Boundary-condition-determined wave function for the ground state of helium and isoelectronic ions

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A simple nonvariational wave function for two electron atoms is described. The radial part is derived from the asymptotic one-electron wave functions that are modified to account for the proper core boundary conditions. The electron-electron correlation is described by an ansatz which has the correct behavior for $r_{12} \to 0$ and $r_{12} \to \infty$. The additional parameter in this ansatz is calculated from a perturbation calculation. This wave function yields ground-state energies for the heliumlike atoms with $Z = 1$ (H$^-$) to 10 (Ne^{8+}) within 0.0021–$0.0068 E_h$ of the exact energies, which is significantly better than obtained with previous models. We also calculated $\langle r^{2n} \rangle$ and multipolar polarizabilities and performed other tests on this wave function. [S1050-2947(96)08510-1]

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I. INTRODUCTION

As the simplest of all quantum systems in which electron-electron correlation has an important effect, the wave functions of two-electron atoms and ions have been investigated ever since the early days of quantum mechanics in great detail [1]. Once this fundamental problem is fully understood the experience gained can be applied to more complicated many-electron systems. These wave functions are needed not only to understand the properties of the free particles but also to describe the behavior of these systems in the presence of external fields, and their interaction with each other and with other systems. A recent particularly interesting application is the demonstration that the He-He van der Waals potential can be fully determined knowing only the ionization energy, the precise asymptotic behavior of the free helium atom wave function, and the dispersion coefficients [2].

The most accurate wave functions of two-electron systems are obtained from variational calculations. A few examples of this approach are the calculations of Chandrasekhar and Herzberg [3], Frankowski and Pekeris [4], and Freund *et al.* [5]. For two-electron systems even high-precision calculations including relativistic and QED corrections can be carried out [6]. However, for a deeper understanding of the atomic properties, it is desirable to have simple, analytic wave functions which can account for the essential important physical features of the exact wave functions. Here we mention several recent efforts in this direction. A systematic expansion in powers of the hyperspherical radius $R = (r_1^2 + r_2^2)^{1/2}$ and $\ln R$, usually designated as the Fock expansion [7], which is especially accurate for small R and formally solves the Schrödinger equation [8], has been considered for two-electron systems [9–11]. In another approach [12], asymptotic wave functions have been obtained by considering a large-r expansion after separating out the leading exponential term. In more recent work [13–15], correlation has been incorporated by including the cusp factor as first suggested by Hirschfelder [16]. While all these approaches have some positive aspects, none of them appears to incorporate all the correct features of the exact wave function.

In Sec. II we review some general properties of the exact two-electron wave function. Then in Sec. III we propose a simple radial wave function which satisfies these important local properties. An ansatz for a correlation function which correctly accounts for the electron-electron interaction in the two limits $r_{12} \to 0$ and $r_{12} \to \infty$ is described. The additional parameter λ of this correlation function is calculated in Sec. IV. In Sec. V we use this wave function to calculate the ground state energies of the two electron systems H$^-$, He, Li$^+$, ..., Ne^{8+}. This wave function yields ground state energies which agree between 0.0021–$0.0068 E_h$ with the exact energies. This wave function is also used to calculate $\langle r^{2n} \rangle$ and multipolar polarizabilities. The reliability of the wave function is demonstrated by subjecting it to several critical tests. Atomic units are used throughout.

II. SOME GENERAL PROPERTIES OF EXACT EIGENFUNCTIONS

The exact eigenstates of the atomic Hamiltonian have several well known properties. For example, the expectation value of the Hamiltonian has a minimum at the exact eigenfunction. Similarly, the virial theorem can be used to relate the average kinetic and potential energies. These properties, which are called global properties, have been the basis of many variational calculations. Here, however, our interest is in the local properties such as the spatial behavior of the wave functions in specific regions of configuration space. By analyzing these properties and incorporating each of them, we have constructed an optimized but simple wave-function which has the proper behavior in all regions.

The *s*-states of a two-electron atom or ion are described by the Hamiltonian

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$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{1}$$

In our approach the wave function is separated into two parts,

$$\Psi(r_1, r_2, r_{12}) = \Phi(r_1, r_2) \times f(r_{12}), \tag{2}$$

where the second factor, which depends only on r_{12}, is called the correlation function $f(r_{12})$. This approximation was already introduced by Hylleraas [17] and used often afterwards [18]. The total wave function of Eq. (2) must satisfy the following three local properties: it has to fulfill specific boundary conditions as either r_1 or r_2 go to zero. On the other hand, if either r_1 or r_2 goes to infinity, the wave function must satisfy the well known asymptotic conditions. If r_{12} goes to zero and the two electrons coalesce, the well-known correlation cusp condition has to be fulfilled. Finally as r_{12} goes to infinity $f(r_{12})$ has to equal unity.

A. Small-r behavior of the total wave function

When r_1 goes to 0, the two leading terms in the Hamiltonian are $\frac{1}{2}\nabla_1^2$ and $-Z/r_1$. From this, one can show that the total wave function of an s-state should start off as [19]

$$\Psi \xrightarrow{\ r_1 \to 0\ } g_0(r_2)(1 - Zr_1). \tag{3a}$$

Similarly

$$\Psi \xrightarrow{\ r_2 \to 0\ } g_0(r_1)(1 - Zr_2), \tag{3b}$$

where $g_0(r_2)$ and $g_0(r_1)$ are only functions of r_2 and r_1, respectively.

These equations follow from Kato's theorem [20] of electron-nucleus coalescence,

$$\lim_{r \to 0}\left(\frac{\partial \Psi}{\partial r}\right)_{av} = -Z\Psi(r=0), \tag{4}$$

where r can be either r_1 or r_2 and ''av'' stands for spherical averaging. Thus the exact eigenfunctions must satisfy these boundary conditions at small values of r_1 and of r_2. For the wave function of Eq. (2) these conditions must be fulfilled by $\Phi(r_1, r_2)$.

