J. Phys. Chem. A **2005,** *109,* 11413−11416

Highly Compact Wave Functions for He-Like Systems[†]

Frank E. Harris*

Department of Physics, University of Utah, Salt Lake City, Utah 84112, and Quantum Theory Project, University of Florida, Gainesville, Florida 32611

Vedene H. Smith, Jr.[‡]

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received: June 9, 2005; In Final Form: August 22, 2005

Wave functions which are compact, but still quite accurate, are extremely valuable as tools for gaining understanding of quantum systems. This paper investigates the use for that purpose of functions that depend exponentially on all the interparticle distances of a few-body system, illustrated by a study of the ground electronic states of the He isoelectronic series (Z from 1 to 10). Using as few as 4 exponential basis functions, it is found that nonrelativistic energies are reproduced to within 38 microhartrees of the exact values, an error far less than for previously reported compact wave functions. Other properties are also well-represented.

I. Introduction

A search for reasonably accurate but highly compact wave functions in small quantum systems has been a recurring theme, motivated by the difficulty in interpreting the essence of accurate wave functions that may be linear combinations of thousands of terms. Of particular interest are studies of two-electron atomic systems (the He isoelectronic series), the simplest systems which exhibit electron correlation effects. As long ago as 1929, Hylleraas[1] showed the effectiveness of a basis that included the interelectron distance r_{12} as an explicit coordinate in He, and the more recent, highly accurate studies of He-like systems have used extensive expansions in terms of r_{12} and the electron−nuclear distances. These computations (see, for example, refs 2 and 3) have focused on extreme accuracy rather than our current objective of reasonable accuracy and great compactness.

An early attempt to find compact, but accurate, He-like wave functions was reported in 1977 by Thakkar and Smith.[4] Their definition of compact was less stringent than we apply here; they found that 66-term wave functions gave excellent results for both energy and other properties. In 1992, Koga[5] revisited the use of Hylleraas-type expansions in He-like systems, obtaining compact wave functions (of up to 6 terms) that yielded a significant improvement in energy relative to expansions of similar length by others. More recently, Kleinekathöfer, Patil, Tang, and Toennies[6] (hereinafter KPTT) proposed a compact He wave function, the form of which is largely determined by requirements that it be asymptotically correct in both the small- and large-distance limits. While the approaches of Koga and KPTT are interesting from a fundamental viewpoint, neither provides the accuracy that is needed for some purposes. The present communication describes an alternative to the work of those authors and involves comparable or less computational effort associated with the use of the compact wave functions, but yields many properties with orders of magnitude less error. Even the properties for which satisfaction is built into the KPTT approach are rendered here with satisfactory accuracy.

We conclude with a look at the prospects for applying the method of this paper to larger and chemically more interesting systems.

II. Method

We consider systems consisting of two electrons and an infinitely massive nucleus of charge Z. In the nonrelativistic limit in which the Hamiltonian consists only of the kinetic energy and coulomb interactions, it is (in hartree atomic units: $m_e = \hbar = e = 4\pi\epsilon_0 = 1$)

$$\mathscr{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \qquad (1)$$

Here, $\mathbf{r}_i$ (with magnitude r_i) describes the position of electron i relative to the nucleus, r_{12} is the interelectron distance $|\mathbf{r}_1 - \mathbf{r}_2|$, and ∇_i is with respect to the coordinates of $\mathbf{r}_i$.

The spatial dependence of the ground-state wave function Ψ will be symmetric in the electron coordinates and depend only on the interparticle distances r_1, r_2, and r_{12}. We construct it from basis functions ϕ_i of the form

$$\phi_i = (1 + \mathscr{P}_{12})\, e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}} \qquad (2)$$

where $\mathscr{P}_{12}$ is an operator interchanging r_1 and r_2. We have chosen to restrict the parameters α_i, β_i, and γ_i to real values. It is not necessary that they all be nonnegative; it is sufficient to require $\alpha_i + \beta_i > 0$, $\alpha_i + \gamma_i > 0$, and $\beta_i + \gamma_i > 0$.

