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Variational calculations for helium-like ions using generalized Kinoshita-type expansions

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Abstract. Variational calculations are reported for the ground states of the helium atom and its isoelectronic ions H^-, Li^+, …, Ne^{8+}. The calculations use generalized Kinoshita expansions with freely optimized, noninteger powers of the Hylleraas coordinates s and u. One hundred-term expansions of this type lead to better energies than any other expansions in the literature with comparable numbers of terms.

Keywords: Helium-like ions – Generalized Kinoshita-type wave functions

1 Introduction

The solution of the Schrödinger equation for the helium atom and its isoelectronic ions is a subject that has attracted a huge amount of effort. Originally, these simple systems constituted a good test of quantum mechanics. Current interest stems partly from use of these systems as test beds for approximate theories of relativistic, quantum-electrodynamic and other effects not included in the Schrödinger equation.

Following the pioneering work of Unsöld [1], Kellner [2], Slater [3], and Hylleraas [4, 5], the variational upper bound to the ground-state energy of the helium atom was gradually lowered by Chandrasekhar and coworkers [6, 7], Schwartz [8], Hylleraas and Midtdal [9, 10], Kinoshita [11], Pekeris [12, 13], Schwartz [14], Frankowski and Pekeris [15, 16], Freund et al. [17], Drake [18], Thakkar and Koga [19], Drake and Yan [20], Bürgers et al. [21], Goldman [22], Drake [23], Korobov [24], Drake et al. [25], and Schwartz [26]. The most recent variational energies [26] have converged to an accuracy of about one part in 10^{36}. Most of the high-accuracy work of the last decade was based upon expansions of the wave function that contain more than 1000 terms. Expansions with 1262, 24497, 8066, 2114, 2200, 2358, and 10259 terms were used by Drake and Yan [18], Bürgers et al. [21], Goldman [22], Drake [23], Korobov [24], Drake et al. [25], and Schwartz [26], respectively.

However, energies accurate to better than one part in 10^{12} have been obtained with two types of variational wave functions containing only a few hundred terms [15, 17, 19]. Frankowski and Pekeris [15, 16] used trial wave functions of the form

$$\psi(\vec{r}_1,\vec{r}_2) = \exp(-\zeta s) \times \sum_{i=1}^{I} c_i s^{l_i} t^{2m_i} u^{n_i} (s^2+t^2)^{j_i/2} (\ln s)^{k_i} \ , \tag{1}$$

in which $s = |\vec{r}_1| + |\vec{r}_2|$, $t = |\vec{r}_1| - |\vec{r}_2|$, and $u = |\vec{r}_1 - \vec{r}_2|$ are the Hylleraas coordinates, ζ and c_i are variational parameters, j_i, k_i, m_i, and n_i are nonnegative integers, and l_i is an integer that may be negative. Their ground-state energy for helium, obtained with a 246-term wave function, is accurate to about 5 parts in 10^{13}. Freund et al. [17] obtained even more compact wave functions of the same type by reordering terms, and by adding terms that have both $k_i \neq 0$ and $l_i < 0$. Their 230-term wave function leads to an energy accurate to about 2 parts in 10^{14}. An advantage that the ansatz (Eq. 1) has over all other expansions is its compatibility with the formal solution of the Schrödinger equation for the ground state of the helium atom [27, 28].

A 252-term wave function that led to an energy accurate to about 1 part in 10^{14} was obtained in our previous work [19] by using both fractional [8, 29] and negative powers [11] of s and u, as well as a novel procedure for varying the powers selected. Specifically, we used the ansatz

$$\psi(\vec{r}_1,\vec{r}_2) = \exp(-\zeta s) \sum_{i=1}^{I} c_i s^{(l_i-n_i)/\lambda} t^{m_i} u^{(n_i-m_i)/\nu} \ , \tag{2}$$

in which ζ, c_i, λ, and ν are variational parameters, l_i, m_i, and n_i are nonnegative integers subject to the inequality

$$0 \leq Ll_i + Mm_i + Nn_i \leq P \ , \tag{3}$$

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and m_i is even to ensure that ψ is symmetric with respect to $\vec{r}_1$ and $\vec{r}_2$. Varying the integers L, M, and N in the inequality (Eq. 3) provides a convenient, systematic, and relatively efficient method for optimization of term-ordering schemes.