B. Large-r behavior of the total wave function

When r_1 goes to ∞, electron 1 is essentially in the Coulomb field of the nucleus shielded by electron 2. Therefore the wave function of electron 1 is determined by its long range asymptotic form which is a Whittaker function [12,21–23]. The leading term is

$$\Psi \xrightarrow{\ r_1 \to \infty\ } \frac{A}{\sqrt{4\pi}} g_1(r_2) r_1^{(Z-1)/\beta - 1} e^{-\beta r_1}, \tag{5}$$

where $\beta = \sqrt{2E_I}$, E_I is the first ionization energy, and A is the asymptotic normalization constant. For $r_1 \to \infty$ the total

energy of the system is $E = -Z^2/2 - E_I$, since $-Z^2/2$ is the energy of the one electron ion core. Therefore β can be written as

$$\beta = \sqrt{-Z^2 - 2E}. \tag{6}$$

Furthermore, the wave function of the residue system is hydrogenic with a nucleus of charge Z,

$$g_1(r_2) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr_2}. \tag{7}$$

Thus it follows from Eq. (5) that

$$\Psi \xrightarrow{\ r_1 \to \infty\ } \frac{Z^{3/2}}{2\pi} A e^{-Zr_2} r_1^{(Z-1)/\beta - 1} e^{-\beta r_1}. \tag{8a}$$

Similarly

$$\Psi \xrightarrow{\ r_2 \to \infty\ } \frac{Z^{3/2}}{2\pi} A e^{-Zr_1} r_2^{(Z-1)/\beta - 1} e^{-\beta r_2}, \tag{8b}$$

where A is the normalization for the asymptotic function. Of course, there are other properties such as relations for higher partial waves similar to Eq. (3) or higher order terms in Eq. (5). They may be important, if higher precision is required [23]. Again with the ansatz of Eq. (2) the asymptotic conditions have to be fulfilled by $\Phi(r_1, r_2)$.

C. The electron-electron correlation function

Clearly in the region where r_{12} is very small relative to r_1 and r_2, the r_{12}^{-1} term will dominate the potential. Kato [20] formally and rigorously showed that

$$\lim_{r_{12} \to 0}\left(\frac{\partial \Psi}{\partial r_{12}}\right)_{av} = \frac{1}{2}\Psi(r_{12} = 0), \tag{9}$$

where the factor of 1/2 is because of the reduced mass of the two electrons, and their charges being both negative. This condition is known as the correlation cusp. As a consequence of Eq. (9) the wave function at small r_{12} must start off as [24]

$$\Psi \xrightarrow{\ r_{12} \to 0\ } \Phi(r_1, r_2) \cdot \left(1 + \frac{1}{2} r_{12} + \cdots\right), \tag{10}$$

where Φ is independent of r_{12}. According to Eq. (10) the logarithmic derivative is equal to $\frac{1}{2}$ at $r_{12} = 0$. Although the wave function may not go to zero for $r_{12} \to 0$ the radial probability density does. This can be easily seen using the coordinate set (r_1, r_2, r_{12}) in which the volume element is proportional to r_{12}.

From Eq. (10) it follows that the simplest correlation function is [25]

$$f(r_{12}) = 1 + \frac{1}{2} r_{12}. \tag{11}$$

This approximate correlation function has recently been used in variational CI quantum chemistry calculations [26–28]. Since this function increases linearly without bound it can give good results only in cases where the wave function is

compact, i.e., the function $\Phi(r_1,r_2)$ is already very small in places where r_{12} becomes large compared to 1. To remove this limitation Hirschfelder [16] proposed a correlation function

$$f(r_{12})=1+\frac{r_{12}}{2}e^{-r_{12}/d} \qquad (12)$$

with d as a variational parameter. This correlation function increases with r_{12} up to $r_{12}=d$, and then decreases reaching an asymptotic value which is the same as the value at $r_{12}=0$. Since there is no *a priori* reason why the correlation function should have a local maximum, the behavior of Eq. (12) is not completely realistic. Nevertheless, this function has been used with some success in several recent calculations [13].

Roothaan and Weiss [29] made a very accurate numerical investigation of the correlation function for the ground state of the He atom. They found that in the vicinity of $r_{12}=0$, the correlation function is linear and satisfies the cusp condition of Eq. (9). It monotonically increases and approaches unity as r_{12} becomes very large [30]. To satisfy both these requirements Parr [31] suggested a piecewise model function,

$$f(r_{12})=\begin{cases}1+gr_{12} & \text{for }r_{12}\leqslant D\\ 1+gD & \text{for }r_{12}\geqslant D.\end{cases} \qquad (13)$$

This function, however, has the disadvantage that the derivative is discontinuous at $r_{12}=D$. As far as we are aware, calculations based on this correlation function have not been reported in the literature. Other, in most cases more complicated, correlation functions have been proposed in literature [32].

In this paper, we propose the following simple correlation function which has the desired properties at $r_{12}=0$ and $r_{12}=\infty$:

$$f(r_{12})=1-\frac{1}{1+2\lambda}e^{-\lambda r_{12}}, \qquad (14)$$

where λ is a variational parameter. Its small r_{12} expansion is

$$f(r_{12})=\frac{2\lambda}{1+2\lambda}\left(1+\frac{1}{2}r_{12}-\frac{\lambda}{4}r_{12}^2+\cdots\right), \qquad (15)$$

so that it satisfies the cusp condition of Eq. (9). On the other hand, as r_{12} becomes large the function Eq. (14) has the desirable feature that it increases monotonically to unity. In the following section we describe how Eq. (14) facilitates the calculation of the ground state energy of two electron atomic systems. In a forthcoming paper, we will use this function to treat the electron-electron correlation in the surface integral method for the exchange energy in a molecular system.

