PHYSICAL REVIEW A VOLUME 15, NUMBER 1 JANUARY 1977

Compact and accurate integral-transform wave functions. I. The 1^1S state of the helium-like ions from H^- through Mg^{10+}

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(Received 6 May 1976)

Accurate and compact integral-transform wave functions are constructed for the 1^1S state of the helium-like ions from H^- through Mg^{10+}. The variational ansatz is of the form $\Psi(r_1, r_2, r_{12}) = (4\pi)^{-1}\Sigma_{k=1}^{N} c_k(1+P_{12}) \exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12})$ where the c_k are found by solving the secular equation and the exponents α_k, β_k, and γ_k are chosen to be the abscissas of Monte Carlo and number-theoretic quadrature formulas for a variationally optimized parallelotope in α-β-γ space. A 66-term function of this type for the helium atom yields an energy of -2.903724363 a.u. as compared with the 1078-term function of Pekeris which yields an energy of -2.903724376 a.u. In order to test the accuracy of the wave functions a number of properties including $\langle r^n \rangle$ and $\langle r_{12}^n \rangle$ with $n = -2, -1, 1, \ldots, 4$, $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$, $\langle \cos\theta_{12} \rangle$, $\langle \delta(\vec{r}_1) \rangle$, and $\langle \delta(\vec{r}_{12}) \rangle$ are computed and compared with the best available results. The electric dipole polarizability is computed from a simple formula due to Thorhallsson, Fisk, and Fraga. Comments on the limiting accuracy of this formula are made. Electron-nuclear and electron-electron cusp condition tests are made for the functions. Detailed convergence studies are presented for H^- and He in the form of a sequence of functions with increasing N. The functions are found to be rather accurate and more compact than any other functions available in the literature with the exception of those containing logarithmic terms. Possible refinements to the basis set used are discussed.

I. INTRODUCTION

The problem of determining variational approximations to the eigenfunctions of the nonrelativistic Hamiltonian for two-electron atoms with infinite-mass nuclei has been extensively studied since the inception of quantum theory.[1] A result of this vast amount of research has been the computation of wave functions and expectation values of various operators for the low-lying states of the helium isoelectronic series to a rather high degree of accuracy.[2]

Nevertheless, our knowledge of the nature of electron correlation[3] in two-electron atoms is far from complete. Much physical insight into the correlation effects contained in an accurate wave function can be obtained by systematic analysis of the wave function. Density matrix analysis,[4] analysis by successive partial orthogonalizations,[5] and analysis of the probability density function for the interelectronic distance[6,7] are among the techniques available for this purpose. Such analyses have not yet been carried out systematically for the most accurate wave functions available for the two-electron ions. This is due primarily to the persisting unavailability of a systematic collection of *compact* and *highly accurate* wave functions expressed in a *relatively simple* basis set for which the necessary manipulations could be carried out without the expenditure of prodigious amounts of man-hours and computer time.

Most of the conventional techniques for constructing accurate wave functions are inadequate for the purpose of building wave functions which satisfy the above criteria. The method of superposition of configurations converges much too slowly[8] to be of use and the explicit introduction of the interelectronic distance r_{12} into the wave function is essential. However, even the Hylleraas[9] type of wave functions obtained by Pekeris[2] contain several hundred, and in some cases more than 2000 terms. The use of negative[10] and fractional[11] powers of r_{12} and of logarithmic terms[12-14] has led to more compact and equally accurate wave functions. However, the presence of these unconventional terms creates formidable difficulties in the computation of quantities required for the analysis of the wave functions.

In this paper we demonstrate that this gap can be filled by suitably constructed integral-transform wave functions, and we present a set of such functions for the ground states of the heliumlike ions.

An outline of the integral-transform method upon which our computations are based, our ansatz, and a discussion of various multidimensional quadrature techniques that we use to select nonlinear parameters are presented in Sec. II. The accuracy of a wave function cannot be gauged from its energy alone, and hence various properties have to be examined. Various moments of the one- and two-electron probability density functions, values of these densities at the origin, cusp conditions, and the static dipole polarizability α_d are among the properties considered in this study. A new form of the electron-electron cusp condition that we have found convenient to work with, an approximate formula for α_d given by Thorhallsson *et al.*,[15] and definitions of the other properties considered are all reported in Sec. II. Detailed convergence studies for the $1\,^1S$ ground states of H^- and He which show that our wave functions yield both energies and other properties to a high degree of accuracy are presented in Sec. III. An estimate is made of the maximum accuracy attainable with the approximate formula for α_d. Wave functions and properties for $1\,^1S$ states of the two-electron ions from Li^+ through Mg^{10+} are also presented in Sec. III. Section IV contains a discussion of the quality of the functions obtained and possibilities of refining the basis sets used.

II. THEORETICAL AND PRACTICAL DETAILS OF THE METHODS USED

A. Integral-transform method

The generator-coordinate method was originally developed by Wheeler and co-workers[16] to study the effect of collective nuclear motion upon nuclear properties. Somorjai[17] has adapted and generalized this method for use in atomic and molecular problems.[18] This is known as the integral-transform method.

Given the problem of finding the eigenfunctions of an N-particle system with Hamiltonian H, the basic idea of the integral-transform method is to systematically generate trial functions Ψ by the prescription

$$\Psi(x_1,x_2,\ldots,x_N)\equiv\Psi(\vec{x}_N)=\int_{D_M} S(\vec{t}_M)\Phi(\vec{x}_N;\vec{t}_M)\,d\vec{t}_M\,. \qquad (1)$$

In the above equation D_M is an M-dimensional integration domain for the parameter space ($\vec{t}$ space), Φ is some known function (and can be thought of as an exact eigenfunction for some model Hamiltonian), and the weight or shape function $S(\vec{t}_M)$ is to be determined. We shall assume that Ψ, Φ, and S are real.

Inserting the ansatz of Eq. (1) into the variational principle yields

$$E\int\Psi(\vec{x}_N)\Psi(\vec{x}_N)\,d\vec{x}_N=\int\Psi(\vec{x}_N)H\Psi(\vec{x}_N)\,d\vec{x}_N\,, \qquad (2)$$

that is,

$$E\int d\vec{t}_M\int d\vec{t}'_M I(\vec{t}_M;\vec{t}'_M)S(\vec{t}_M)S(\vec{t}'_M)=\int d\vec{t}_M\int d\vec{t}'_M K(\vec{t}_M;\vec{t}'_M)S(\vec{t}_M)S(\vec{t}'_M)\,, \qquad (3)$$

where

$$I(\vec{t}_M;\vec{t}'_M)=\int d\vec{x}_N[\Phi(\vec{x}_N;\vec{t}_M)\Phi(\vec{x}_N;\vec{t}'_M)]_{\rm sym}\,, \qquad (4)$$

$$K(\vec{t}_M;\vec{t}'_M)=\int d\vec{x}_N[\Phi(\vec{x}_N;\vec{t}_M)H\Phi(\vec{x}_N;\vec{t}'_M)]_{\rm sym}\,. \qquad (5)$$

In the above $[f\hat{0}g]_{\rm sym}\equiv[f\hat{0}g+g\hat{0}f]$ and hence it is clear that the Hamiltonian kernel K and the overlap kernel I are Hermitian.

A common procedure[18] has been to proceed from Eq. (3) using parametrized trial weight functions S. Alternatively, one may vary Eq. (3) with respect to $S(\vec{t}_M)$ to obtain the Fredholm-type integral equation

$$E\int d\vec{t}_M I(\vec{t}_M;\vec{t}'_M)S(\vec{t}_M)=\int d\vec{t}_M K(\vec{t}_M;\vec{t}'_M)S(\vec{t}_M) \qquad (6)$$

for the unknown $S(\vec{t}_M)$. Equation (6) may now be solved by approximate numerical integration. This produces the familiar secular equations

$$\sum_{i=1}^{L} W_i S(\vec{t}_i)[K(\vec{t}_i;\vec{t}'_j)-EI(\vec{t}_i;\vec{t}'_j)]=0\,, \qquad (7)$$

for $j=1,2,\ldots,L$. The W_i and $\vec{t}_i$ are weights and abscissas, respectively, for the numerical integration. If the sets $\{\vec{t}_i\}$ and $\{\vec{t}'_i\}$ are different, as in Galerkin-type methods, then one obtains an unbounded estimate of E which converges[19] to the true energy as $L\to\infty$. On the other hand, if the sets $\{\vec{t}_i\}$ and $\{\vec{t}'_i\}$ are chosen to coincide, one then obtains a convergent sequence of upper bounds to the true energy. This latter procedure has been used previously[20-22] and is the one we shall adopt.