The purpose of this brief paper is to assess the maximum accuracy that can be attained for variational energies of the ground states of the helium-like ions using 100-term wave functions that are essentially of the form of Eq. (2) but with fewer restrictions on the powers. No attempt is made to produce the most accurate ground-state energies to date. Hartree atomic units are used throughout.

2 Computational method

The powers of s and u in the generalized Kinoshita-type (GK) ansatz, (Eq. 2) are restricted to integer multiples of the real numbers $1/\lambda$ and $1/\nu$ respectively. Moreover, use of the inequality (Eq. 3) invariably means that some terms that make relatively small contributions to the energy will be included at the expense of others that could make larger contributions. We drop both these restrictions and simply optimize, term-by-term, the powers to be included in the expansion. Hence, it is convenient to rewrite the GK ansatz in the form

$$\psi(\vec{r}_1,\vec{r}_2) = \exp(-\zeta s) \sum_{i=1}^{I} c_i s^{(l_i-n_i)} t^{m_i} u^{(n_i-m_i)} \ , \qquad (4)$$

where the l_i and n_i are real-valued, variational parameters. The m_i are restricted to non-negative, even integers so that the spatial wave function (Eq. 4) remains symmetric with respect to $\vec{r}_1$ and $\vec{r}_2$, and the overall wave function $\psi\Theta$, where $\Theta = \alpha\beta - \beta\alpha$ is the two-electron singlet spin function, satisfies the Pauli principle.

We performed systematic calculations in five stages with increasingly more general powers of s and u allowed in the expansion. In the first four stages, denoted GK1, GK2, GK4, and GK8, respectively, l_i and n_i are allowed to be non-negative integers, half integers, quarter integers and eighths of an integer. At the final stage, denoted GKR, the l_i and n_i are allowed to be non-negative, real numbers. An advantage of this multi-stage approach is that an excellent starting point for the optimization of the GK2, GK4, GK8, and GKR wave functions is provided by the optimized wave function for the previous stage.

The variational optimization of these wave functions involved a computationally demanding, four-level iterative procedure as follows.

1. Iterate until the energy converges.
2. Iterate over the $i = 1, 2, \ldots, I$ terms of the wave function.
3. Vary the powers of the ith term to minimize the energy.
4. Vary ζ by Powell's method [30] to minimize the energy for the current powers.

The details of the level 3 iteration were different for different types of wave functions. For the GKj $(j = 1, 2, 4, 8)$ expansions, m_i was varied by increments of ±2, and l_i and n_i were varied by increments of $\pm 1/j$ to minimize the energy. For the GKR expansion, the energy was minimized by varying the l_i and n_i using Powell's method [30], and varying the m_i by increments of ±2. We found that the optimal m_i for the GKR expansion were almost identical to those for GK8 and GK4, and could therefore simply be frozen at those values. Moreover, we noticed that ζ did not change very much upon variation of the powers of a single term in an expansion with 50 or more terms. Hence, for the 50- and 100-term expansions, it was computationally expedient to optimize ζ in the level 4 iteration by using virial scaling [31, 32]. Quadruple precision (≈ 32 significant figure) arithmetic was used throughout. The computational effort required for this optimization is significantly greater than for the ansatz in Eq. (2).