III. A MODEL WAVE FUNCTION

A wave function satisfying the boundary conditions and properties expressed by Eqs. (3), (8), and (14) can be expected to provide a realistic description of the spatial dependence of the wave function in the entire configuration space of the electrons. Consistent with the ''different orbitals for different spins'' approach [33] we therefore propose the fol-

lowing total wave function which has all these three properties for the ground state:

$$\begin{aligned}\Psi(r_1,r_2,r_{12})&=\Phi(r_1,r_2)f(r_{12})\\ &=B[e^{-Zr_1}(1+cr_2)^{(Z-1)/\beta-1}e^{-\beta r_2}\\ &\quad+e^{-Zr_2}(1+cr_1)^{(Z-1)/\beta-1}e^{-\beta r_1}]\\ &\quad\times\left(1-\frac{1}{1+2\lambda}e^{-\lambda r_{12}}\right),\end{aligned} \qquad (16)$$

where B is related to the normalization constant A of the asymptotic wave function by

$$B=\frac{AZ^{3/2}}{2\pi}c^{1-(Z-1)/\beta}. \qquad (17)$$

The only additional parameter c is determined below from the small-r limiting behavior. Note that Eq. (16) is symmetric with respect to the interchange of r_1 and r_2. To determine c we expand Eq. (16) in the region of small r_1 (or r_2),

$$\begin{aligned}\Psi\xrightarrow{r_1\to0}&\left\{(1-Zr_1+\cdots)(1+cr_2)^{(Z-1)/\beta-1}e^{-\beta r_2}\right.\\ &\quad+\left(1+c\left[\frac{Z-1}{\beta}-1\right]r_1+\cdots\right)(1-\beta r_1+\cdots)e^{-Zr_2}\right\}\\ &\quad\times\left(1-\frac{1}{1+2\lambda}e^{-\lambda r_{12}}\right)\\ =&\left((1-Zr_1+\cdots)(1+cr_2)^{(Z-1)/\beta-1}e^{-\beta r_2}\right.\\ &\quad+\left\{1+\left[c\left(\frac{Z-1}{\beta}-1\right)-\beta\right]r_1+\cdots\right\}e^{-Zr_2}\right)\\ &\quad\times\left(1-\frac{1}{1+2\lambda}e^{-\lambda r_{12}}\right).\end{aligned} \qquad (18)$$

Then the electron-nucleus coalescence condition of Eq. (3) is only satisfied if

$$c\left(\frac{Z-1}{\beta}-1\right)-\beta=-Z. \qquad (19)$$

Therefore c becomes

$$c=\frac{(\beta-Z)\beta}{Z-\beta-1}. \qquad (20)$$

Finally we call attention to the fact that the wave function in Eq. (16) with β given by Eq. (6) and c by Eq. (20) has all the required properties discussed in Sec. II, i.e., the correct behavior for r_1 or $r_2\to0$ and ∞, and for $r_{12}\to0$ and ∞. Only one parameter λ remains, which may be determined variationally or from some other considerations as discussed in the next section.

TABLE I. The energies and parameters for heliumlike atoms from the present wave function with λ calculated by Eq. (31) and from a variational calculation. The fraction of the correlation energy (Corr.) recovered by the present calculations is calculated as $[E(\text{present})-E(\text{HF})]/[E(\text{exact})-E(\text{HF})]$. The Hartree-Fock energies $E(\text{HF})$ are taken from Ref. [42] and the exact energies from Ref. [37]. All energies are in atomic units.

System	Z	λ determined by Eq. (31)			λ determined variationally			$-E(\text{exact})$
		λ	$-E(\text{present})$	Corr.	λ	$-E(\text{present})$	Corr.	
H^-	1	0.083	0.5257	95%	0.155	0.5265	97%	0.5278
He	2	0.50	2.9000	91%	0.48	2.9000	91%	2.9037
Li^+	3	0.92	7.2749	89%	0.86	7.2749	89%	7.2799
Be^{2+}	4	1.33	13.6499	87%	1.24	13.6499	87%	13.6556
B^{3+}	5	1.75	22.0249	87%	1.63	22.0249	87%	22.0310
C^{4+}	6	2.17	32.4000	86%	2.02	32.4000	86%	32.4062
N^{5+}	7	2.58	44.7750	86%	2.41	44.7750	86%	44.7814
O^{6+}	8	3.00	59.1500	85%	2.80	59.1500	85%	59.1566
F^{7+}	9	3.42	75.5250	85%	3.19	75.5250	85%	75.5317
Ne^{8+}	10	3.83	93.9000	85%	3.61	93.9000	85%	93.9068

IV. THE CORRELATION PARAMETER λ

The customary way to determine the only remaining parameter λ is to invoke the variational method and determine the energy E self-consistently. First, with an assumed β (for example, $\beta=Z$), we vary λ until a minimum in the energy E calculated according to

$$E = \frac{-\langle\Psi|\nabla_1^2|\Psi\rangle + 2Z\left\langle\Psi\left|\frac{1}{r_1}\right|\Psi\right\rangle + \left\langle\Psi\left|\frac{1}{r_{12}}\right|\Psi\right\rangle}{\langle\Psi|\Psi\rangle} \tag{21}$$

is achieved. With this E, we calculate β according to Eq. (6) and then repeat the process. This iteration converges quickly, usually after two or three cycles. The calculations of the matrix elements in Eq. (21) are straightforward, and some of the details are given in the Appendix. The only input parameter for different systems is the nuclear charge Z. Values of λ and the corresponding energies are listed in Table I.