In order to apply this method to a specific problem one must choose (i) a functional form for $\Phi(\vec{x}_N;\vec{t}_M)$ in Eq. (1), (ii) an appropriate integration domain D_M in Eq. (1), and (iii) a quadrature scheme. The choice of these quantities forms the subject of Sec. II B.

B. Choice of Φ, D_M, and a quadrature scheme for the S states of the two-electron ions

For the S states of the two-electron ions we chose $\Phi(\vec{x}_N;\vec{t}_M)$ to be

$$\Phi(r_1,r_2,r_{12};\alpha,\beta,\gamma)=(4\pi)^{-1}(1\pm P_{12})\times\exp(-\alpha r_1-\beta r_2-\gamma r_{12})\,, \qquad (8)$$

where P_{12} is the permutation operator defined by

$$P_{12}f(r_1,r_2,r_{12})=f(r_2,r_1,r_{12})$$

and the plus and minus signs correspond to the singlet and triplet states, respectively. This choice of Φ corresponds to the variational ansatz

$$\Psi(r_1, r_2, r_{12}) = (4\pi)^{-1} \sum_{k=1}^{N} C_k(1 \pm P_{12}) \times \exp[-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}]. \tag{9}$$

In effect the nonlinear parameters are chosen to be the lattice points of a three-dimensional quadrature formula, and the linear coefficients are found by solving the secular equation. This ansatz is uncommon but not new. It was first used by Hylleraas[9(b)] with $N = 1$, and later by Rosenthal,[23] Somorjai and Power,[21,24] and Winkler and Porter.[22] However, other types of functions containing exponential correlation factors are quite common in the literature[25] and date back to Slater[26] and Hylleraas.[9(b)]

Note that for the ansatz of Eq. (9) all integrals required for the calculation of the energy and various other expectation values, probability density functions, and lower bounds can be done analytically.[27-29,24]

Next the integration domain D_3 must be chosen. It is evident that we may restrict attention to finite values of α_k, β_k, and γ_k, and so D_3 can be chosen to be a parallelotope in three-space. Thus we may write

$$\alpha_k \in [A_1, A_2], \quad \beta_k \in [B_1, B_2], \quad \gamma_k \in [G_1, G_2], \tag{10}$$

for $k = 1, 2, \ldots, N$. The parallelotope is not completely arbitrary. Since we are considering bound states we must have

$$\min \alpha_k > 0, \quad \min \beta_k > 0, \tag{11}$$

where the minimum is to be taken over all $k \in \{1, 2, \ldots, N\}$. Some previous researchers[21-24] have also restricted the γ_k's to be positive. This, however, is an artificial restriction, as shown by the following pair of arguments. (a) Consider a wave function of the type given by Eq. (9), with $N = 1$. Such a wave function can satisfy the Kato[30] electron-electron cusp condition if and only if $\gamma_1 = -\frac{1}{2}$. (b) A wave function of the type $f(r_1)f(r_2)\chi(r_{12})$ has been considered by Baber and Hassé,[25] who showed that $\chi(r_{12})$ asymptotically behaves as $e^{-kr_{12}}$, with $k < 0$, as $r_{12} \to \infty$. Hence we allow the γ_k's to take on negative values. However, in order to ensure that all of the integrals required for the computation of the energy and other properties exist, we impose the following constraints:

$$\begin{aligned} &\min(\alpha_k + \alpha_l + \gamma_k + \gamma_l) > 0, \\ &\min(\beta_k + \beta_l + \gamma_k + \gamma_l) > 0, \\ &\min(\alpha_k + \beta_l + \gamma_k + \gamma_l) > 0, \end{aligned} \tag{12}$$

where the minimum in all of the above cases is to be taken over all $k \in \{1, 2, \ldots, N\}$ and all $l \in \{1, 2, \ldots, N\}$.

Thus D_3 is chosen to be a parallelotope defined by Eq. (10), with A_1, A_2, B_1, B_2, G_1, and G_2 being variational parameters subject to the constraints of Eqs. (11) and (12).

Finally, it is necessary to choose a quadrature scheme. The classical method of performing three-dimensional numerical integration is to use the tensor product of three one-dimensional Gaussian quadrature formulas.[31] In this method the total number of quadrature points is $N = n_1 n_2 n_3$, where n_i is the number of quadrature points in the ith dimension. Consider the usual case $n_1 = n_2 = n_3 = n$, so that $N = n^3$. Clearly the major drawback of this scheme is that N grows too rapidly with n for it to be practicable to use even a moderately sized n. Winkler and Porter[22] used Gaussian quadratures and found it expedient to use only a selected subset of $\frac{1}{6}n(n+1)(n+2)$ points out of the total set of n^3 points. Even with their scheme N already reaches 165 for $n = 9$. Moreover, their complicated selection procedure suffers from a high degree of arbitrariness,[29] and hence we will not consider it further.

In recent years various other multidimensional schemes have become available.[31,32] Of these, we reject interpolatory nonproduct formulas because *in the present context* their symmetry properties invariably lead to linear dependencies[29] among the various terms in Eq. (9). Monte Carlo methods[32,33] are popular because the number of quadrature points required for satisfactory accuracy is smaller than in traditional methods. We use one particular method[34] that seems to be quite successful. In this method the quadrature points are pseudorandom numbers in the unit cube which may be mapped into the required parallelotope by an affine transformation. In this scheme, which we refer to as scheme P in the rest of this paper, the N nonlinear parameters in Eq. (9) are generated by the following equations:

$$\begin{aligned} \alpha_k &= \eta[(A_2 - A_1)\langle \tfrac{1}{2}k(k+1)\sqrt{2}\rangle + A_1], \\ \beta_k &= \eta[(B_2 - B_1)\langle \tfrac{1}{2}k(k+1)\sqrt{3}\rangle + B_1], \\ \gamma_k &= \eta[(G_2 - G_1)\langle \tfrac{1}{2}k(k+1)\sqrt{5}\rangle + G_1], \end{aligned} \tag{13}$$

for all $k = 1, 2, \ldots, N$. In the above $\langle x \rangle$ is defined to be the fractional part of x. A_1, A_2, B_1, B_2, G_1, and G_2 are the variational parameters that define the parallelotope of Eq. (10). In principle $\eta = 1$. Note that if A_1, A_2, B_1, B_2, G_1, and G_2 were truly variationally optimized our wave function would satisfy the virial theorem. However, the optimization algorithm we use is not perfect, and hence we scale the wave function so that it satisfies the virial theorem.[35] η serves this purpose, and as will be seen in later sections of this paper η rarely differs from unity by more than 10^{-7} for

TABLE I. $a_{i,N}$ constants for scheme Z.

N/i	1	2	3
21	1	3	8
35	1	11	16
44	1	14	20
66	1	9	23

our wave functions. Somorjai and Power[21] used a similar scheme.

Number-theoretical multidimensional integration formulas which have been shown to be extremely economical and accurate are also available.[36,37] Hence we also use the method of "good lattice points."[37,38] In this method the quadrature points for the unit cube are found by a complicated procedure which utilizes concepts from number theory and from the theory of multiply periodic functions. In this scheme, which we refer to as scheme Z in the rest of this paper, the N nonlinear parameters in Eq. (9) are generated by the following equations:

$$\begin{aligned} \alpha_k &= \eta[(A_2 - A_1)\langle k a_{1,N}/N\rangle + A_1]\,, \\ \beta_k &= \eta[(B_2 - B_1)\langle k a_{2,N}/N\rangle + B_1]\,, \qquad (14) \\ \gamma_k &= \eta[(G_2 - G_1)\langle k a_{3,N}/N\rangle + G_1]\,, \end{aligned}$$

for all $k = 1, 2, \ldots N$. In the above $\langle x\rangle$ is defined to be the fractional part of x, and the $a_{i,N}$ are listed in Table I. All of the other quantities appearing in Eq. (14) have the same meanings as in Eq. (13). Note that in the remainder of this paper we use $\langle x\rangle$ to denote the quantum-mechanical expectation value of x. Empedocles[20] has used other number-theoretic quadrature schemes in the construction of radial limit integral-transform wave functions for He, Li, and Be.

C. Properties other than energy

It is well known that the accuracy of a wave function cannot be assessed solely from the energy. Hence we have computed a variety of other expectation values which can help indicate the accuracy of our wave functions.

