|3,2)dv_3$$
$$-\psi_{1s}(2)\int\psi_{1s}(3)\psi_A{}^0(2s,2s|1,3)dv_3+\psi_{1s}(1)\psi_{1s}(2)\int\psi_{1s}(3)\psi_{1s}(4)\psi_A{}^0(2s2s|3,4)dv_3dv_4, \quad (5.5)$$

where $\psi_A{}^0$ is the spatial part of the nonorthogonal $\phi_A{}^0$. On the other hand the spatial part of the function satisfying (5.2) has the following form:

$$\psi_A(2s,2s|1,2)=\psi_A{}^0(2s,2s|12)-\psi_{1s}(1)\int\psi_{1s}(3)\psi_A{}^0(2s,2s|32)dv_3-\psi_{1s}(2)\int\psi_{1s}(3)\psi_A{}^0(2s,2s|13)dv_3$$
$$+\psi_{1s}(1)\psi_{1s}(2)\int\psi_{1s}(3)\psi_{1s}(4)\psi_A{}^0(2s,2s|3,4)dv_3dv_4-\psi_{2s}(1)\int\psi_{2s}(3)\psi_A{}^0(2s,2s|3,2)dv_3$$
$$-\psi_{2s}(2)\int\psi_{2s}(3)\psi_A{}^0(2s2s|13)dv_3+\psi_{2s}(1)\psi_{2s}(2)\int\psi_{2s}(3)\psi_{2s}(4)\psi_A{}^0(2s,2s|3,4)dv_3dv_4$$
$$+\psi_{1s}(1)\psi_{2s}(2)\int\psi_{1s}(3)\psi_{2s}(4)\psi_A{}^0(2s,2s|3,4)dv_3dv_4+\psi_{2s}(1)\psi_{1s}(2)\int\psi_{2s}(3)\psi_{1s}(4)\psi_A{}^0(2s,2s|3,4)dv_3dv_4. \quad (5.6)$$

In order to get the matrix components in the secular equation we have to form the expectation value of the Hamiltonian with respect to the functions (5.5) and (5.6), respectively. A typical integral occurring in the matrix components is of the form:

$$I=\int\psi_A{}^*(2s,2s|12)r_{12}{}^{-1}\psi_A(2s,2s|12)dv_1dv_2. \quad (5.7)$$

Now if we form this integral with (5.5) we get an expression containing 16 integrals; if we form it with (5.6) we get an expression containing 81 integrals. It is clear that the function (5.5) which is the result of the orthogonality condition (5.1) involves much less numerical work than the function (5.6) which is the result of the orthogonality condition (5.2).

Now let us compare the results obtained with the two different sets of orthogonality conditions. We consider here the functions used by Geller, Taylor, and Levine:[24]

$$\Psi=\mathcal{A}\{(\psi_1(1)\psi_1(2) + \langle\psi_3(1)\psi_3(2)\rangle[1+\langle a_1r_{12}\rangle+\langle a_2(r_1+r_2)\rangle + \langle a_3r_{12}{}^2\rangle+\langle a_4(r_1-r_2)^2\rangle])\psi_2(3)\psi_2(4)w\}, \quad (5.8)$$

where the angular brackets around the function symbols mean that these terms are orthogonalized to the 1*s* orbitals as well as to the 2*s* orbitals, i.e., they are put in the form satisfying the conditions (5.2). For comparison let us consider one of our functions used above:

$$\Psi=\mathcal{A}\{(\psi_1(1)\psi_1(2) +\psi_3(1)\psi_3(2)[1+a_1r_{12}+a_2(r_1+r_2)+a_3r_{12}{}^2 +a_4(r_1{}^2+r_2{}^2)+a_5r_1r_2])\psi_2(3)\psi_2(4)w\}, \quad (5.9)$$

in which we have no restrictive orthogonality conditions, i.e. the two-electron functions satisfy only (5.1). In both wave functions ψ_1 and ψ_2 are the H-F orbitals and ψ_3 is the Slater function (3.19); in (5.8) $Z_3=3.6$ and in (5.9) $Z_3=3.7$. It is clear that the nonorthogonalized two-electron functions are almost identical in both functions. The essential difference is that by using (5.8), Geller, Taylor, and Levine used the orthogonality condition (5.2); by using (5.9) we used the simpler condition (5.1).

The results are as follows: (5.8) yielded the correlation energy $E_c=-0.0421$ a.u. and (5.9) gave $E_c=-0.0415$ a.u. The difference is very small (1.4%). Therefore the two functions gave essentially the same results.