Next we show that in fact λ can be determined analytically. For this we split the Hamiltonian into a perturbation, which is $1/r_{12}$, and a zeroth-order Hamiltonian given by the remaining terms in Eq. (1). The wave function $\Phi(r_1,r_2)$ is assumed to be the eigenfunction of this zeroth-order Hamiltonian so that the total wave function is given by

$$\Psi(r_1,r_2,r_{12}) = \Phi_0(r_1,r_2)f(r_{12}) = e^{-Z(r_1+r_2)}f(r_{12}). \tag{22}$$

This approximate wave function has the correct small-r behavior but the asymptotic, $r\rightarrow\infty$ condition is not properly fulfilled. Inserting Eq. (22) into the Schrödinger equation with the full Hamiltonian, we obtain

$$E\Psi = E_0\Psi - \frac{1}{2}\Phi_0\nabla_1^2 f - \frac{1}{2}\Phi_0\nabla_2^2 f + (\vec{\nabla}_1\Phi_0)\cdot(\vec{\nabla}_1 f)$$

$$+ (\vec{\nabla}_2\Phi_0)\cdot(\vec{\nabla}_2 f) + \frac{1}{r_{12}}\Psi \tag{23}$$

with the eigenenergy $E_0=-Z^2$ of the zeroth-order Hamiltonian. The terms $\vec{\nabla}_1\Phi_0$ and $\vec{\nabla}_2\Phi_0$ are easily calculated. After dividing both sides by Φ_0, a differential equation for $f(r_{12})$ is then obtained,

$$(E-E_0)f = -\frac{1}{2}\nabla_1^2 f - \frac{1}{2}\nabla_2^2 f - Z\frac{\vec{r_1}}{r_1}\cdot(\vec{\nabla}_1 f) - Z\frac{\vec{r_2}}{r_2}\cdot(\vec{\nabla}_2 f)$$

$$+ \frac{1}{r_{12}}f. \tag{24}$$

To solve for $f(r_{12})$ in the limit $r_{12}\rightarrow 0$, $f(r_{12})$ is assumed to be a regular function for small r_{12} and can therefore be written as a power series,

$$f(r_{12}) = \sum_i c_i r_{12}^i. \tag{25}$$

Thus Eq. (24) becomes

$$-\frac{1}{2}\sum_i c_i i(i+1)r_{12}^{i-2} - \frac{Z}{2}\left(\frac{\vec{r_1}\cdot\vec{r_{12}}}{r_1} - \frac{\vec{r_2}\cdot\vec{r_{12}}}{r_2}\right)\sum_i c_i i r_{12}^{i-2}$$

$$+ \sum_i c_i r_{12}^{i-1} = (E-E_0)\sum_i c_i r_{12}^i. \tag{26}$$

With the expansion $r_2 = r_1 - \vec{r_1}\cdot\vec{r_{12}}/r_1 + \cdots$ one can show that the second term in Eq. (26) is of order $O(r_{12})$. Equating all terms proportional to r_{12}^{-1} in Eq. (26) yields

$$c_1 = \frac{1}{2}c_0, \tag{27}$$

which is equivalent to Kato's cusp condition Eq. (9). Equating the terms proportional to 1 yields

$$c_2 = \frac{1}{6}\left(\frac{1}{2} - (E-E_0)\right)c_0. \tag{28}$$

TABLE II. The present values for the expectation values $\langle r^{2n} \rangle$, dipolar and quadupolar polarizabilities, along with the predictions of some other calculations which are enclosed in parentheses.

	$\langle r^2 \rangle$	$\langle r^4 \rangle$	$\langle r^6 \rangle$	α_1	α_2
He	2.329	7.262	4.45×10^1	1.33	2.01
	(2.39)	(7.93)[a]	(5.03×10^1)[b]	(1.38)[a]	(2.44)[a]
	(2.34)	(7.6)[b]		(1.37)[b]	
Li$^+$	0.874	0.979	2.08	0.184	9.54×10^{-2}
	(0.892)[a]	(1.03)[b]	(2.35)[b]	(0.192)[a]	(1.11×10^{-1})[b]
	(0.88)[b]			(0.190)[b]	
Be^{2+}	0.456	0.264	0.287	5.06×10^{-2}	1.33×10^{-2}
	(0.455)[b]	(0.272)[b]	(0.315)[b]	(5.1×10^{-2})[b]	(1.49×10^{-2})[b]
B^{3+}	0.280	9.89×10^{-2}	6.54×10^{-2}	1.91×10^{-2}	3.04×10^{-3}
C^{4+}	0.189	4.50×10^{-2}	2.00×10^{-2}	8.74×10^{-3}	9.36×10^{-4}

[a]Reference [43].
[b]Reference [12].

This equation contains the unknown energy difference $(E - E_0)$ which can be approximated by its perturbative value

$$E - E_0 = \left\langle \Phi_0(r_1, r_2) \left| \frac{1}{r_{12}} \right| \Phi_0(r_1, r_2) \right\rangle = \frac{5Z}{8}. \quad (29)$$

We thus have

$$c_2 = \frac{1}{12} \left(1 - \frac{5Z}{4} \right) c_0. \quad (30)$$

With c_1 and c_2 determined in Eq. (27) and Eq. (30) a direct comparison with the expansion of the correlation function Eq. (15) becomes possible. The unknown parameter λ is calculated to be

$$\lambda = \frac{5}{12} Z - \frac{1}{3}. \quad (31)$$

Thus in this approximation λ is a simple linear function of Z. It may be noted that since the perturbative value in Eq. (29) is more accurate for larger values of Z, the expression for λ in Eq. (31) is particularly accurate for larger values of Z.

V. RESULTS

We now present the results of the calculations of the energies, expectation values $\langle r^{2n} \rangle$, and dipolar and quadrupolar polarizabilities for the two-electron isoelectronic sequence, using our wave function in Eq. (16) with the parameters defined in Eqs. (6), (20), and (31). The parameter β, which depends on the ionization energy of the system, is determined iteratively.