Since our wave functions are scaled to satisfy the virial theorem, the latter cannot be used to test the accuracy of the functions. A set of expectation values which can be used to probe the details of the charge density are its moments defined by

$$\langle r^n\rangle \equiv \langle r_1^n + r_2^n\rangle\,. \qquad (15)$$

Values of $\langle r^n\rangle$ for $n = -2, -1, 1, 2, 3$, and 4 have been computed. Similarly, the moments of the probability density function for r_{12} serve as useful probes of the accuracy of the wave functions. Values of $\langle r_{12}^n\rangle$ for $n = -2, -1, 1, 2, 3$, and 4 have been computed. Two expectation values that reflect the angular correlation contained in the wave function, $\langle \vec{r}_1 \cdot \vec{r}_2\rangle$ and $\langle \cos\theta_{12}\rangle$, have also been computed. θ_{12} is the angle subtended at the nucleus by the position vectors of the two electrons.

The sensitive "point" properties $\langle \delta(\vec{r}_1)\rangle$ and $\langle \delta(\vec{r}_{12})\rangle$ which play a role in the relativistic[1(a)] and radiative[39] corrections to the ground-state energy are two other properties that have been computed. Cusp conditions and the static dipole polarizability provide other probes and are discussed below.

D. Approximate formula for the static dipole polarizability

If an atom is in a uniform static electric field F_Z its energy E and dipole moment m_Z may be written as power series in F_Z,

$$E = E_0 + E_2 F_Z^2 + E_4 F_Z^4 + \cdots\,, \qquad (16)$$

$$M_Z = -\left(\frac{\partial E}{\partial F_Z}\right) = \alpha_d F_Z + \frac{\gamma F_Z^3}{6} + \cdots\,, \qquad (17)$$

where the dipole polarizability $\alpha_d = -2E_2$, and $\gamma = -24E_4$ is the "second hyperpolarizability." When a weak field is under consideration the perturbed function Φ may be approximated as

$$\Phi = \Psi(1 + \omega)\,, \qquad (18)$$

where Ψ represents the unperturbed function or a variational approximation to it, and ω denotes a symmetric function to be determined by a variational treatment. Thorhallsson, Fisk, and Fraga[15] (TFF) have proposed the use of

$$\omega = \sum_i u(\vec{r}_i)\,, \qquad (19)$$

where the summation extends over all the electrons in the system and

$$u(\vec{r}) = F_Z(\mu r + \nu r^2)\cos\theta\,. \qquad (20)$$

They then minimize the energy with respect to μ and ν to obtain E_2 and hence obtain

$$\alpha_d = -\left[M_0\mu^2 + 2M_2\nu^2 + \tfrac{4}{3}(N_0\mu + 2M_1\mu\nu + N_1\nu)\right]\,, \qquad (21)$$

where

$$\mu = (4M_1N_1 - 6M_2N_0)/(9M_0M_2 - 8M_1^2)\,, \qquad (22)$$

$$\nu = (4M_1N_0 - 3M_0N_1)/(9M_0M_2 - 8M_1^2)\,. \qquad (23)$$

In the above,

$$M_k = \left\langle \Psi \,\middle|\, \sum_i r_i^k \,\middle|\, \Psi\right\rangle. \qquad (24)$$

$$N_k = \left\langle \Psi \,\middle|\, \sum_{i,j} r_i^k(\vec{r}_i \cdot \vec{r}_j) \,\middle|\, \Psi\right\rangle. \qquad (25)$$

TFF proposed this ansatz for ω for use with a restricted Hartree-Fock Ψ. Clearly the use of such an unperturbed function together with the TFF ansatz for ω amounts to an approximate uncoupled Hartree-Fock scheme. In view of the relative success[15] of the TFF scheme for many atoms other than the transition metals[40] we feel that it is of some interest to assess the limiting accuracy of the TFF ansatz for ω.

It has been known for some time[41] that α_d is extremely sensitive to the choice of the field-free wave function Ψ but relatively insensitive to the correction $\Psi\omega$. Formally the leading errors in a variational-perturbation calculation of α_d are first order in the error of the unperturbed wave function but only second order with respect to the error in the perturbative correction.[42,43] Hence one may attempt to assess the limiting accuracy of the TFF ansatz for ω by using their formulas to compute α_d with a sequence of increasingly accurate unperturbed wave functions and comparing the results with the best available values.[43-46]

We have used our wave functions for the helium-like ions for this purpose. It should be emphasized that our calculations of α_d do *not* serve as a probe of the accuracy of our wave functions, because we have restricted ourselves to the use of the TFF ansatz for ω.

E. Cusp conditions

Cusp conditions which an exact wave function must satisfy arise from a consideration of the singularities of the Hamiltonian. They constitute rather sensitive tests of an approximate wave function.

It has been shown[30] that the Kato electron-nuclear (Coulomb) cusp condition for *S states of any N-electron system* implies that

$$\lim_{r\to 0}\left(-\frac{1}{2}\,\frac{\rho'(r)}{\rho(r)}\right)=Z\,, \tag{26}$$

where Z is the nuclear charge, $\rho'(r)=d\rho/dr$, and ρ is the electron density defined by

$$\rho(r)=(4\pi)^{-1}\int_0^{\pi}\int_0^{2\pi}\Gamma^{(1)}(\vec{r}\,|\,\vec{r})\,d\phi\,\sin\theta\,d\theta\,, \tag{27}$$

where $\vec{r}=(r,\theta,\phi)$ and $\Gamma^{(1)}(\vec{r}\,|\,\vec{r}')$ is the spin-traced one-electron reduced-density matrix. Recall that the spin-traced p-electron reduced-density matrix is defined by[4(a)]

$$\begin{aligned}\Gamma^{(p)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_p\,|\,\vec{r}_1',\vec{r}_2',\ldots,\vec{r}_p') &= \binom{N}{p}\int\Psi(x_1,x_2,\ldots,x_N)\\ &\quad\times\Psi^*(x_1',x_2',\ldots,x_p',x_{p+1},\ldots,x_N)\\ &\quad\times(ds)(dV_i)\,,\end{aligned} \tag{28}$$

where $x_i=(\vec{r}_i,\zeta_i)$ is a combined space-spin coordinate, (ds) indicates a trace operation over the spin coordinates of all electrons, and (dV_i) indicates integration over the spatial coordinates of all but the first p electrons.

We have recently shown[29,47] that the Kato electron-electron (correlation) cusp condition for *singlet S states of any N-electron system* implies that

$$\lim_{r_{12}\to 0}\left(\frac{1}{2}\,\frac{h'(r_{12})}{h(r_{12})}\right)=\frac{1}{2}\,, \tag{29}$$

where $h'=dh/dr_{12}$, and $h(r_{12})$ is defined by

$$h(r_{12})=(4\pi)^{-1}\int_0^{\pi}\int_0^{2\pi}J(\vec{r}_{12},\vec{r}_{12})\,d\beta\,\sin\alpha\,d\alpha\,. \tag{30}$$

In the above $\vec{r}_{12}=(r_{12},\alpha,\beta)$ and $J(\vec{r}_{12},\vec{r}_{1'2'})$ is the intracule matrix[48] which is obtained from the spin-traced two-electron reduced-density matrix $\Gamma^{(2)}$ as follows:
Define

$$\vec{R}=\tfrac{1}{2}(\vec{r}_1+\vec{r}_2)\,, \tag{31}$$

$$\vec{r}_{12}=\vec{r}_1-\vec{r}_2\,, \tag{32}$$

and similarly for $\vec{R}'$ and $\vec{r}_{1'2'}$. Then change coordinates to obtain

$$\tilde{\Gamma}^{(2)}(\vec{R},\vec{r}_{12}\,|\,\vec{R}',\vec{r}_{1'2'})=\Gamma^{(2)}(\vec{r}_1,\vec{r}_2\,|\,\vec{r}_1',\vec{r}_2')\,, \tag{33}$$

and, finally, integrate over the extracular coordinates to obtain the intracule matrix

$$J(\vec{r}_{12},\vec{r}_{1'2'})=\int\tilde{\Gamma}^{(2)}(\vec{R},\vec{r}_{12}\,|\,\vec{R},\vec{r}_{1'2'})\,d\vec{R}\,. \tag{34}$$

Note that J, as defined above, is normalized to $\binom{N}{2}$, while Coleman[48] normalizes J to unity. Note also that $h(r_{12})$ is related to the electron-electron distribution[7] function $P_0(r_{12})$ by

$$P_0(r_{12})=4\pi r_{12}^2\,h(r_{12})\,. \tag{35}$$

A discussion of other properties of $h(r_{12})$ and a derivation of Eq. (29) may be found elsewhere.[29,47]

We have computed the quantities

$$C_{\mathrm{EN}}=\lim_{r\to 0}\left(-\frac{1}{2}\,\frac{\rho'(r)}{\rho(r)}\right)\,, \tag{36}$$

$$C_{\mathrm{EE}}=\lim_{r_{12}\to 0}\left(\frac{1}{2}\,\frac{h'(r_{12})}{h(r_{12})}\right) \tag{37}$$

for all of our wave functions as a check on how well they satisfy the cusp conditions (26) and (29).