Note that eq 2 differs from the more frequently used Hylleraas ansatz (that employed by Koga) in that the exponentials are not multiplied by powers of r_1, r_2, or r_{12}, and that the parameter γ_i is not set to zero. The needed dependence on the interelectron distance is obtained here by the exponential factor $\exp(-\gamma_i r_{12})$. Unlike the custom with Hylleraas basis sets of taking a fixed value of $\alpha = \beta$ and using many different powers of the r_i and r_{12}, the present approach obtains wave function flexibility by assigning individual values of α, β, and γ to each ϕ_i.

[†] Part of the special issue "Jack Simons Festschrift".

* Corresponding author. Electronic address: harris@qtp.ufl.edu.

[‡] Electronic address: vhsmith@chem.queensu.ca.

10.1021/jp0531098 CCC: $30.25

For given values of α_i, β_i, and γ_i, the coefficients C_i in a wave function of the form

$$\Psi = \sum_i C_i \phi_i \tag{3}$$

were determined variationally, minimizing the energy expectation value $E = \langle \Psi | \mathscr{H} | \Psi \rangle$ by standard methods. The matrix elements needed for this purpose were calculated using formulas that have been extensively documented in the literature[7,8] and need not be repeated here. It suffices to observe that the procedures are rapid, convenient, and numerically stable.

Optimum values of the α_i, β_i, and γ_i were then determined variationally, minimizing E (obtained as described in the preceding paragraph) with respect to these nonlinear parameters by application of a conjugate gradient method. We found that, for a given Z, the parameter space contained several local energy minima, and it was necessary to carry out multiple searches from a number of different starting points to reach a reasonable level of assurance that the global energy minimum had been located. An indication that global minima were indeed obtained is provided by the fact that the energy errors vary smoothly with Z, as do the nonlinear parameters (with the exception noted toward the end of the next section of this paper).

We note parenthetically that from a technical perspective the optimization of the nonlinear parameters is a demanding task. In the limit of large numbers of configurations, the wave function becomes completely independent of the parameter values, and even for the expansion lengths reported here (four configurations, vide infra), the optimization is exceedingly ill-conditioned.

III. Wave Functions and Energies

Using the procedures described in the preceding section, we studied two-electron systems with Z values from 1 through 10 (H^-, He, Li^+, ..., Ne^{8+}). We report here results for the ground electronic states of H^-, He, and Ne^{8+}; data for the other systems will be presented in a forum without length restrictions. We found the quality of the wave functions (with respect to both energy and other properties) to be highly dependent on the completeness of the optimization. Examining the carefully optimized results as a function of the number of ϕ_i used (i.e., the number of configurations), we came to the conclusion that an optimized four-configuration wave function yielded an excellent compromise of the desirable but conflicting features of compactness and accuracy.

Table 1 gives the nonlinear parameters of the optimized four-configuration wave functions for H^-, He, and Ne^{8+}, and Table 2 compares the ground-state energies for our wave functions with those obtained from other recent studies (those of Koga and KPTT). The first observation to be made now is that our four-configuration wave functions yield surprisingly accurate energies, all within 38 μhartree of the exact values. These errors are about 2 orders of magnitude less than those of KPTT, a factor of 20 to 60 less than those of the Koga four-term function (his expansion of length similar to ours), and about an order of magnitude more precise than Koga's six-term function. It should also be noted that, unlike the other studies, our results do not deteriorate with increasing Z. An optimum compact expansion should have this property, as electron correlation becomes relatively less important as Z increases and, in fact, approaches a constant limiting value at infinite Z (see discussions of the $1/Z$ expansion for this system, e.g., in a paper by Dalgarno[9]). Our results in fact represent the recovery of about 99.9% of the correlation energy throughout the He isoelectronic series.

TABLE 1: Nonlinear Parameters (bohr^{-1}) of Optimized Four-Configuration Wave Functions, of Functional Form Given in Eq 2[a]

	cfg no.	*a*	*b*	*g*
H^-	1	0.857 017	0.751 909	0.101 595
	2	0.841 729	0.762 291	0.105 682
	3	1.021 337	0.310 090	−0.016 292
	4	0.814 655	0.814 651	−0.212 153
He	1	2.373 427	1.823 077	0.190 179
	2	2.508 989	1.767 884	0.130 308
	3	2.068 441	2.022 821	0.264 338
	4	2.106 452	1.395 750	−0.096 177
Ne^{8+}	1	13.283 463	9.675 289	2.615 987
	2	13.850 848	9.397 064	2.461 465
	3	11.180 907	11.180 904	2.949 205
	4	10.497 988	9.007 933	−0.119 465

[a] Configurations in descending order of importance.