A. Energies

The values of the energies for the two-electron isoelectronic sequence with $Z = 1 - 10$ calculated for λ determined from Eq. (31), and variationally, are listed in Table I. The difference in the energies for these two calculations is so small for $Z = 2 - 10$ that it does not appear within the five significant figures given in Table I. Only in the case of H$^-$ is

there a slight difference. The present results are, to the best of our knowledge, the lowest parameter-free energies that have been reported up to now. Our results are much better than the simplest conventional one-parameter variational calculation which introduces an effective nuclear charge [34]. They are also far superior to other more involved one-parameter calculations [35,36]. Particularly striking is the nonvariational energy of $-0.5257 E_h$ for H$^-$, which is very close to the exact result of $-0.5278 E_h$ [37]. The present value should be compared with the earlier two-parameter results of $-0.506 E_h$ [38] and $-0.5206 E_h$ [39] and the three-parameter results of $-0.5213 E_h$ [40] and $-0.5254 E_h$ [41]. The importance of the asymptotic condition for H$^-$ was already seen in a former one-parameter calculation, reported by one of the present authors, which gave an energy of $-0.5226 E_h$ [36]. The present nonvariational calculation recovers 95% of the correlation energy defined as the difference between the exact [37] and the HF [42] energies. This is improved to 97% by using λ as a variational parameter $(E = -0.5265 E_h)$.

B. Expectation values $\langle r^{2n} \rangle$

Some important and useful properties of atomic isoelectronic sequences are the expectation values of r^{2n}. We have presented the values for these quantities, obtained from our nonvariational wave functions, in Table II, along with the results of other calculations. In particular, the expectation value $\langle r^2 \rangle$ is known to be equal to 6χ, where χ is the diamagnetic susceptibility. For He, Li$^+$, and Be^{2+}, for which other values have been reported [43,12], there is good agreement. Previous results for B^{3+} and C^{4+} are not available.

C. Multipolar polarizabilities

Our wave functions can be used to calculate multipolar polarizabilities. In the presence of a multipolar potential, the perturbed part of the wave function, $\delta\Psi(r_1, r_2, r_{12})$, satisfies the inhomogeneous equation

$$(E_0 - H_0)\delta\Psi = [r_1^l P_l(\cos\theta_1) + r_2^l P_l(\cos\theta_2)]\Psi(r_1, r_2, r_{12}), \quad (32)$$

where $\Psi(r_1, r_2, r_{12})$ is the unperturbed wave function given in Eq. (16). We obtain the first two terms for $\delta\Psi$ in the asymptotic expansion,
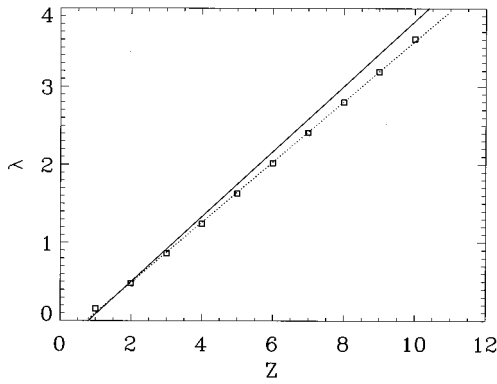
FIG. 1. The two sets of values for the parameter λ are plotted against the nuclear charge Z. The solid line is calculated using Eq. (31). The variational points (squares) can be fitted by a straight line $\lambda = 0.386 \times Z - 0.283$ (dashed). All quantities are in atomic units.

$$
\delta \Psi = - \left[\left\{ \frac{1}{(l+1)\beta} r_1 + \frac{(Z-1)[2l+1+(Z-1)/\beta]}{2\beta^3 l(l+1)} \right\} \right.
$$
$$
\times r_1^l P_l(\cos\theta_1) + \left\{ \frac{1}{(l+1)Z} r_2 + \frac{1}{lZ^2} \right\} r_2^l P_l(\cos\theta_2) \right]
$$
$$
\left. \times (1+cr_1)^{(Z-1)/\beta-1} e^{-\beta r_1} e^{-Z r_1} f(r_{12}) + (r_1 \leftrightarrow r_2). \right.
$$
$$
(33)
$$

The multipolar polarizability α_l is given by

$$
\alpha_l \langle \Psi | \Psi \rangle = \left(\frac{4}{2l+1} \right) \int \Psi(r_1, r_2, r_{12})
$$
$$
\times \left[\left\{ \frac{1}{(l+1)\beta} r_1 + \frac{(Z-1)[2l+1+(Z-1)/\beta]}{2\beta^3 l(l+1)} \right\} \right.
$$
$$
\times r_1^{2l} + \left\{ \frac{1}{(l+1)Z} r_2 + \frac{1}{lZ^2} \right\} r_2^{2l} \right]
$$
$$
\left. \times (1+cr_1)^{(Z-1)/\beta-1} e^{-\beta r_1} e^{-Z r_1} f(r_{12}) d^3 r_1 d^3 r_2. \right.
$$
$$
(34)
$$

Here we have left out the cross-terms which are expected to be unimportant. The values of the polarizabilities obtained for $l=1,2$ are given in Table II, along with the results of some other calculations [43,12]. Again the agreement with other work is quite satisfactory.

D. Dependence of the correlation function on Z

In Fig. 1 we have plotted the λ-values given by Eq. (31) and those from the variational calculation as a function of the nuclear charge Z. The variational results can be fitted very well by a straight line $\lambda = 0.386 \times Z - 0.283$ which comes close to the perturbation calculation Eq. (31), $\lambda = 0.417 \times Z - 0.333$. Although, as shown in Fig. 1 the two sets of λ-values differ somewhat from each other, only in the case of H$^-$ is there a significant difference in the energies.