It is important to realize that the cusp conditions (26) and (29) are based on derivations which involve a number of averaging procedures.[29,30,47] Therefore as far as approximate wave functions for ${}^1S$ states of two-electron atoms are concerned a check of these cusp conditions is less stringent than a test based on the Fock expansion.[49, 50] The latter test consists of expanding an approximate wave function in a Fock-like expansion and comparing the coefficients thus obtained with the exact ones.

An examination of the coefficients of the Fock expansion of our wave functions for the ^1S states of the two-electron atoms has been initiated and it is hoped that results will become available in the near future.

F. Computational methods

All integrals required for the energy, overlap, and most other expectation values were computed with the recursion relations given by Sack *et al.*[28] The computation of certain integrals required for $\langle r^{-2}\rangle$ and $\langle r_{12}^{-2}\rangle$ is described in the Appendix. The formulas for $\langle\delta(\vec{r}_1)\rangle$, $\langle\delta(\vec{r}_{12})\rangle$, C_{EN}, and C_{EE} are special cases of formulas for $\rho(r)$, $\rho'(r)$, $h(r_{12})$, and $h'(r_{12})$, which are given elsewhere.[29]

The optimization of the variational parameters A_1, A_2, B_1, B_2, G_1, and G_2 [cf. Eqs. (10), (13), and (14)] was carried out using Powell's algorithm[51] modified by the inclusion of a barrier function to handle the constraints given by Eqs. (11) and (12). All of the algorithms used for solution of the secular equation were taken from Wilkinson and Reinsch.[52] During the preliminary optimization cycles the sequential combination of *reduc*1, *tred*1 and *ratqr* was used. In the final cycle the sequential combination of *reduc*1, *tred*2, *tql*2, and *rebaka* was used.

The preliminary optimization cycles were carried out on an IBM 360/91 computer using a 56-bit (~16 significant figure) mantissa. *All* final calculations were carried out on a Burroughs B6700 computer using a 78-bit (~23 significant figure) mantissa.

III. WAVEFUNCTIONS AND PROPERTIES

A. $1\,^1S$ state of the helium atom

The ground state of the helium atom is the natural one to consider first, because it is the most extensively studied of the two-electron ions.

Sequences of wave functions with increasing numbers of terms (N) were constructed using both the Z and P schemes [cf. Eqs. (14) and (13), respectively] for choosing the nonlinear parameters. The parameters defining the parallelotope [cf. Eq. (10)] were separately optimized for each value of N.

Table II lists values of N, A_1, A_2, B_1, B_2, G_1, G_2, $1-\eta$ (instead of η, for convenience), and the energy for each of these functions. Not surprisingly, the intuitively appealing inequalities

$$A_1 < Z < A_2\ , \tag{38}$$

$$B_1 < Z < B_2\ , \tag{39}$$

where $Z=2$ is the nuclear charge, are seen to be satisfied in all cases. The values of G_1 are all negative, and negative γ_k's do occur, confirming our arguments in Sec. II B that negative values of the γ_k's are necessary. The small magnitudes of $1-\eta$ show that our optimization scheme was rather effective at finding at least local minima in the parameter space. Finally, note that the energy values are converging smoothly toward the "exact" value of Frankowski and Pekeris[13]. With roughly 45 terms the wave functions are already energetically accurate to 10^{-7} a.u., and the 60- and 66-term wave functions yield energies that have errors of only 27×10^{-9} and 14×10^{-9} a.u., respectively.

Table III lists values of $\langle r^n\rangle$ ($n=-2,-1,1\ldots,4$) for each of the wave functions. Here the convergence patterns are not monotonic. This is to

TABLE II. Parallelotope parameters and energies for He. The "exact" energy is from Ref. 13. Note that in this table, as in Tables III–VIII, all quantities are in atomic units and the format A–B stands for $A\times10^{-B}$.

Scheme	N	A_1	A_2	B_1	B_2	G_1	G_2	$1-\eta$	$-E$
Z	21	1.8060	2.5120	1.3260	2.4190	–0.0740	1.4290	–2.942–8	2.903 723 415
	35	1.9900	2.4600	1.4180	2.2730	–0.0390	1.1920	–1.717–8	2.903 724 053
	44	1.8960	2.1690	1.3970	2.7280	–0.0160	2.5520	–1.089–8	2.903 724 280
	66	1.4612	4.1453	1.2897	3.5514	–0.2894	1.0938	9.308–9	2.903 724 363
P	10	1.0420	2.0250	1.2110	2.2800	–0.1670	0.9590	2.581–7	2.903 713 181
	20	1.7130	2.5790	1.4050	2.2840	–0.2400	1.5610	–2.505–8	2.903 722 730
	30	1.7280	2.7650	1.3110	2.3950	–0.1900	1.1750	–5.069–9	2.903 724 019
	35	1.6630	2.7170	1.4530	2.2820	–0.2550	1.6210	3.427–8	2.903 724 168
	40	1.4160	2.9510	1.4300	2.3830	–0.2420	2.0330	–2.705–9	2.903 724 279
	45	1.4230	2.9300	1.4350	2.3630	–0.2080	2.0100	–2.209–8	2.903 724 301
	50	1.4130	2.9520	1.4790	2.3400	–0.2110	1.9610	–3.128–8	2.903 724 316
	60	0.9950	3.8860	1.5460	2.7610	–0.2890	1.8440	2.070–8	2.903 724 350
Exact									2.903 724 377

TABLE III. $\langle r^n \rangle$ values for He. The "exact" values are from Ref. 2.

Scheme	N	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^{2}\rangle$	$\langle r^{3}\rangle$	$\langle r^{4}\rangle$
Z	21	12.035 182 0	3.376 634 072	1.858 929 361	2.386 849 83	3.935 148 01	7.942 673 1
	35	12.034 480 0	3.376 633 352	1.858 945 772	2.386 977 16	3.935 962 39	7.947 508 6
	44	12.034 672 3	3.376 633 567	1.858 944 772	2.386 966 96	3.935 889 48	7.947 019 2
	66	12.034 829 9	3.376 633 603	1.858 944 392	2.386 964 34	3.935 883 22	7.947 026 3
P	10	12.036 697 4	3.376 635 708	1.858 896 030	2.386 614 42	3.934 192 39	7.938 420 3
	20	12.035 416 0	3.376 634 334	1.858 941 289	2.386 955 31	3.935 910 94	7.947 415 6
	30	12.034 630 5	3.376 633 440	1.858 943 277	2.386 956 10	3.935 820 29	7.946 575 0
	35	12.034 779 4	3.376 633 431	1.858 944 728	2.386 964 66	3.935 882 13	7.947 028 9
	40	12.034 717 7	3.376 633 540	1.858 944 508	2.386 966 02	3.935 890 24	7.947 067 6
	45	12.034 764 3	3.376 633 556	1.858 944 776	2.386 966 03	3.935 879 83	7.946 922 3
	50	12.034 782 3	3.376 633 589	1.858 944 425	2.386 963 24	3.935 862 46	7.946 809 5
	60	12.034 818 1	3.376 633 583	1.858 944 438	2.386 964 75	3.935 886 68	7.947 065 9
Exact		12.034 814 2	3.376 633 592	1.858 944 594	2.386 966 02		

be expected, since no bounding principle for these properties is being used. $\langle r^{-1}\rangle$ shows the most rapid convergence. This is not surprising, since $\langle r^{-1}\rangle$ occurs in the expression for the energy. In increasing order of n, the $\langle r^n\rangle$ values seem to have converged to accuracies of roughly 3×10^{-5}, 1×10^{-8}, 2×10^{-7}, 2×10^{-6}, 2×10^{-5}, and 1×10^{-4} a.u., respectively. The slow convergence of $\langle r^{-2}\rangle$ is not unexpected. It could have been predicted on the basis of the well-documented[2,10] observation that lower bounds to the energy that depend on $\langle H^2\rangle$ converge relatively slowly.