TABLE 2: Error in the Ground-State Energy (μhartrees)[a]

		$^\infty H^-$	$^\infty He$	$^\infty Ne^{8+}$
KPTT[b]		1251.0	3724.4	6806.5
Koga[c]	(4 term)	823.6	952.1	1941.3
	(6 term)	181.3	271.6	556.3
this research		37.9	36.4	32.8

[a] The "exact" energies used and the energies computed in this research are included in Table 3. [b] Ref 6. [c] Ref 5.

TABLE 3: Exact[a] and Compact-Function Ground-State Properties, Respectively Labelled E and C[b]

	$^\infty H^-$	$^\infty He$	$^\infty Ne^{8+}$
E_C	−0.527 713 1	−2.903 688 0	−93.906 773 7
E_E	−0.527 751 0	−2.903 724 4	−93.906 806 5
$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle_C$	−0.684 555	−0.064 667	−0.000 402 503
$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle_E$	−0.687 313	−0.064 737	−0.000 402 542
$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle_C$	0.032 967	0.158 902	1.217 620
$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle_E$	0.032 880	0.159 069	1.217 079
$\langle \delta(\mathbf{r}_1) \rangle_C$	0.164 154	1.807 310	297.541
$\langle \delta(\mathbf{r}_1) \rangle_E$	0.164 553	1.810 429	297.623
$\langle \delta(\mathbf{r}_{12}) \rangle_C$	0.002 865	0.108 314	32.709
$\langle \delta(\mathbf{r}_{12}) \rangle_E$	0.002 738	0.106 345	32.620
$\langle \delta(\mathbf{r}_1)\delta(\mathbf{r}_2) \rangle_C$	0.005 128	1.884	80 775
$\langle \delta(\mathbf{r}_1)\delta(\mathbf{r}_2) \rangle_E$	0.005 064	1.869	80 763
$\nu_{1,C}$	−0.996	−1.992	−9.992
$\nu_{1,E}$	−1.000	−2.000	−10.000
$\nu_{12,C}$	+0.437	+0.437	+0.445
$\nu_{12,E}$	+0.500	+0.500	+0.500

[a] From high-accuracy computations in refs 3 and 8. [b] Data are in hartree atomic units ($m_e = \hbar = e = 4\pi e_0 = 1$). The quantities ν are cusp strengths, defined in eq 4.

Looking next at the wave functions themselves, we see that in all cases there occur configurations with negative values of the parameter γ: this is necessary to obtain a good description in the neighborhood of the electron−electron cusp. There is a qualitative change in the optimum wave function as one proceeds from $Z = 1$ to $Z = 2$; what is actually happening is that there are two low-lying relative minima, with that corresponding to the H^- wave function becoming less favored as Z increases. For He, the H^--type minimum is only about 4 μhartree above the global minimum; when Ne^{8+} is reached, this difference has widened to over 1 millihartree.

It is interesting to note that a phenomenon parallel to that discussed in the previous paragraph can be seen in the work of Koga. He found that the most important configurations were different for H^- than for He and the ions with $Z > 2$.

IV. Properties

Table 3 compares various properties obtained with the wave functions of this study against exact values from high-accuracy computations. For completeness, we include the total energies that were used to compute the numbers in Table 2.

Since the wave functions used here were not constrained to give exact values of specific properties, it is of particular interest to see how well they do for quantities other than the energy. They all exactly satisfy the virial theorem, but that is a consequence of the fact that it is automatically satisfied for the wave functions used here when the nonlinear parameters are optimally scaled. Table 3 shows that the correlation in electron positions, as measured by $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$, is reproduced to within a few parts per thousand; even higher accuracy is noted for the momentum correlation $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$. It should be remembered that $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$ and $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$ are defined entirely by correlation effects; both these quantities vanish in the independent-particle limit.