3. Results and discussion

The energies for helium computed with 10, 20, 30, 50, and 100 terms and each of the five expansion methods are listed in Table 1. A convenient measure of the error in the relative energy is

$$\epsilon = \log_{10}(1 - E/E_{\mathrm{r}}) \ , \qquad (5)$$

where E_{r} is the most accurate value currently available [26]; E_{r} for helium is given in the legend to Table 1. The relative energy errors for helium are shown as a function of the logarithm of the number of expansion terms, I, in Fig. 1. As expected, the convergence with respect to I improves in the sequence GK1, GK2, GK4, GK8, and GKR as the domain of allowable values of the powers of s and u is enlarged. Observe that GK2 converges much faster than GK1, and that GKR

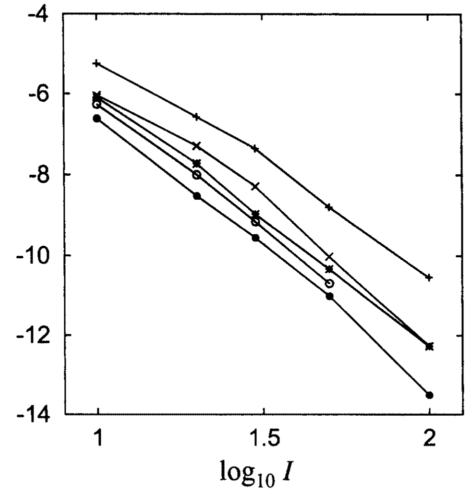

Fig. 1. Decrease of energy errors for the ground state of He with expansion length I. GK1 (+); GK2 (×); GK4 (∗); GK8 (○); GKR (●)

Table 1. Ground-state energies (hartrees) for the helium atom obtained with I-term generalized Kinoshita expansions of five types. The most accurate, variational, upper bound currently known [26] is $E_{\mathrm{r}} = -2.903724377034119598311159245194404 4\ldots$

Type	$I = 10$	20	30	50	100
GK1	−2.9037077	−2.903723608	−2.903724249	−2.90372437240	−2.90372437695472
GK2	−2.9037217	−2.903724228	−2.903724362	−2.90372437676	−2.90372437703254
GK4	−2.9037220	−2.903724322	−2.903724374	−2.90372437690	−2.90372437703258
GK8	−2.9037228	−2.903724348	−2.903724375	−2.90372437697	
GKR	−2.9037237	−2.903724368	−2.903724376	−2.90372437701	−2.90372437703403

converges much faster than GK2. In contrast, the improved convergence of GK4 and GK8 relative to GK2 is much smaller. This is particularly marked for 100-term expansions where the improvement of GK4 over GK2 is so small, see Table 1, that it cannot be seen on the scale of Fig. 1. In view of this, we did not construct a 100-term GK8 wave function. For 100 terms, the most general GKR expansion is about 3 orders of magnitude more accurate than the GK1 expansion. The 100-term GKR energy is accurate to about 3 parts in 10^{14}. Similar results were obtained for H^- and Li^+ (not shown). Convergence was slower in H^- than in He or Li^+ because our single-exponent ansatz is more efficient at describing angular correlation than radial correlation which is most important in H^-.

The 100-term GKR wave functions were then constructed for Be^{2+} to Ne^{8+}. Table 2 shows that the energies of the 100-term GKR wave functions for the helium isoelectronic sequence from H^- to Ne^{8+} are more accurate than the 203-term (214-term for H^-) results of Thakkar and Koga [19] but less accurate than their 308-term (455-term for H^-) results. The 100-term GKR expansions for the ground states of the helium atom and its isoelectronic ions lead to more accurate energies than any found to date with other expansions using comparable numbers of terms.

The structure of the GK wave functions can be appreciated by an examination of Table 3, which shows the optimal values of (l_i, m_i, n_i) and ζ for the 20-term wave functions. The first three terms, $(0,0,0)$, $(1,0,1)$ and $(2,2,2)$, occur in each of the GK1, GK2, GK4, and GK8 expansions, and terms with almost exactly these values of (l_i, m_i, n_i) are also found in the GKR expansion. The importance of the $(2,2,2)$ term is manifested by the presence of several other terms with very similar values of (l_i, m_i, n_i); see, for example, terms 6 and 8 in the GK4 expansion, and terms 6, 8 and 15 in the GKR expansion. The values of ζ are almost identical for GK2, GK4, GK8 and GKR, and are close to that for GK1.