Table IV lists values of $\langle r_{12}^n\rangle$ ($n=-2,-1,\ldots,4$) for each of the wave functions. Trends similar to those observed for $\langle r^n\rangle$ can be seen here as well. None of the convergence patterns are monotonic, $\langle r_{12}^{-1}\rangle$, which is a part of $\langle H\rangle$, converges rapidly, and $\langle r_{12}^{-2}\rangle$, which is a part of $\langle H^2\rangle$, converges slowly. In increasing order of n, the $\langle r_{12}^n\rangle$ values seem to have converged to accuracies of roughly 1×10^{-5}, 3×10^{-8}, 3×10^{-7}, 1×10^{-6}, 1×10^{-5}, and 3×10^{-4} a.u., respectively. The relatively consistent values of $\langle r_{12}^{-2}\rangle$ for most of the functions with 40 or more terms could lead one to the conclusion that the true value of $\langle r_{12}^{-2}\rangle$ is closer to 1.464 783 a.u. than it is to the Pekeris[2(a)] value of 1.464 773 a.u. However, the 44-term scheme-Z function, for which $\langle r_{12}^{-2}\rangle = 1.464\,777$ a.u., warns one that this conclusion could be erroneous. It will be seen shortly that this warning is worth heeding.

Values of $\langle\delta(\vec{r}_1)\rangle$, $\langle\delta(\vec{r}_{12})\rangle$, $\langle\vec{r}_1\cdot\vec{r}_2\rangle$, $\langle\cos\theta_{12}\rangle$, C_{EN}, C_{EE}, and α_d for each of the wave functions are listed in Table V. $\langle\delta(\vec{r}_1)\rangle$, $\langle\vec{r}_1\cdot\vec{r}_2\rangle$, and $\langle\cos\theta_{12}\rangle$ seem to have converged to accuracies of roughly 5×10^{-5}, 2×10^{-7}, and 1×10^{-7} a.u., respectively.

The α_d values are very interesting. They seem to have converged to a value of 1.379 36 ± 0.000 01 a.u. There is no question however that the Buckingham-Hibbard[46] (BH) value of 1.383 19 a.u. is much more accurate. The latter was computed with a 180-term Kinoshita-type[10] unperturbed function and an 84-term perturbing function (ω in the notation of Sec. II D). Moreover, Weinhold[43] has obtained a rigorous lower bound of 1.3817 a.u. and

TABLE IV. $\langle r_{12}^n\rangle$ values for He. The "exact" values are from Ref. 2.

Scheme	N	$\langle r_{12}^{-2}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle r_{12}\rangle$	$\langle r_{12}^{2}\rangle$	$\langle r_{12}^{3}\rangle$	$\langle r_{12}^{4}\rangle$
Z	21	1.464 842	0.945 821 315	1.422 053 25	2.516 320 66	5.307 327 1	12.977 396 2
	35	1.464 824	0.945 818 598	1.422 070 51	2.516 438 16	5.307 984 2	12.981 022 7
	44	1.464 777	0.945 818 574	1.422 069 66	2.516 432 99	5.307 956 8	12.980 868 0
	66	1.464 784	0.945 818 481	1.422 070 08	2.516 437 83	5.307 998 1	12.981 178 3
P	10	1.465 456	0.945 845 053	1.421 981 60	2.515 909 24	5.304 878 9	12.962 039 0
	20	1.464 971	0.945 823 210	1.422 051 61	2.516 353 68	5.307 748 8	12.980 864 1
	30	1.464 835	0.945 818 843	1.422 068 27	2.516 414 02	5.307 771 5	12.979 301 0
	35	1.464 793	0.945 818 527	1.422 070 62	2.516 438 69	5.307 983 1	12.980 974 0
	40	1.464 786	0.945 818 523	1.422 070 76	2.516 443 12	5.308 029 5	12.981 347 5
	45	1.464 787	0.945 818 511	1.422 070 10	2.516 435 84	5.307 967 6	12.980 862 0
	50	1.464 786	0.945 818 545	1.422 070 08	2.516 436 59	5.307 976 0	12.980 922 1
	60	1.464 783	0.945 818 466	1.422 070 20	2.516 438 54	5.308 003 5	12.981 236 3
Exact		1.464 773	0.945 818 451	1.422 070 26	2.516 439 34		

TABLE V. Various properties for He. The "exact" value for $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ is from Ref. 2, the exact values of C_{EN} and C_{EE} are from Eqs. (26)–(29), and the rest of the "exact" values are from Ref. 46.

Scheme	N	$\langle \delta(\vec{r}_1) \rangle$	$\langle \delta(\vec{r}_{12}) \rangle$	$\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$	$\langle \cos\theta_{12} \rangle$	α_d	C_{EN}	C_{EE}
Z	21	1.810 897	0.106 495	−0.064 735 414	−0.064 200 775	1.378 96	2.001 812	0.489 54
	35	1.810 023	0.106 466	−0.064 730 502	−0.064 202 403	1.379 42	1.998 526	0.491 38
	44	1.810 252	0.106 365	−0.064 733 012	−0.064 202 196	1.379 37	1.999 306	0.497 83
	66	1.810 456	0.106 387	−0.064 736 747	−0.064 202 621	1.379 36	2.000 183	0.495 90
P	10	1.811 787	0.107 172	−0.064 647 414	−0.064 173 033	1.378 84	2.002 980	0.466 26
	20	1.811 037	0.106 728	−0.064 699 188	−0.064 199 783	1.379 47	2.002 003	0.476 03
	30	1.810 199	0.106 482	−0.064 728 956	−0.064 202 765	1.379 36	1.999 152	0.490 65
	35	1.810 383	0.106 397	−0.064 737 014	−0.064 202 010	1.379 35	1.999 886	0.496 14
	40	1.810 336	0.106 389	−0.064 738 553	−0.064 202 491	1.379 35	1.999 753	0.495 86
	45	1.810 380	0.106 397	−0.064 734 902	−0.064 202 435	1.379 36	1.999 888	0.494 88
	50	1.810 384	0.106 393	−0.064 736 675	−0.064 202 576	1.379 35	1.999 815	0.495 40
	60	1.810 424	0.106 385	−0.064 736 893	−0.064 202 638	1.379 36	1.999 945	0.496 00
Exact		1.810 433	0.106 352	−0.064 736 665		1.383 19	2	0.5

a variation perturbation estimate of 1.383 16 a.u. Weinhold's unperturbed wave function yields an energy of − 2.903 724 333 a.u. and has an overlap parameter $\epsilon = 2 \times 10^{-4}$, where ϵ is defined by

$$\epsilon = (1 - S^2)^{1/2}\,, \tag{40}$$

in which S is the Weinberger[53] lower bound for the overlap between an approximate and the exact wave function. By comparison our scheme-Z 66-term unperturbed wave function yields an energy of − 2.903 724 363 a.u. and has[29] an overlap parameter $\epsilon = 1 \times 10^{-4}$. In view of the above comparison it seems that the discrepancy between our value of α_d and the BH and Weinhold values must be ascribed to our choice of ω [cf. Eqs. (19) and (20)]. This enables us to conclude that the limiting error inherent in the TFF ansatz for ω is roughly 4×10^{-3} a.u. for the ground state of the helium atom.

The $\langle \delta(\vec{r}_{12}) \rangle$ values have certainly converged to an accuracy of roughly 5×10^{-5} a.u. However, the relative consistency of these values could lead one to the conclusion that the true value of $\langle \delta(\vec{r}_{12}) \rangle$ lies between 0.106 38 and 0.106 40 a.u., as opposed to the BH value of 0.106 35 a.u. A warning that this may be a false conclusion is once again sounded by the 44-term scheme-Z function. Turning to the cusp-condition checks for our wave functions, we see that our suspicions about the apparent convergence of $\langle r_{12}^{-2} \rangle$ and $\langle \delta(\vec{r}_{12}) \rangle$ to values slightly different from the best values available in the literature were indeed well founded. This is evident from the fact that the 44-term scheme-Z function which prevented us from jumping to false conclusions satisfies the electron-electron cusp condition more closely than any of the other functions. Since $\langle r_{12}^{-2} \rangle$, $\langle \delta(\vec{r}_{12}) \rangle$, and C_{EE} are all sensitive to the behavior of the wave function at small values of r_{12}, it is obvious that the 44-term function is the most reliable one as far as these properties are concerned. Hence the apparent convergence of $\langle r_{12}^{-2} \rangle$ and $\langle \delta(\vec{r}_{12}) \rangle$ to values different from the Pekeris[2] and BH[46] values, respectively, is illusory.

