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Ground-state energies for the helium isoelectronic series

Ajit J. Thakkar
Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B 6E2, Canada

Toshikatsu Koga
Department of Applied Chemistry, Muroran Institute of Technology, Muroran, Hokkaido 050, Japan

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Variational calculations are reported for the ground state of the helium isoelectronic series. An ansatz is introduced and it achieves an accuracy comparable to that hitherto achieved only with basis functions containing logarithmic terms. Energies accurate to better than one part in 10^{14} are obtained for the ground states of He through Ne^{8+} using 308-term expansions, and the ground state of H^- using 455 terms.

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The solution of Schrödinger's equation for two-electron atoms has attracted an enormous amount of interest since the emergence of quantum mechanics. Originally, these systems constituted a good test of quantum mechanics. Current interest is partly due to the use of these systems as test beds for approximate theories of relativistic, radiative, and other effects not included in Schrödinger's description. Another strong motivation for studying two-electron atoms is the hope that lessons learned in constructing accurate wave functions for these small systems will be applicable to larger ones.

The most compact representations discovered so far [1] for the ground-state wave functions of the two-electron atoms have the form

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

in which $u=r_{12}$ is the interelectronic distance,

$$s=r_1+r_2 , \quad t=r_1-r_2 , \qquad (2)$$

j_i, k_i, m_i, n_i are non-negative integers, l_i is an integer that may be negative under certain conditions, and ζ and c_i are variational parameters. With 246-term expansions of this sort, Frankowski and Pekeris [1] obtained variational energies that were not surpassed for almost two decades. In 1984, Freund and co-workers [2] reported even more accurate 230-term expansions of this form. Their improvements were achieved essentially by reordering the terms so that more important ones came before less important ones and by adding terms that have both $k_i \neq 0$ and l_i negative.

No other wave functions that combine comparable accuracy and compactness have been found to date. The purpose of this paper is to report an ansatz that simultaneously achieves comparable accuracy and compactness without the use of logarithmic terms.

Our ansatz is based on several observations that are summarized below. Wave functions of the form

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\exp(-\zeta s)\sum_{i=1}^{I} c_i s^{l_i} t^{2m_i} u^{n_i} , \qquad (3)$$

in which l_i, m_i, n_i are non-negative integers, have been used since the trailblazing work of Hylleraas [3]. Optimization of ζ and careful ordering of terms [4] results in relatively rapid convergence. For example, with a 204-term expansion of this type, Koga, Kasai, and Thakkar [5] obtained $-2.904\,724\,373$ hartress for the ground state energy of He which is 4 nhartrees higher than the best available upper bound of $-2.904\,724\,377\,034\,07$ hartrees [2,6]. Schwartz [7] and Schwartz [8] demonstrated that fractional powers of s and u improve the convergence of the ansatz (3). Thus, with a 189-term expansion in which half integral powers of s were included, Schwartz [8] obtained $-2.904\,724\,376\,16$ hartrees for the ground-state energy of He which is 0.87 nhartrees above the best available energy [2,6]. Kinoshita [9] showed that including certain negative powers of s and u improves the convergence of the Hylleraas ansatz (3). Thus, his form was

$$\psi(\mathbf{r}_i,\mathbf{r}_2)=\exp(-\zeta s)\sum_{i=1}^{I} c_i s^{l_i-n_i} t^{2m_i} u^{n_i-2m_i} , \qquad (4)$$

in which l_i, m_i, n_i are non-negative integers.

With the above considerations in mind, we first tried fractional powers of s and u in the ansatz

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\exp(-\zeta s)\sum_{i=1}^{I} c_i s^{l_i/\lambda} t^{2m_i} u^{n_i/2} , \qquad (5)$$

in which λ is a small, positive, fixed integer, and l_i, m_i, n_i are non-negative integers subject to the inequality

$$0 \le Ll_i+2Mm_i+Nn_i \le P . \qquad (6)$$

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TABLE I. Ground-state energies for helium ($Z=2$) through Ne^{8+} ($Z=10$) in hartrees as predicted by our [Thakkar and Koga (TK)] 203, 252, and 308 term expansions and the 230-term wave functions [Freund, Huxtable, and Morgan (FHM)] of Freund and co-workers [2].