As a result of the linear increase of λ with Z, the relative effect of the correlation becomes less important for heavier multiple charged ions. This is also confirmed in Fig. 2, where the correlation function is plotted for the different nuclear
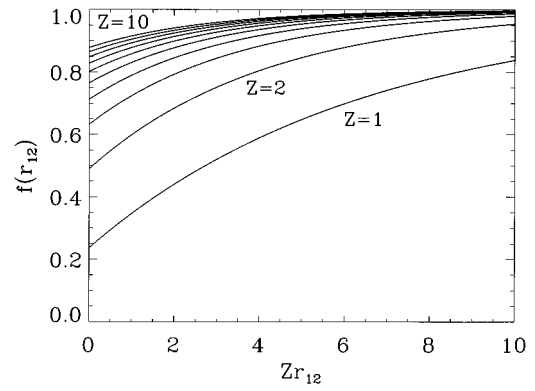

FIG. 2. The correlation functions are plotted against Zr_{12} for Z from 1 to $10a_0$. λ was calculated using Eq. (31). The correlation functions are normalized to 1 for $r_{12} \to \infty$. The slope at $r_{12}=0$ is $\lambda/(1+2\lambda)$. All quantities are in atomic units.

charges. The small value of λ for H$^-$ seen in Fig. 2 indicates that the long range behavior of the correlation function is most important in this diffuse system whose two electrons are least tightly bound to the nucleus. Thus H$^-$ provides the most exacting test of the new correlation function. For larger Z, the values of the correlation function at $r_{12}=0$ approach 1. Since the total energy increases rapidly with Z^2 but the correlation energy is almost the same for all Z [42], the relative importance of correlation decreases with increasing Z. This is clearly illustrated in Fig. 2.

VI. DISCUSSION AND CONCLUSIONS

There are several properties which a good wave function must possess. Of course the expectation value of the Hamiltonian must be close to the eigenvalue. However, the expectation value is rather insensitive to the large-r region, except in the case of H$^-$, and hence is usually not a very good indicator of the overall quality of the wave function. We consider other, more detailed tests.
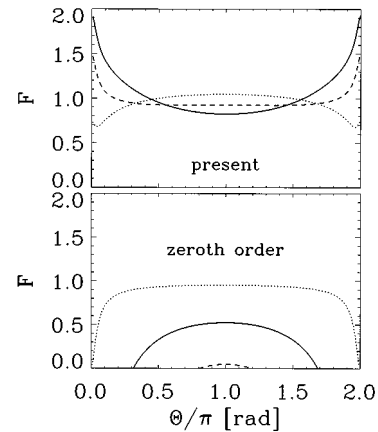

FIG. 3. The local energy test for H$^-$. The ratio between r_2 and r_1 is 1.1. The solid line shows F for $r_1=0.5$, the dashed line for $r_1=1$, and the dotted line for $r_1=10$. The upper panel shows the local energy for the present wave function Eq. (16) with λ from Eq. (31) and the lower one for the zeroth order wave function $\Psi = Z^3 e^{-Z(r_1+r_2)}/\pi$.
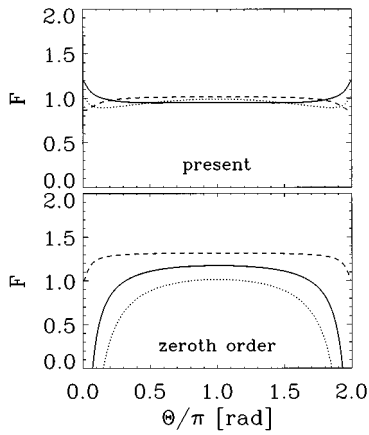
FIG. 4. The same as in Fig. 3 for He.

A. Local energy test

In the local energy test, or more descriptively, local satisfaction of the Schrödinger equation, one considers the function [44]

$$F(r_1, r_2, r_{12}) = \frac{H\Psi}{\langle \Psi | H | \Psi \rangle \Psi}. \tag{35}$$

If the trial wave function is a good wave function, the function $F(r_1, r_2, r_{12})$ should be 1 everywhere. The function is plotted in Figs. 3 and 4 for H^- and He, respectively, as a function of the angle Θ between $\vec{r}_1$ and $\vec{r}_2$ for three different values of r_1 and a constant ratio $r_2/r_1 = 1.1$. It is observed to be close to 1 except for angles Θ close to 0 or 2π. This is the region where the two electrons come closest to each other and the electron density is small there anyway.

Also plotted in Figs. 3 and 4 are the same functions F for an uncorrelated zeroth order wave function $\Psi = Z^3 e^{-Z(r_1 + r_2)}/\pi$. In this case F is simply given by

$$F(r_{12}) = \frac{-Z^2 + \dfrac{1}{r_{12}}}{-Z^2 + \dfrac{5Z}{8}}. \tag{36}$$

The figures show that the function F for the present wave function is much closer to 1 than the function F for the zeroth order wave function. This local energy test is certainly

an indicator of the good quality of our wave function, in particular, the correlation function we have proposed.

B. Virial theorem and the correlation test

If the wave functions are exact eigenstates, then they must satisfy the condition

$$\langle \Psi | [H, O] | \Psi \rangle = 0, \tag{37}$$

where O is any operator. This can be used as a test for the quality of the model wave function. If O is $\vec{r}_1 \cdot \vec{p}_1 + \vec{r}_2 \cdot \vec{p}_2$, then Eq. (37) leads to the virial theorem. For our problem, this is

$$\langle (p_1^2 + p_2^2) \rangle = Z \left\langle \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right\rangle - \left\langle \frac{1}{r_{12}} \right\rangle. \tag{38}$$

The term on the left is proportional to the average kinetic energy and the term on the right is the average potential energy. The first two columns of Table III list the present potential energies and the ratios between the two energies for four systems. The good agreement with the result for the exact wave function, which is 2, is again an indicator of the good quality of our wave functions.