Deviations from the electron-nuclear cusp condition do not exceed 0.003 for any of the functions. The 60- and 66-term functions show deviations of 0.000 05 and 0.000 18, respectively. None of the functions with 30 or more terms deviates from the electron-electron cusp condition by more than 0.01, and the 60- and 66-term functions show deviations of 0.004. Finally, note that there is essentially no difference between the scheme-Z and scheme-P functions when all of the properties are considered.

B. Ground state of the hydride ion

Next we consider the ^1S ground state of the H^- ion, which is of interest because of its astrophysical significance and because the restricted Hartree-Fock model predicts that it is unbound.

21-, 35-, 44-, and 66-term scheme-Z and 10-, 20-, 30-, 40-, 50-, and 60-term scheme-P wave functions were constructed for the purpose of a convergence study. The tables listing parallelotope parameters, energies, expectation values, and cusp-condition checks for all of these wave functions are presented elsewhere.[29] These tables have been omitted from this paper for the sake of brevity.[54] Here we present only a discussion of the convergence studies and a summary of the expectation values for the two best functions (see Table VI).

Except in the case of the ten-term function, the nuclear charge $Z = 1$ lies[29] between A_1 and A_2, and B_1 and B_2, as intuitively expected, and the rela-

TABLE VI. Parallelotope parameters, expectation values, and cusp-condition checks for H^-. The "exact" energy is from Ref. 13, the "exact" value of α_d is from Ref. 43, the exact values of C_{EN} and C_{EE} are from Eqs. (26)–(29), and the rest of the "exact" values are from Ref. 2.

(Scheme) N	(Z) 66	(P) 60	"Exact"
A_1	0.2180	0.1280	
A_2	1.5100	1.2460	
B_1	0.8710	0.8890	
B_2	1.5000	1.2030	
G_1	−0.1000	−0.1100	
G_2	0.1820	0.3420	
$1-\eta$	−6.223—8	−2.314—9	
$-E$	0.527 750 985	0.527 750 940	0.527 751 016
$\langle r^{-2}\rangle$	2.233 320	2.233 315	
$\langle r^{-1}\rangle$	1.366 523 52	1.366 523 85	
$\langle r\rangle$	5.420 350 83	5.420 322 33	5.420 356 62
$\langle r^2\rangle$	23.827 222	23.826 674	23.827 384
$\langle r^3\rangle$	152.0415	152.0387	
$\langle r^4\rangle$	1290.17	1290.79	
$\langle r_{12}^{-2}\rangle$	0.155 108	0.155 112	
$\langle r_{12}^{-1}\rangle$	0.311 021 55	0.311 021 97	
$\langle r_{12}\rangle$	4.412 688 50	4.412 661 45	4.412 694 52
$\langle r_{12}^2\rangle$	25.201 856	25.201 291	25.202 010
$\langle r_{12}^3\rangle$	180.601	180.598	
$\langle r_{12}^4\rangle$	1590.0	1590.6	
$\langle \cos\theta_{12}\rangle$	−0.105 147 89	−0.105 147 97	
α_d	202.629	202.626	206.04
$\langle \delta(\vec{r}_1)\rangle$	0.164 547	0.164 545	0.164 547
C_{EN}	0.999 825	0.999 828	1
$\langle \delta(\vec{r}_{12})\rangle$	0.002 742	0.002 745	0.002 740
C_{EE}	0.494 077	0.491 068	0.5

tively small magnitude of $1-\eta$ indicates that our optimization procedure did not fare too badly. The energies seem to be converging toward the "exact" value,[13] and the 60- and 66-term energies are in error by only 76×10^{-9} and 31×10^{-9} a.u., respectively. The G_1 values are again all negative and negative γ_k's do occur, lending further support to our claim that negative γ_k's are necessary.

Values of $\langle r^n\rangle$ and $\langle r_{12}^n\rangle$ $(n=-2,-1,1,\ldots,4)$ for all of these wave functions reveal[29] nonmonotonic convergence patterns, and show that $\langle r^{-1}\rangle$ and $\langle r_{12}^{-1}\rangle$, which form part of $\langle H\rangle$, converge more rapidly than $\langle r^{-2}\rangle$ and $\langle r_{12}^{-2}\rangle$, which form part of $\langle H^2\rangle$. Errors in the 66-term values of $\langle r^n\rangle$ and $\langle r_{12}^n\rangle$ are estimated to be no more than 5×10^{-5}, 1×10^{-6}, 1×10^{-5}, 5×10^{-4}, 1×10^{-1}, and 1 a.u., in order of increasing n. The 66-term values of $\langle\delta(\vec{r}_1)\rangle$ and $\langle\delta(\vec{r}_{12})\rangle$ do not differ from those of Pekeris[2] by more than 2×10^{-6} a.u. The $\langle\cos\theta_{12}\rangle$ value from the 66-term function is estimated to have a maximum error of 1×10^{-6} a.u.

The dipole polarizability α_d seems to have converged to roughly 202.6 ± 0.2 a.u. However, Weinhold[43] and Chung[45] both have obtained accurate variation-perturbation estimates of 206.0 a.u., and Weinhold gives 201.8 a.u. as a rigorous lower bound. As opposed to the case of He, Weinhold's bound does not exclude the α_d values obtained by us from unperturbed wave functions with 40 or more terms. Weinhold's unperturbed function gave an energy of − 0.527 750 799 a.u. and an overlap parameter [cf. Eq. (40)] $\epsilon=2.8\times10^{-3}$. By comparison our scheme-Z 66-term function gives an energy of − 0.527 750 985 a.u. and an overlap parameter $\epsilon=1.1\times10^{-3}$. On the basis of the above facts, we estimate that the limiting error of the TFF ansatz[15] for ω is roughly 3 a.u. for the ground state of H^-.

The deviations from the cusp conditions are larger than in the case of He. The best (60 and 66 term) functions deviate from the electron-nuclear and electron-electron cusp conditions by 0.0002 and 0.01, respectively. Once again, the Z and P schemes fare equally well when all the properties are taken into account.

C. $1\,^1S$ state of the two-electron ions from Li^+ through Mg^{10+}

A set of wave functions for the ground state of all the two-electron ions from Li^+ through Mg^{10+} were constructed using scheme P. The parallelotope parameters, various expectation values, and the cusp checks for these functions are listed in Tables VII and VIII.

The function for Li^+ contains 45 terms, while all of the rest are 25-term functions. Comparison with with the Frankowski-Pekeris values[13] shows that the errors in the energies are 4.1×10^{-7}, 6.2×10^{-6}, 1.6×10^{-6}, 6.6×10^{-6}, 5.1×10^{-6}, 5.1×10^{-6}, 2.4×10^{-6}, and 6.5×10^{-6} a.u. for Li^+ through Ne^{8+} in order of increasing nuclear charge. Comparison with the Pekeris values[55] shows that for Li^+ the errors in $\langle r\rangle$, $\langle r^2\rangle$, $\langle r_{12}\rangle$, $\langle r_{12}^2\rangle$, $\langle\delta(\vec{r}_1)\rangle$, and $\langle\delta(\vec{r}_{12})\rangle$ are 3×10^{-8}, 4×10^{-7}, 9×10^{-8}, 5×10^{-7}, 1.5×10^{-4}, and 9×10^{-5} a.u., respectively. The electron-nuclear and electron-electron cusp deviations for Li^+ are 0.0001 and 0.002, respectively. For the other ions the electron-nuclear cusp deviations range from 0.0002 to 0.003, while the electron-electron cusp deviations are ~0.02. For α_d, Weinhold's rigorous lower bound[43] of 0.192 35 a.u. and variation-perturbation estimate of 0.192 452 a.u. show that for the ground state of Li^+ the limiting accuracy of the TFF ansatz[15] for ω is roughly 2×10^{-4} a.u. For Be^{2+} and B^{3+} Weinhold gives variation-perturbation estimates of 0.052 268 5 and 0.019 631 4 a.u., respectively. The discrepancies between these values of α_d and those in Table VII are 7×10^{-5} and 7×10^{-6} a.u. for Be^{2+} and B^{3+}, respectively. Discrepancies of the same order of magnitude exist between the values of α_d in Tables VII and VIII and Weinhold's extrapolated values for $6\leq Z\leq 10$.