In summary, the data in Table 3 reinforce the earlier assertion that these compact four-configuration wave functions provide good descriptions of a wide range of properties in addition to the energy, and the form of the wave function makes it easy to use and interpret.

Turning now to local properties, we first look at the probabilities that particle positions coincide, corresponding to the δ-function expectation values in Table 2. We also examine the cusp strength, with the electron−nuclear cusp defined as

$$\nu_1 = \frac{\langle \delta(\mathbf{r}_1)\partial/\partial r_1 \rangle}{\langle \delta(\mathbf{r}_1) \rangle} \tag{4}$$

The electron−electron cusp, ν_{12}, is defined analogously. It is apparent that the compact wave functions provide a nearly quantitative description of behavior in the vicinity of the nucleus. The electron−electron cusp is not as well described (with an error of over 10%), presumably due to the small energetic importance of that feature.

One of the virtues of a compact description is the ability to use it to examine additional features of the electron distribution without the necessity of repeating extensive computations to recreate complicated wave functions. We illustrate here by presenting the pair distribution functions in He as given by the compact wave function. Figure 1 shows the electron−nuclear radial probability distribution $D(r_1)$ and the charge density $\rho(r_1) = D(r_1)/4\pi r_1^2$, where $D(r_1)$ has the definition

$$D(r_1) = 2(4\pi r_1^{\,2}) \int d\mathbf{r}_2 |\Psi(r_1, r_2, r_{12})|^2 \tag{5}$$

We follow the notation of Thakkar and Smith,[10] who give formulas for evaluation of $D(r_1)$ and $P(r_{12})$ (vide infra). The electron−electron pair distribution $P(r_{12})$ is defined analogously to $D(r_1)$ (but without the prefactor 2). Figure 2 shows $P(r_{12})$ and $h(r_{12}) = P(r_{12})/4\pi r_{12}^2$ (the latter known as the *intracule function*).

The radial distributions are qualitatively what is expected: $D(r_1)$ has a maximum at an r_1 value somewhat greater than $1/Z$, corresponding to partial shielding of the nucleus by the other electron, while r_{12} at the maximum in $P(r_{12})$ is somewhat larger than $\sqrt{2}$ times the r_1 value at the maximum of $D(r_1)$, reflecting the effect of electron−electron repulsion. The plots of $\rho(r_1)$ and $h(r_{12})$ clearly show the effects of the nuclear−electron and electron−electron cusps. Note that the electron−electron cusp is entirely due to electron correlation; an independent-particle wave function cannot cause $h(r_{12})$ to have a local minimum at $r_{12} = 0$. The vertical intercept of $\rho(r_1)$ corresponds to $2 \times \langle \delta(\mathbf{r}_1) \rangle$, reflecting the fact that ρ describes the entire electron density (not that of one electron only), and the intercept of $h(r_{12})$ is, as it must be, consistent with the value tabulated for $\langle \delta(\mathbf{r}_{12}) \rangle$. All four graphs appear nearly identical to those for He in ref 10, indicating that our compact wave function has captured the essence of the electron distribution in this system.

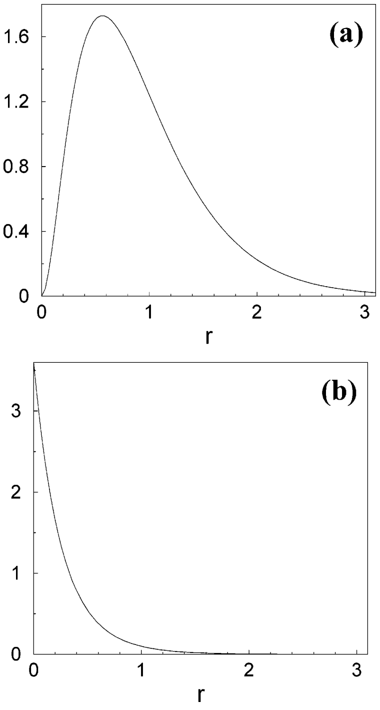

Figure 1. Electron−nuclear radial distribution function for He: (a) $D(r_1)$; (b) $\rho(r_1)$, computed from the compact wave function.