Z	TK—203[a]	FHM—230[b]	TK—252[a]	TK—308[a]
2	−2.903 724 377 033 89	−2.903 724 377 034 07	−2.903 724 377 034 085	−2.903 724 377 034 114 4
3	−7.279 913 412 669 14	−7.279 913 412 669 2	−7.279 913 412 669 284	−7.279 913 412 669 302 0
4	−13.655 566 238 423 43	−13.655 566 238 423 5	−13.655 566 238 423 566	−13.655 566 238 423 582 9
5	−22.030 971 580 242 62	−22.030 971 580 242 7	−22.030 971 580 242 761	−22.030 971 580 242 777 7
6	−32.406 246 601 898 37	−32.406 246 601 898 4	−32.406 246 601 898 510	−32.406 246 601 898 526 5
7	−44.781 445 148 772 54	−44.781 445 148 772 6	−44.781 445 148 772 684	−44.781 445 148 772 700 8
8	−59.156 595 122 757 76	−59.156 595 122 757 8	−59.156 595 122 757 905	−59.156 595 122 757 921 7
9	−75.531 712 363 959 32	−75.531 712 363 959 4	−75.531 712 363 959 471	−75.531 712 363 959 487 2
10	−93.906 806 515 037 37	−93.906 806 515 037 4	−93.906 806 515 037 529	−93.906 806 515 037 545 5

[a] This work.
[b] Freund and co-workers [2].

A systematic exploration of different ordering schemes was made by variation of L,M,N in the above. Two of our best results for the He ground state were as follows. A 203-term expansion with $\lambda=2$, $P=11$, $L=M=N=1$, led to an energy of −2.904 724 376 957 51 hartrees which is 0.077 nhartrees above the best available one [2,6]. An even better 204-term expansion with $\lambda=3$, $P=14$, $L=2$, $M=1$, and $N=1$, led to an energy of −2.904 724 377 007 69 hartrees which is only 0.026 nhartrees above the best one [2,6].

The above results are better than those of Schwartz [8] but not as good as those obtained with logarithmic terms [1,2]. Thus we tried the more general ansatz:

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\exp(-\zeta s)\sum_{i=1}^{I} c_i s^{(l_i-n_i)/\lambda} \times t^{2m_i} u^{(n_i-2m_i)/\nu} , \tag{7}$$

in which λ and ν are non-negative parameters that need not be integers, and l_i, m_i, n_i are non-negative integers subject to the inequality:

$$0 \le Ll_i + 2Mm_i + Nn_i \le P . \tag{8}$$

TABLE II. Nonlinear parameters in our best wave functions. The wave function for H^- contains 455 terms ($P=28$) and the rest contain 308 terms ($P=13$).

Z	L	M	N	ζ	λ	ν
1	2	1	3	0.575 76	4.608 84	3
2	1	1	1	1.650 09	6.342 16	2
3	1	1	1	2.740 68	6.028 59	2
4	1	1	1	3.798 24	5.774 40	2
5	1	1	1	4.845 75	5.620 23	2
6	1	1	1	5.888 14	5.518 53	2
7	1	1	1	6.927 35	5.448 06	2
8	1	1	1	7.964 36	5.397 45	2
9	1	1	1	8.999 65	5.360 03	2
10	1	1	1	10.033 56	5.332 16	2

This eclectic ansatz allows both fractional and negative powers of s and u. Moreover, variation of L,M,N in inequality (8) permits a systematic optimization of term ordering schemes. Exploratory calculations led us to choose $\nu=2$, and $L=M=N=1$ as optimal for He through Ne^{8+}. This leads to 203, 252, and 308 term wave functions for $P=11$, 12, and 13, respectively. A noninteger ν does not improve the results significantly for expansions of this length. Table I compares our resulting energies with those of Freund and co-workers [2]. Our 203-term energies are no more than 2 phartrees above their 230-term results which in turn are higher than our 252- and 308-term energies by no more than 0.1 phartree. Our 308-term energies seem to be converged to about 1 part in 10^{14}.

The hydride anion is very different from the other two electron atoms. Systematic exploratory calculations with the ansatz of Eq. (7) led us to choose $\nu=3$, and $L=2$, $M=1$, $N=3$ as optimal for H^-. With $P=21$, this choice led to a 214-term expansion that yielded an energy of −0.527 751 016 499 7 hartrees which is lower than the 230-term best result of Freund and co-workers [2], the 246-term best result of Frankowski and Pekeris [1], and the 250-term energy of Drake [6]. By using 455 terms ($P=28$), we obtained an energy of −0.527 751 016 544 240 hartrees which is 0.037 phartrees lower than Drake's 616-term best result of −0.527 751 016 544 203 hartrees [6].

Table II summarizes nonlinear parameters defining our 308-term wave functions for He through Ne^{8+} and the 455-term wave function for the hydride anion. We are exploring the use of ansatz (7) and further generalizations for the low lying S states of the two-electron atoms.

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