From the above comparisons and the analogous ones for H^- and He it is clear that the error inherent in the TFF ansatz for ω decreases as Z increases. This can easily be understood by noting that the TFF ansatz for ω [Eqs. (19) and (20)] weights regions of space close to the nucleus, and hence is better suited to describing distortions of the compact charge distributions of the ions of higher nuclear charge than distortions of the more diffuse charge distributions of the ions with smaller nuclear charges. The above argument also indicates that the TFF ansatz for ω should be poor for excited states. That this is indeed the case is verified by our calculations on excited states.[56]

In the absence of convergence studies and of values computed from wave functions of Pekeris-type accuracy we are unable to make quantitative error estimates for the remaining properties. They should, however, be useful, since no comparable calculations seem to be available in the literature.

Note that for $Z\leq 8$ G_1 is negative but for $Z>8$ it

TABLE VII. Parallelotope parameters, expectation values, and cusp-condition checks for the ions from Li^+ through N^{5+}.

	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}
N	45	25	25	25	25
A_1	2.9840	3.7640	4.7670	5.7070	6.6420
A_2	3.8310	4.8840	5.9260	7.1870	8.4460
B_1	2.0750	3.1960	3.4580	4.1870	4.9270
B_2	3.2710	4.4320	5.0240	6.1390	7.2600
G_1	−0.2570	−0.4120	−0.2810	−0.3960	−0.5090
G_2	2.5790	3.1840	4.5820	5.6080	6.6110
$1-\eta$	−1.767—8	−6.074—9	−6.004—9	−2.903—9	−3.254—9
$-E$	7.279 913 27	13.655 565 0	22.030 970 4	32.406 245 4	44.781 443 9
$\langle r^{-2}\rangle$	29.855 23	55.679 17	89.506 70	131.3342	181.1622
$\langle r^{-1}\rangle$	5.375 848 77	7.375 500 61	9.375 327 81	11.375 230 6	13.375 170 9
$\langle r\rangle$	1.145 548 33	0.828 566 830	0.649 111 369	0.533 587 601	0.452 984 671
$\langle r^2\rangle$	0.892 558 44	0.464 135 81	0.283 937 90	0.191 478 67	0.137 808 77
$\langle r^3\rangle$	0.882 558 7	0.328 440 6	0.156 515 7	0.864 576 1—1	0.526 970 5—1
$\langle r^4\rangle$	1.059 22	0.281 131	0.104 168	0.470 789—1	0.242 825—1
$\langle r_{12}^{-2}\rangle$	4.082 25	8.029 19	13.3075	19.9186	27.8625
$\langle r_{12}^{-1}\rangle$	1.567 719 8	2.190 872 5	2.814 698 3	3.438 893 0	4.063 308 3
$\langle r_{12}\rangle$	0.862 315 292	0.618 756 549	0.482 435 504	0.395 316 696	0.334 839 523
$\langle r_{12}^2\rangle$	0.927 064 28	0.477 947 16	0.290 791 20	0.195 363 20	0.140 219 12
$\langle r_{12}^3\rangle$	1.188 56	0.440 530	0.209 243	0.115 294	0.701 370—1
$\langle r_{12}^4\rangle$	1.7660	0.470 69	0.174 58	0.789 07—1	0.406 90—1
$\langle\cos\theta_{12}\rangle$	−0.436 321 37—1	−0.329 412 29—1	−0.264 373 66—1	−0.220 722 07—1	−0.189 418 40—1
α_d	0.192 258	0.522 424—1	0.196 380—1	0.896 196—2	0.465 477—2
$\langle\delta(\vec{r}_1)\rangle$	6.852 017	17.195 912	34.757 907	61.442 019	99.159 910
$\langle\delta(\vec{r}_{12})\rangle$	0.533 808	1.524 587	3.314 775	6.144 791	10.252 929
C_{EN}	3.000 098	3.998 591	4.999 827	5.999 730	6.999 632
C_{EE}	0.497 907	0.483 364	0.486 551	0.485 833	0.485 292

TABLE VIII. Parallelotope parameters, expectation values, and cusp checks for the ions from O^{6+} through Mg^{10+}.

	O^{6+}	F^{7+}	Ne^{8+}	Na^{9+}	Mg^{10+}
N	25	25	25	20	20
A_1	7.5800	8.7940	9.8000	11.0370	12.1410
A_2	9.6910	9.8720	10.6000	11.8600	12.9070
B_1	5.6790	7.3910	8.8100	10.3030	11.3090
B_2	8.3820	9.1490	10.0000	11.4990	12.4270
G_1	−0.6180	0.4850	0.6260	0.0904	0.4410
G_2	7.5910	5.9800	3.7600	4.9150	7.3430
$1-\eta$	2.348—9	−1.033—8	−1.735—7	−1.601—7	8.485—8
$-E$	59.156 593 8	75.531 710 8	93.906 802 4	114.281 879	136.656 944
$\langle r^{-2}\rangle$	238.9905	304.8203	378.6468	460.4830	550.3112
$\langle r^{-1}\rangle$	15.375 131 6	17.375 104 4	19.375 084 9	21.375 070 3	23.375 059 1
$\langle r\rangle$	0.393 543 432	0.347 895 504	0.311 738 189	0.282 389 885	0.258 092 574
$\langle r^2\rangle$	0.103 910 52	0.811 410 63—1	0.651 123 43—1	0.534 036 23—1	0.445 912 41—1
$\langle r^3\rangle$	0.344 599 1—1	0.237 558 3—1	0.170 639 0—1	0.126 670 4—1	0.965 993 3—2
$\langle r^4\rangle$	0.137 632—1	0.837 257—2	0.538 149—2	0.361 464—2	0.251 699—2
$\langle r_{12}^{-2}\rangle$	37.1395	47.7496	59.6946	72.9708	87.5802
$\langle r_{12}^{-1}\rangle$	4.687 865 0	5.312 517 9	5.937 243 8	6.562 015 1	7.186 820 6
$\langle r_{12}\rangle$	0.290 406 322	0.256 381 467	0.229 491 864	0.207 706 138	0.189 697 482
$\langle r_{12}^2\rangle$	0.105 507 51	0.822 530 18—1	0.659 174 10—1	0.540 050 52—1	0.405 523 78—1
$\langle r_{12}^3\rangle$	0.457 941—1	0.315 302—1	0.226 254—1	0.167 812—1	0.127 882—1
$\langle r_{12}^4\rangle$	0.230 56—1	0.140 21—1	0.901 00—2	0.605 01—2	0.421 18—2
$\langle \cos\theta_{12}\rangle$	−0.165 879 84—1	−0.147 538 69—1	−0.132 852 82—1	−0.120 810 25—1	−0.110 772 94—1
α_d	0.265 218—2	0.162 004—2	0.104 471—2	0.703 613—3	0.491 056—3
$\langle\delta(\vec{r}_1)\rangle$	149.821 756	215.344 766	297.612 966	398.605 860	520.140 668
$\langle\delta(\vec{r}_{12})\rangle$	15.877 968	23.257 758	32.643 199	44.247 599	58.326 082
C_{EN}	7.999 591	9.000 658	9.999 378	11.002 604	12.002 086
C_{EE}	0.484 777	0.486 389	0.479 460	0.483 004	0.481 670

is positive. In fact, negative γ_k's occur only for $Z \leq 5$. The inequalities of Eqs. (38) and (39) are invariably satisfied for $Z \leq 9$ but not always for $Z > 9$. These results are slightly surprising, and probably are artifacts of the optimization procedure used. The latter claim is supported by the fact that we encountered convergence problems with the optimization algorithm for atoms with nuclear charges greater than 9.

IV. DISCUSSION

In Sec. I it was pointed out that a goal of this work was to construct compact and accurate wave functions using a relatively simple basis set. Do the functions constructed in this work meet these requirements? We believe that they do. As pointed out earlier, the basis set used in this work is indeed simple, since the integrals required to compute a wide variety of properties [including lower bounds, $\rho(r)$ and $h(r_{12})$, and those properties presented in Sec. III] can be done analytically. Furthermore, it was shown in Sec. III that our wave functions yield rather accurate values for a host of properties, including the energy. It remains to examine how well our functions satisfy the criterion of compactness.