If we take $O = \vec{r}_1 \cdot \vec{p}_2 + \vec{r}_2 \cdot \vec{p}_1$, one obtains the relation [45]

$$2 \langle \vec{p}_1 \cdot \vec{p}_2 \rangle = Z \left\langle \vec{r}_1 \cdot \vec{r}_2 \left(\frac{1}{r_1^3} + \frac{1}{r_2^3} \right) \right\rangle + \left\langle \frac{1}{r_{12}} \right\rangle. \tag{39}$$

This relation, which may be regarded as a generalization of the virial theorem, can only be satisfied by wave functions which correctly account for the correlation. For example, in the independent particle approximation, the left-hand side and the first term on the right-hand side are both zero whereas $\langle 1/r_{12} \rangle$ is not zero, so this relation is not satisfied. In Table III we have also listed the calculated values of the two sides for different members of the isoelectronic sequence. The near equality of the two sides except for H^- is a strong indication of the reliability of our wave function in general and the correlation function in particular. We note that in the case of H^-, since λ is quite small, the correlation is very sensitive to the value of λ, and for this reason we have in addition given the values of the two sides of Eq. (39) for the variational value of $\lambda = 0.155$.

TABLE III. The potential energies (PE) and the ratios of the potential and the kinetic energies (KE) calculated with the present wave function are listed in the first two columns. According to the virial theorem this ratio should be equal to 2. Also the right-hand side and the left-hand side of the correlation test [Eq. (39)] are compared with the exact values. Without correlation the value of $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ is equal to zero.

	$-$PE	$-$PE/KE	$2\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$	$Z\langle \vec{r}_1 \cdot \vec{r}_2 (r_1^{-3} + r_2^{-3}) \rangle + \langle r_{12}^{-1} \rangle$	$2\langle \vec{p}_1 \cdot \vec{p}_2 \rangle_{\text{exact}}$ [a]
H^-	1.015	2.074	0.0628	-0.0408	0.0657
			(0.0577) [b]	(0.0357) [b]	
He	5.721	2.028	0.309	0.284	0.320
Li^+	14.435	2.016	0.555	0.537	0.551
Be^{2+}	27.143	2.012	0.852	0.813	0.847

[a]Reference [45].
[b]Calculated with the variational value $\lambda = 0.155$.

TABLE IV. Negative values of the total ground state energy for the systems H^-, He, and Li^+ calculated with different correlation functions (atomic units). λ was calculated using Eq. (31).

	$f(r_{12})=1$	$f(r_{12})=1+\frac{1}{2}r_{12}$	$f(r_{12})=1-\dfrac{1}{1+2\lambda}e^{-\lambda r_{12}}$	Exact
H^-	0.5082	0.5204	0.5257	0.5278
He	2.8591	2.8851	2.9000	2.9037
Li^+	7.2286	7.2490	7.2749	7.2799

We have also compared our values of $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ with those calculated using Pekeris exact wave functions [45,37]. From the values given in Table III, one observes that the agreement is quite satisfactory.

C. Other correlation functions

In order to demonstrate the importance of the correlation function, we have calculated the energies of H^-, He, and Li^+ using different correlation functions. The results are shown in Table IV. The $\Phi(r_1,r_2)$ parts were the same as discussed in Sec. II and only the $f(r_{12})$ part was changed. The simplest correlation function $f(r_{12})=1$ neglects the effect of correlation entirely, the second one $f(r_{12})=1+\frac{1}{2}r_{12}$ includes the cusp condition in its simplest way, and the third correlation function is the one proposed in the present paper. It is clearly seen that the present correlation function leads to an improvement in the energy. Additional calculations revealed that the Hirschfelder correlation function Eq. (12) leads to almost the same results as with the present proposed correlation function although its large-r_{12} behavior is incorrect. For the asymptotic normalization constant A in Eq. (8) one has with the present correlation function a value of 2.34 which is much closer to the *ab initio* value of 2.91 [46] compared to the value of 1.18 obtained with Hirschfelder's function. This illustrates the extreme sensitivity of A to the long range behavior of the correlation function.

D. Conclusions

The present calculation illustrates the importance of the asymptotic behavior, the small-r behavior, and the correlation factor for a proper description of the two-electron wave function. As far as we are aware it is the first successful derivation of a nonvariational wave function for simple two-electron atoms and ions. Because of its simplicity and accuracy this wave function should prove very useful for calculating the effect of collective properties of two-electron systems. It would be interesting to extend these methods to atoms with more than two electrons. It should also be possible to extend this treatment to excited states, diatomic molecules, and atom-surface interactions. In this connection it is interesting to note that Le Sech and co-workers have used a related ansatz, but with two variationally determined parameters, to calculate the excited states of some two-electron atoms [13], the triplet states of H_2 and He_2^{2+} [14], and recently the atom-metal surface potential [15]. It is already clear that the correlation function presented here is preferable to other forms also for molecular calculations [47].