4. Concluding remarks

The 100-term GKR expansions for the ground states of the helium atom and its isoelectronic ions from H^- to Ne^{8+} lead to more accurate energies than any other

Table 2. Energies (hartrees) of He and its isoelectronic ions obtained with 100-term GKR expansions. Energies from the 203 and 308-term wave functions of Thakkar and Koga (TK) [19] are listed for comparison; for H^-, the TK energies correspond to 214- and 455-term wave functions

	TK(203)	GKR(100)	TK(308)
H^-	−0.5277510164997	−0.52775101654263	−0.527751016544240
He	−2.90372437703389	−2.903724377034030	−2.9037243770341144
Li^+	−7.27991341266914	−7.279913412669241	−7.2799134126693020
Be^{2+}	−13.65556623842343	−13.655566238423488	−13.6555662384235829
B^{3+}	−22.03097158024262	−22.030971580242644	−22.0309715802427777
C^{4+}	−32.40624660189837	−32.406246601898378	−32.4062466018985265
N^{5+}	−44.78144514877254	−44.781445148772592	−44.7814451487727008
O^{6+}	−59.15659512275776	−59.156595122757784	−59.1565951227579217
F^{7+}	−75.53171236395932	−75.531712363959344	−75.5317123639594872
Ne^{8+}	−93.90680651503737	−93.906806515037406	−93.9068065150375455

Table 3. Parameters for the 20-term GK expansions

	GK1			GK2			GK4			GK8			GKR		
i	l_i	m_i	n_i	l_i	m_i	n_i	l_i	m_i	n_i	l_i	m_i	n_i	l_i	m_i	n_i
1	0	0	0	0	0	0	0	0	0	0	0	0	0.000	0	0.000
2	1	0	1	1	0	1	1	0	1	1	0	1	1.049	0	1.007
3	2	2	2	2	2	2	2	2	2	2	2	2	1.967	2	1.887
4	1	0	2	1	0	2	1.25	0	1.75	1.25	0	1.75	1.506	0	2.065
5	5	0	0	4	0	0	4	0	0	3.875	0	0	3.452	0	0.001
6	1	2	2	1	2	2	1.25	2	1.75	1.5	2	1.75	1.903	2	1.851
7	2	0	0	1.5	0	0	1.5	0	0	1.5	0	0	1.446	0	0.000
8	2	2	3	2	2	3	2	2	2.25	2	2	2.125	2.027	2	1.860
9	4	2	2	4	2	2	3.5	2	1.75	3.5	2	1.875	4.008	2	1.904
10	3	0	1	2.5	0	1	2.5	0	1	2.5	0	1	2.574	0	1.130
11	0	0	3	0	0	2.5	0.75	0	1.75	0.625	0	1.625	0.865	0	1.329
12	2	0	2	1.5	0	1.5	1.75	0	2.25	1.75	0	2.625	1.384	0	1.814
13	2	0	3	1.5	0	3.5	1.75	0	2.5	2.375	0	1.875	2.701	0	1.447
14	4	0	2	4.5	0	1	4.5	0	0.75	4.75	0	0.625	4.680	0	0.803
15	2	0	4	3.5	0	1.5	2.75	0	1.75	2.125	2	1	1.968	2	1.701
16	3	0	0	2	2	2.5	3	2	1.5	6	2	2.125	7.210	2	2.050
17	1	2	1	6	2	1.5	6.75	2	2.25	3.25	4	3.375	3.082	4	3.592
18	2	2	4	3	4	3	3.25	4	3.5	3.375	4	4	3.105	4	3.794
19	2	4	1	3.5	4	4.5	3.25	4	4.25	6.75	4	4	6.443	4	4.246
20	6	4	5	7.5	4	4	5.5	4	3.75	5.375	6	3.375	5.274	6	3.653
ζ		1.944			1.995			1.994			1.991			2.008	

expansions with comparable numbers of terms. The 100-term GKR energies are better than those obtained with roughly twice as many terms using our previous [19] expansion (Eq. 2), or the ansatz (Eq. 1) involving logarithmic terms [15, 16]. We think that it would be worthwhile to attempt a calculation for the ground state of the lithium atom in which fractional powers of the interelectronic distances are used.

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