Let us consider the ground state of He. For lack of sufficient data in the literature we must restrict our attention to the energy. The 60-term function presented in Table II yields an energy of $-2.903\,724\,350$ a.u. Functions of the Pekeris type in perimetric coordinates would require roughly 400 terms to achieve similar accuracy, as indicated by the 252- and 444-term energies of $-2.903\,724\,290$ and $-2.903\,724\,356$ a.u., respectively.[2] With the scale parameter fully optimized, a Hylleraas-type function would require roughly 115 terms to attain similar accuracy. This is indicated by the recently computed 95- and 125-term energies of $-2.903\,724\,306$ and $-2.903\,724\,371$ a.u., respectively.[57] If half-integral powers of $r_1 + r_2$ are used in addition to the usual Hylleraas-type terms, then a 99-term function[11] yields an energy of $-2.903\,724\,349$ a.u. Finally, the complicated ansatz

$$\Psi(s,u,t) = \phi(ks,ku,kt)\ , \tag{41}$$

with

$$\phi = e^{-s/2} \sum_{n,l,m,i,j} C(n,l,m,i,j) s^n t^{2l} u^m \times (s^2 + t^2)^{i/2} (\ln s)^j \tag{42}$$

and $s = r_1 + r_2$, $t = r_2 - r_1$, and $u = r_{12}$, has been employed by Frankowski and Pekeris.[13] With 59 terms they obtained an energy of $-2.903\,724\,351$ a.u. Clearly the 60-term function of Table II and the Frankowski-Pekeris function are the two most compact functions available. For H^- the 60-term function of Table VI yields an energy of $-0.529\,775\,094$ a.u., which is close to the value of $-0.529\,775\,098$ a.u. obtained[13] with a 101-term function of the type given by Eqs. (41) and (42).

From the above comparisons it is evident that our functions are more compact than any others in the literature, with the exception of the Frankowski-Pekeris functions. The latter are, however, more complicated and more difficult to manipulate.

Why has it been possible for the present ansatz of Eq. (9) to yield such a combination of compactness, simplicity, and accuracy? We believe that this is chiefly due to the large number ($3N$) of nonlinear parameters in an N-term function of this type. The direct optimization of these $3N$ exponents would be a virtually impossible task. The generator-coordinate formalism has enabled the use of quadrature formulas to generate these exponents while optimizing only six parallelotope parameters. This latter optimization *cannot* be dispensed with. That this is so is evident from the energy of $-2.903\,724\,111$ a.u. for $1\,^1S$ He obtained[22] with a 165-term function of this type, with the quadrature domain chosen to be the totally positive octant of α-β-γ space. Note, however, that there seems to be little to choose between the Z and P schemes of this work. The P scheme is marginally more convenient because there is no restriction on the number of terms, N, that can be used. The Z scheme is, of course, restricted to those N for which "good lattice points" modulo N exist.[38]

Not surprisingly there is a price to be paid for the success of the method used in this paper. The higher roots of the secular equations provide very poor upper bounds to excited-state energies. Separate optimization of the integration domain seems to be necessary for each state that one wishes to study. Excited states are dealt with in detail in the next paper of this series.[56] Other problems that can arise during the computational stage include near-linear dependencies among the basis functions. These, however, can usually be overcome by not allowing the edges of the parallelotope to become too short.

A computational nuisance is that multiple-precision arithmetic is required in order to avoid loss of accuracy due to cancellation. This, however, is not at all surprising. Accad *et al.*[2] and Aashamar *et al.*[58] have also noted that the more flexible the basis set used, the more severe the loss of accuracy due to cancellation. In order to monitor these cancellations we calculated separately the positive and negative contributions to various expectation values. For the 60-term $1\,^1S$ He function it was found that the leading four to six significant figures of the positive and negative contributions canceled each other. It appears that if our calculations were to be extended to 100 or more terms, arithmetic of higher precision than that used by us (see Sec. II F) would be necessary.[59]

A number of avenues for future work seem promising. It may be worth investigating the possible use of the techniques described in this paper for variational-perturbation calculations of the Z^{-1} expansion for two-electron atoms.[60] Refinements of the basis set used in this work are possible. An interesting approach would be to use an ansatz of the form

$$\Psi(r_1, r_2, r_{12}) = (4\pi)^{-1} \sum_{k=1}^{N} C_k(1 \pm P_{12}) \exp(-\alpha_k r_1 - \beta_k r_2) \times (1 + \tfrac{1}{2} r_{12} e^{-\gamma_k r_{12}}) . \qquad (43)$$

The idea behind such an ansatz is to force the correct behavior of Ψ for small r_{12}. The correlation factor in Eq. (43) is given by Hirschfelder.[61] Another interesting question is how much improvement would be possible by adding a correction term to Eq. (9) [or for that matter to Eq. (43)] in an attempt to force the correct asymptotic behavior when one electron is far away from the nucleus. Such a correction term could be the Hulthen type:

$$\psi_{\text{add}} = C_{N+1}(1 \pm P_{12}) e^{-Z r_1} r_2^{-1} (e^{-\delta r_2} - e^{-\epsilon r_2}) , \qquad (44)$$

where $\delta = (2|I_p|)^{1/2}$, with I_p equal to the ionization potential; Z is the nuclear charge and ϵ is a parameter. Rotenberg and Stein[62] obtained a significant improvement by adding such a term to a Hylleraas-type ansatz. Equation (44) is only an approximation to the asymptotic behavior. A more sophisticated approach would be to use the complicated but rigorous asymptotic form given by Slaggie and Wichmann.[63] Yet another approach would be to use the scheme suggested by Armstrong,[64] which is based on a zero-momentum Fourier analysis.

Finally, it would be useful to analyze the wave functions constructed in this work by one of the techniques mentioned in Sec. I. Analysis of the intracule function $h(r_{12})$ is underway in our laboratory.

ACKNOWLEDGMENTS

This research was supported in part by a grant from the National Research Council of Canada. We wish to thank Professor G. L. Hofacker for his hospitality at the Technical University of Munich. A portion of the work was carried out while the authors were guests of the Molecular

Physics Group of the Max Planck Institute for Physics and Astrophysics. The interest of Dr. E. Trefftz and Dr. G. H. Diercksen is gratefully acknowledged.

APPENDIX

In order to compute $\langle r^{-2}\rangle$ and $\langle r_{12}^{-2}\rangle$ from wave functions of the type used in this work [cf. Eq. (9)] certain integrals which require careful handling are encountered. Their computation is described below.

Define

$$I(a,b,c;l,m,n) = (4\pi)^{-2}\int dv_1\, dv_2 \exp[-ar_1 - br_2 - cr_{12}] \times r_1^{l-1} r_2^{m-1} r_{12}^{n-1}\,, \tag{A1}$$

where $a+b>0$, $a+c>0$, and $b+c>0$. For $l, m, n \geq 0$ these integrals can easily be computed by the recursion scheme given by Sack *et al.*[28] However, $I(a,b,c;-1,1,1)$, $I(a,b,c;1,-1,1)$, and $I(a,b,c;1,1,-1)$ are also needed. Note that only $I(a,b,c;-1,1,1)$ need be considered, since, by symmetry arguments, we have

$$I(a,b,c;1,-1,1) = I(b,a,c;-1,1,1)\,, \tag{A2}$$

$$I(a,b,c;1,1,-1) = I(c,b,a;-1,1,1)\,. \tag{A3}$$

Transforming to perimetric coordinates and bearing the Frullanian character[65] of the integral in mind, it can be shown that

$$I(a,b,c;-1,1,1) = \frac{2}{(b^2-c^2)^2}\left[\frac{b}{(a+c)} + \frac{c}{(a+b)} - \frac{4bc}{(b^2-c^2)}\ln\left(\frac{a+b}{a+c}\right)\right]\,. \tag{A4}$$

When $|(b-c)/(a+c)| = |\tau|$ becomes small, formula (A4) is numerically unstable and hence we expand the logarithm to obtain an alternative form,

$$I(a,b,c;-1,1,1) = \frac{2}{(b+c)^3}\left\{\frac{1}{(a+b)}\left[1 + \frac{b}{(a+c)} + \frac{2bc}{(a+c)^2}\right] - \frac{4bc}{(a+c)^3}\,\mathcal{S}\right\}\,, \tag{A5}$$

where

$$\mathcal{S} = \sum_{k=3}^{\infty} \frac{(-1)^{k+1}}{k}\,\tau^{k-3}\,. \tag{A6}$$

The series $\mathcal{S}$ converges fairly rapidly for small values of $|\tau|$ and, if necessary, can easily be accelerated with the Euler transformation.[66] Equation (A4) for $|\tau| > 0.1$ and Eqs. (A5) and (A6) for $|\tau| \leq 0.1$ provided satisfactory computational access to $I(a,b,c;-1,1,1)$ for all values of a, b, and c encountered in this work.

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