Summarizing the comparison between the two orthogonality conditions (5.1) and (5.2) we conclude that the condition (5.2) involves much more numerical work; on the other hand the results are essentially the same with both conditions.

6. DISCUSSION

A. The Main Result of the Calculations

The main result is that in the case of the beryllium atom, the Hylleraas-type expansion gives better results than the superposition of configurations. This is true not only in the (1*s*) shell, for which this fact was evident before the present calculation, but it is also true in the (2*s*) shell. As we have discussed above previously it was believed by several workers that the correlation between the two (2*s*) electrons is such that the best way of describing it is to write the wave function in the form of the superposition of the two configurations $(2s)^2+(2p)^2$. It was generally believed that this wave function gives better results than the Hylleraas expansion. The present calculations show, however, that a Hylleraas-type expansion if carried far enough gives better results than the superposition of configurations.

It is evident now that in the case of the atoms, He,[2] Li,[13,25] and Be the Hylleraas method proved to be effective. There is a fair probability that it will be effective also in the case of more complex atoms.

B. The Mathematical Difficulties

In the earlier literature of the many-body problem it was generally stated that the Hylleraas method is too complicated to be applied to more complex atoms. In the set of previous publications[1] we have shown that this is not the case. We emphasize here that the method of correlated wave functions[1] is formulated in such a way that it can be applied to atoms with any number of electrons. The calculations for the beryllium atom presented in this paper are special cases of a general formalism which can be applied to atoms with any number of electrons.

The mathematical difficulties may be characterized as follows: In the variation method the solution of the problem boils down to the calculation of the energy from the secular equation. The only problem is therefore essentially the calculation of the matrix components occurring in the secular equation.

In a previous paper[11] we have shown that the complexity of the integrals occurring in the secular equation does not increase with the increase of the number of electrons. We have shown that if the calculations are restricted to two-electron correlations, i.e., if the wave functions (2.5) is used, and the two-electron functions $\Phi(i,k)$ are written in the form of Hylleraas series, then the matrix components can be reduced to six types of relatively simple basic integrals. (See the Appendix where the technique of computing these integrals is described.) From these six integrals five can be computed easily in closed form. The only difficulty arises from the sixth type [Eq. (A5)] which, like some of the many-center integrals of the molecular physics, can be computed only in the form of a series. If there are many such integrals to compute for a particular atom, the calculations become very time consuming, since the convergence of the series may not be very fast for some cases. In the present calculation for the beryllium, we had only *one* such integral in each diagonal matrix component which was always very small compared to the other integrals; therefore in this particular case this was a minor problem. For larger atoms, however, the formalism would require the computation of a much larger number of such integrals which may not be small compared to others, therefore it will require a careful treatment. The recent paper by Roberts[26] is a significant development toward the solution of this problem. Roberts suggested a method by which even these integrals could be computed in closed form.

If the method of Roberts can be effectively applied to machine calculations, then one of the major difficulties is removed from the application of the theory of correlated wave functions to larger atoms.

We may summarize the mathematical side of the problem as follows. The calculation of a Hylleraas-type function for an atom with small number of electrons $(2\leqq N\leqq 30)$ is much more complicated than an atomic H-F calculation but much less complicated than a calculation using a linear combination of atomic orbitals for a diatomic molecule of the size of, say Na_2. In our opinion no serious difficulty stands in the way of applying the method to larger atoms.

C. The Additivity of Correlated Energy

If we are making a calculation in which only two-electron correlations are considered, we have to use the function (2.5) in which all two-electron correlations are included but the higher-order correlation effects are neglected. However, it is clear from the presentation in Sec. III that from the function (2.5) it does not follow that the correlation energy is additive in pairs. As we have seen, we can compute the correlation energy for each electron pair separately or we can compute the total two-electron correlation by taking into account all pairs simultaneously. We have seen above that the correlation energies computed in the two different ways are different; the difference which we have denoted by E_Δ may be positive or negative, depending on the wave functions used. This result is somewhat unexpected since in the beryllium atom the overlap between the (1*s*) and (2*s*) shells is very small, and therefore one would expect that the correlation effects in the two shells are independent; however, the calculations show that this is not the case.

D. The Higher-Order Correlation Effects

We have pointed out in Sec. IV that the size of the higher-order (more than two-electron) correlation effects in the Be atom is about -0.0060 a.u., which is con-

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[25] E. Burke, Phys. Rev. **130**, 1871 (1963).