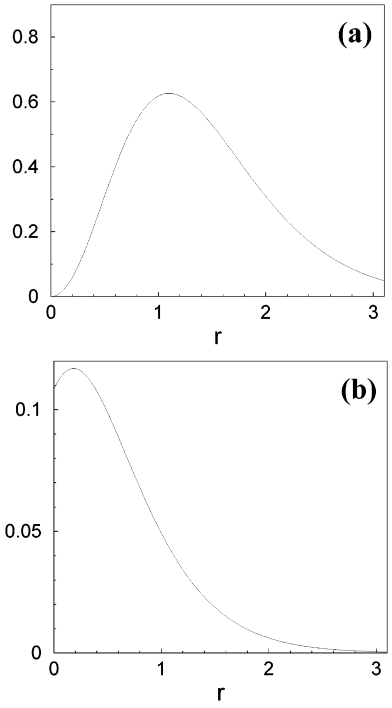

Figure 2. Electron-electron radial distribution function for He: (a) $P(r_{12})$; (b) $h(r_{12})$, computed from the compact wave function.

V. Concluding Remarks

It would be desirable if the type of analysis illustrated here could be extended to systems containing larger numbers of nuclei or electrons. However, a key feature (namely the occurrence of all the interparticle distances r_{ij} in exponents) makes the evaluation of the necessary matrix elements very difficult. It is, nevertheless, possible to treat four-body systems (e.g., the Li atom) by the present methods. All the matrix elements arising in energy computations on such systems can be evaluated analytically using closed formulas first obtained by Fromm and Hill;[11] see also further development of the formulation by a group that includes the present authors.[12,13] Another possibility, not yet significantly exploited, would be to represent the correlated exponentials by linear combinations of correlated Gaussians, for which general formulas are now available.[14]

One closing observation: The present work shows that, although it is difficult to obtain an optimum description of a simple atomic or molecular system within a modest basis containing nonlinear parameters, such bases may permit better and more economical representations than is generally realized.

Acknowledgment. We acknowledge helpful discussions with Dr. A. M. Frolov. It is a pleasure to thank the Natural Sciences and Engineering Research Council of Canada for financial support. One of us (F.E.H.) also acknowledges support from the U. S. National Science Foundation, grant PHY-0303412.

References and Notes

(1) Hylleraas, E. *Z. Phys.* **1929**, *54*, 347.

(2) Frankowski, K.; Pekeris, C. L. *Phys. Rev.* **1966**, *146*, 46; **1966**, *150*, 366(E).

(3) Frolov, A. M. *Phys. Rev. A* **1998**, *57*, 2436.

(4) Thakkar, A. J.; Smith, V. H., Jr. *Phys. Rev. A* **1977**, *15*, 1.

(5) Koga, T. *J. Chem. Phys.* **1992**, *96*, 1276.

(6) Kleinekathöfer, U.; Patil, S. H.; Tang, K. T.; Toennies, J. P. *Phys. Rev. A* **1996**, *54*, 2840.

(7) Abbott, P. C.; Maslen, E. N. *J. Phys. B* **1986**, *19*, 1595.

(8) Frolov, A. M.; Smith, V. H., Jr. *J. Phys. B* **2004**, *37*, 2917; **2004**, *37*, 4037(E).

(9) Dalgarno, A. In *Quantum Theory I. Elements*; Bates, D. R., Ed; Academic: New York, 1961; p 193.

(10) Thakkar, A. J.; Smith, V. H., Jr. *J. Chem. Phys.* **1977**, *67*, 1191.

(11) Fromm, D. M.; Hill, R. N. *Phys. Rev. A* **1987**, *36*, 1013.

(12) Harris, F. E. *Phys. Rev. A* **1997**, *55*, 1820.

(13) Harris, F. E.; Frolov, A. M.; Smith, V. H., Jr. *J. Chem. Phys.* **2003**, *119*, 8833.

(14) Harris, F. E.; Monkhorst, H. J. *Int. J. Quantum Chem.* (in press).