APPENDIX

In this appendix we describe how to calculate the matrix elements for the energy calculation using Eq. (21). To make the calculations more systematic we write the correlation function Eq. (14) as

$$f(r_{12})=1-\frac{1}{1+2\lambda}e^{-\lambda r_{12}}=\sum_{i=1}^{2}\alpha_i e^{-\lambda_i r_{12}}, \qquad (A1)$$

where $\alpha_1=1$, $\alpha_2=-1/(1+2\lambda)$, $\lambda_1=0$, and $\lambda_2=\lambda$. Therefore the total wave function Ψ Eq. (16) can be written as

$$\Psi(\vec{r}_1,\vec{r}_2)=\Psi_1(\vec{r}_1,\vec{r}_2)+\Psi_2(\vec{r}_1,\vec{r}_2), \qquad (A2)$$

$$\Psi_1(\vec{r}_1,\vec{r}_2)=\sum_{i=1}^{2}\alpha_i e^{-Zr_1}(1+cr_2)^{-\gamma}e^{-\beta r_2}e^{-\lambda_i r_{12}}, \qquad (A3)$$

$$\Psi_2(\vec{r}_1,\vec{r}_2)=\sum_{i=1}^{2}\alpha_i e^{-Zr_2}(1+cr_1)^{-\gamma}e^{-\beta r_1}e^{-\lambda_i r_{12}}, \qquad (A4)$$

with $\gamma=1-(Z-1/)\beta$. The norm is given by

$$\langle\Psi|\Psi\rangle=2\sum_{i,j}\alpha_i\alpha_j[K(\lambda_i+\lambda_j,2\gamma,0,0,0)$$
$$+L(\lambda_i+\lambda_j,\gamma,\gamma,0,0,0)]. \qquad (A5)$$

Here we have

$$K(\eta,\gamma,l,m,n)=\int e^{-2Zr_1-2\beta r_2-\eta r_{12}}(1+cr_2)^{-\gamma}$$
$$\times\frac{1}{r_1^l r_2^m r_{12}^n}d^3r_1 d^3r_2$$
$$=8\pi^2\int I_n(\eta,r_1,r_2)e^{-2Zr_1-2\beta r_2}$$
$$\times(1+cr_2)^{-\gamma}\frac{1}{r_1^l r_2^m}r_1^2 dr_1 r_2^2 dr_2, \qquad (A6)$$

$$I_n(\eta,r_1,r_2)=\int \frac{e^{-\eta r_{12}}}{r_{12}^n} d\cos\Theta_{12}, \tag{A7}$$

$$r_{12}=[r_1^2+r_2^2-2r_1r_2\cos\Theta_{12}]^{1/2}, \tag{A8}$$

specifically for $n=0$ and $n=1$,

$$I_0(\eta,r_1,r_2)=\frac{1}{r_1r_2}\left[\frac{e^{-\eta|r_1-r_2|}|r_1-r_2|-e^{-\eta(r_1+r_2)}(r_1+r_2)}{\eta}\right.$$
$$\left.+\frac{e^{-\eta|r_1-r_2|}-e^{-\eta(r_1+r_2)}}{\eta^2}\right], \tag{A9}$$

$$I_1(\eta,r_1,r_2)=\frac{1}{r_1r_2}\left[\frac{e^{-\eta|r_1-r_2|}-e^{-\eta(r_1+r_2)}}{\eta}\right]. \tag{A10}$$

The integral $L(\eta,\gamma_1,\gamma_2,l,m,n)$ is given by

$$L(\eta,\gamma_1,\gamma_2,l,m,n)=\int e^{-(Z+\beta)(r_1+r_2)-\eta r_{12}}(1+cr_1)^{-\gamma_1}$$
$$\times(1+cr_2)^{-\gamma_2}\frac{1}{r_1^l r_2^m r_{12}^n}d^3r_1 d^3r_2$$
$$=8\pi^2\int I_n(\eta,r_1,r_2)e^{-(Z+\beta)(r_1+r_2)}$$
$$\times(1+cr_1)^{-\gamma_1}(1+cr_2)^{-\gamma_2}$$
$$\times\frac{1}{r_1^l r_2^m}r_1^2 dr_1 r_2^2 dr_2. \tag{A11}$$

For calculating the kinetic energy, we have

$$\langle\Psi|\nabla_1^2|\Psi\rangle=\sum_{i,j}\alpha_i\alpha_j[(Z^2+\beta^2-2\lambda_i\lambda_j)\{K(\lambda_i+\lambda_j,2\gamma,0,0,0)+L(\lambda_i+\lambda_j,\gamma,\gamma,0,0,0)\}-2Z\{K(\lambda_i+\lambda_j,2\gamma,1,0,0)$$
$$+L(\lambda_i+\lambda_j,\gamma,\gamma,1,0,0)\}+\gamma(\gamma+1)c^2\{K(\lambda_i+\lambda_j,2\gamma+2,0,0,0)+L(\lambda_i+\lambda_j,\gamma,\gamma+2,0,0,0)\}$$
$$+2\beta\gamma c\{K(\lambda_i+\lambda_j,2\gamma+1,0,0,0)+L(\lambda_i+\lambda_j,\gamma,\gamma+1,0,0,0)\}-2\gamma c\{K(\lambda_i+\lambda_j,2\gamma+1,0,1,0)$$
$$+L(\lambda_i+\lambda_j,\gamma,\gamma+1,0,1,0)\}-2\beta\{K(\lambda_i+\lambda_j,2\gamma,0,1,0)+L(\lambda_i+\lambda_j,\gamma,\gamma,0,1,0)\}]. \tag{A12}$$

In writing this expression, we have used some of the techniques described in Ref. [13]. Finally, one also needs

$$\left\langle\Psi\left|\frac{1}{r_1}\right|\Psi\right\rangle=\sum_{i,j}\alpha_i\alpha_j[K(\lambda_i+\lambda_j,2\gamma,0,1,0)+K(\lambda_i+\lambda_j,2\gamma,1,0,0)+2L(\lambda_i+\lambda_j,\gamma,\gamma,1,0,0)], \tag{A13}$$

and

$$\left\langle\Psi\left|\frac{1}{r_{12}}\right|\Psi\right\rangle=2\sum_{i,j}\alpha_i\alpha_j[K(\lambda_i+\lambda_j,2\gamma,0,0,1)+L(\lambda_i+\lambda_j,\gamma,\gamma,0,0,1)]. \tag{A14}$$

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