[26] P. J. Roberts, Proc. Phys. Soc. (London) **88**, 53 (1966).

siderable compared to the total correlation $E=-0.0944$ a.u. (6.3%). According to Watson[17] the higher-order effects are coming mostly from simultaneous excitations in the $(1s)$ and $(2s)$ shells which could be taken into account by using quadruple substitution configurations. The fact that the many-electron effects are fairly large even for the Be atom which has only four electrons emphasizes that the function (2.5) is only an approximation, although it is a much better approximation than the H-F method. It is clear, however, that results which are as accurate as the results of Hylleraas for the He atom can be obtained for more complex atoms only if the higher-order effects are included in the wave functions, i.e., if the complete function (2.8) is used.

E. The Choice of Orbitals in the Correlated Wave Functions

Our results presented in Sec. III show that using the same correlation factor g_i we get very different results depending on the choice of the one-electron orbitals in the wave functions. This means that the rate of convergence depends on the choice of the one-electron orbitals used in the wave function. From the combinations tested we have found that the combination H-F orbitals for the determinantal part-Slater functions for the correlated part, gives the best results.

As was mentioned in Sec. 3A we have investigated in a previous publication[13] what kind of one- and two-electron functions give the absolute minimum for the energy with an ansatz of the type (2.5). It was pointed out that the equations found for the one-electron orbitals[27] are quite different from the H-F equations. In the light of our present results we conclude that the H-F orbitals are probably good approximations to the solutions of the equations, defining the best orbitals in an ansatz of type (2.5).[28] It must be emphasized, however, that the results of our calculations for *one* atom does not allow us to draw general conclusions regarding the nature of the best orbital combinations in an ansatz of the type (2.5). In the present calculations the combination H-F/Slater orbitals gave a good result, but we have tested only a very limited number of other combinations, and we do not know whether the convergence would be faster with an entirely different combination.

In our opinion the central difficulty with calculations of this type is, and is going to be, that we have to search for the best orbitals by doing the calculations on a trial and error basis, which means that in future calculations we shall have to test again different orbital combinations and check which gives the best results. Fortunately, the mathematical technique is developed in such a way that one electron orbitals of any form can be used.

APPENDIX: THE CALCULATION OF THE MATRIX COMPONENTS OF THE SECULAR EQUATION

As stated in Sec. 3, and shown first in Ref. 10, all matrix components occurring in the secular Eq. (2.22) can be reduced to the following six basic integrals (the notation is from Ref. 10):

$$I_1=\int \rho_{AB}(1)\rho_{CD}(2)r_1^{\kappa}r_2^{\lambda}r_{12}^{\delta}dv_1dv_2\,, \tag{A1}$$

$$I_2=\int \rho_{AB}(1)\rho_{CD}(2)\rho_{EF}(3)r_i^{\kappa}r_2^{\lambda}r_3^{\mu}r_{12}^{\delta}r_{32}^{\epsilon}dv_1dv_2dv_3\,, \tag{A2}$$

$$I_3=\int \rho_{AB}(1)\rho_{CD}(2)\rho_{EF}(3)\rho_{GH}(4)r_1^{\kappa}r_2^{\lambda}r_3^{\mu}r_4^{\nu}r_{12}^{\delta}r_{32}^{\epsilon}r_{42}^{\rho}dv_1dv_2dv_3dv_4\,, \tag{A3}$$

$$I_4=\int \rho_{AB}(1)\rho_{CD}(2)\rho_{EF}(3)\rho_{GH}(4)r_1^{\kappa}r_2^{\lambda}r_3^{\mu}r_4^{\nu}r_{12}^{\delta}r_{32}^{\epsilon}r_{41}^{\rho}dv_1dv_2dv_3dv_4\,, \tag{A4}$$

$$I_5=\int \rho_{AB}(1)\rho_{CD}(2)\rho_{EF}(3)r_1^{\kappa}r_2^{\lambda}r_3^{\mu}r_{13}^{\delta}r_{23}^{\epsilon}r_{12}^{-1}dv_1dv_2dv_3\,, \tag{A5}$$

$$I_6=\int \psi_A^*(1)\rho_{BC}(2)r_1^{\delta}r_2^{\omega}r_{12}^{\gamma}[-\tfrac{1}{2}\Delta_1](\psi_D(1)\rho_{EF}(3)r_1^{\tau}r_3^{\delta}r_{13}^{\epsilon})dv_1dv_2dv_3\,. \tag{A6}$$

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[27] See Eqs. (4.12), (6.6), and (7.2) of Ref. 13.

[28] At least for the Be atom.

Let us consider (A1). Let us assume that $\rho_{AB}=\psi_A\psi_B$ and $\rho_{CD}=\psi_C\psi_D$ depend on r_1 and r_2 only. Then putting the z axis of the coordinate system into $\mathbf{r}_1$ and introducing r_2 and r_{12} as integration variables we get

$$g_{CD}{}^{\lambda\mu}(r_1)\equiv\int\rho_{CD}(r_2)r_2{}^{\lambda}r_{12}{}^{\mu}dv_2=\frac{1}{2(\mu+2)}\sum_{k=0}^{\mu+2}\binom{\mu+2}{k}\Gamma(k)$$

$$\times\left\{r_1{}^{\mu+1-k}\int_0^{r_1}P_{CD}(r_2)r_2{}^{\lambda+k-1}dr_2+r_1{}^{k-1}\int_{r_1}^{\infty}P_{CD}(r_2)r_2{}^{\lambda+\mu+k-1}dr_2\right\},\quad\text{(A7)}$$

where $P_{CD}(r_2)=4\pi r^2\rho_{CD}(r_2)$ and $\Gamma(k)=1-(-1)^k$. With (A7) we get

$$I_1=\int\rho_{AB}(r_1)r_1{}^{\kappa}g_{CD}{}^{\lambda\mu}(r_1)dv_1.\quad\text{(A8)}$$

The calculation of I_1 is carried out in such a way that first (A7) is computed by numerical integration which can be done easily for any $\rho_{CD}(r_1)$ and for any combination of λ, μ. After (A7) is tabulated, I_1 is computed by numerical integration from (A8). The integrations can be carried out without changing the interval length by introducing[29] the new independent variable $\sigma=r^{1/4}$. Since the Slater functions, as well as the Roothaan-type H-F orbitals are given in analytic form, there is no difficulty in tabulating them in σ scale.

The integrals I_2, I_3, I_4 can be obtained similarly as I_1. We get, for instance,

$$I_2=\int g_{AB}{}^{\kappa\delta}(r_2)g_{EF}{}^{\mu\epsilon}(r_2)\rho_{CD}(r_2)r_2{}^{\lambda}dv_2,\quad\text{(A9)}$$

which again can be computed by 3 successive numerical integrations. Similar procedures can be applied to I_3 and I_4.

The calculation of I_5 was described elsewhere before.[30] The calculation of I_6 is also straightforward since we can integrate first with respect to dv_3:

$$g_{EF}{}^{\delta\epsilon}(r_1)=\int\psi_E(r_3)\psi_F(r_3)r_3{}^{\delta}r_{13}{}^{\epsilon}dv_3.\quad\text{(A10)}$$

The Laplacian Δ_1 operates on this function, which does not lead to any difficulties since g depends only on r_1. The necessary formulas are

$$\frac{dg_{EF}{}^{\delta\epsilon}}{dr_1}=\frac{1}{2(\epsilon+2)}\sum_{k=0}^{\epsilon+2}\binom{\epsilon+2}{k}\Gamma(k)\left\{(\epsilon+1-k)r_1{}^{\epsilon-k}\int_0^{r_1}P_{EF}(r_2)r_2{}^{\delta+k-1}dr_2+(k-1)r_1{}^{k-2}\int_{r_1}^{\infty}P_{EF}(r_2)r_2{}^{\delta+\epsilon+1-k}dr_2\right\}\quad\text{(A11)}$$

and

$$\frac{d^2g_{EF}{}^{\delta\epsilon}}{dr^2}=\frac{1}{2(\epsilon+2)}\sum_{k=0}^{\epsilon+2}\binom{\epsilon+2}{k}\Gamma(k)\left\{(\epsilon+1-k)(\epsilon-k)\right.$$

$$\left.\times r_1{}^{\epsilon-k-1}\int_0^{r_1}P_{EF}(r_2)r_2{}^{\delta+k-1}dr_2+(k-1)(k-2)r_1{}^{k-3}\int_{r_1}^{\infty}P_{EF}(r_2)r_2{}^{\delta+\epsilon+1-k}dr_2\right\},\quad\text{(A12)}$$

where $P_{EF}=4\pi r^2\psi_E\psi_F$. Again (A11) and (A12) can be computed easily by numerical integrations. Following the above procedures all six integrals are computed numerically; the procedure is the same regardless of the special form of the one-electron wave functions.

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[29] E. Trefftz, A. Schluter, K. Deitman, and J. Jorgens, Z. Astrophys. 44, 1 (1957).
[30] L. Szasz, J. Chem. Phys. 35, 1072 (1961).