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

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In the early days of quantum mechanics, Hylleraas[1-3] determined a very accurate wave function for the helium atom (see Refs. 4 and 5 for a review). Using the variables $s = r_1 + r_2$, $t = r_1 - r_2$, and $u = r_{12}$ (which are often called the Hylleraas variables), he expanded the wave function for the ground-state helium atom as

$$\Psi_n = \exp(-\zeta s) \sum_{i=1}^{n} c_i s^{n_i} t^{2l_i} u^{m_i}, \tag{1}$$

where ζ and $\{c_i\}$ are variational parameters. The six-term function Ψ_6 given by

$$\Psi_6 = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2), \tag{2}$$

has been introduced in several quantum chemistry books (see, e.g., Refs. 6–10) as a typical function that manifests the spirit of the expansion (1) and yet gives an accurate energy comparable to the experimental one.

During our recent study on the electron correlation problem of two-electron atoms, we have encountered a situation where we have to know the accurate parameter values of Eq. (2). Since the literature values[2,6,7,10] do not have sufficient significant figures for our purpose, we have been obliged to redo the variational calculation of the helium atom with the trial function (2). Our calculations do *not* reproduce the energy given in the literature, but show that the Hylleraas six-term wave function (2) associates an energy much lower than the value hitherto believed. The results are reported in the following. (Atomic units are used throughout.)

The two-electron atomic Hamiltonian in the Hylleraas coordinates is given in Refs. 2–5 and 11. To avoid trivial mistakes, we have processed all the algebraic manipulations including differentiations and integrations by a software for algebraic computation.[12] The generated expressions for the Hamiltonian and overlap matrix elements have been directly incorporated into a FORTRAN program by which the energy and parameters are determined.

We have first minimized the energy E as a function of the six parameters involved in Eq. (2) by using the Powell method of conjugate directions.[13] In Table I, the results for the helium atom are summarized and compared with the literature values. Our calculations give an energy $-2.903\,329\,354$ which is lower than the known value by about 0.0001.

To verify the above result, we have examined two more different methods. One method finds the optimum parameters by the minimization of the energy derivative sum $|\partial E/\partial\zeta| + \Sigma_{i=1}^{5} |\partial E/\partial c_i|$, where all the derivatives are analytically evaluated. The other method determines the energy E and the linear parameters $\{c_i\}$ by the solution of a generalized eigenvalue problem[2-5,11] for a given exponent ζ. The nonlinear parameter ζ is iteratively determined so as to achieve $\partial E/\partial\zeta = 0$. However, none of these calculations has altered the present results given in Table I.

If we restrict some linear coefficients in Eq. (2) to be zero, we obtain simpler Hylleraas functions such as

$$\Psi_2 = \exp(-\zeta s)(1 + c_1 u), \tag{3a}$$

$$\Psi_2' = \exp(-\zeta s)(1 + c_2 t^2), \tag{3b}$$

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TABLE I. The Hylleraas six-term wave function for helium.

	Hylleraas (Ref. 2)	Pauling–Wilson (Ref. 6.)	Slater (Refs. 7 and 10)	Present
E	− 2.903 24	− 2.903 24	− 2.903 24	− 2.903 329 354
V/T[a]	...	...	...	− 2.000 000 000
ζ	1.82	1.818	1.82	1.755 656
c_1	0.353 8	0.353	0.353 808	0.337 294
c_2	0.128 5	0.128	0.128 521	0.112 519
c_3	− 0.100 8	− 0.101	− 0.100 828	− 0.145 874
c_4	0.033 1	0.033	0.033 124	0.023 634
c_5	− 0.031 8	− 0.032	− 0.031 799	− 0.037 024

[a] Virial ratio.

TABLE II. The Hylleraas six-term wave functions for helium-like atoms.

	H^-	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
$-E$	0.526 464 363	7.279 286 233	13.654 798 53	22.030 114 07	32.405 327 30	44.780 480 85	59.155 596 65	75.530 687 06	93.905 759 59
ζ	0.701 186	2.784 751	3.808 557	4.830 494	5.851 559	6.872 143	7.892 429	8.912 514	9.932 455
c_1	0.260 181	0.354 317	0.361 318	0.365 071	0.367 395	0.368 970	0.370 106	0.370 962	0.371 630
c_2	0.072 248	0.154 657	0.197 144	0.239 794	0.282 531	0.325 319	0.368 139	0.410 978	0.453 831
c_3	− 0.143 860	− 0.127 225	− 0.107 497	− 0.087 704	− 0.067 960	− 0.048 275	− 0.028 643	− 0.009 057	+ 0.010 487
c_4	0.004 360	0.042 220	0.060 818	0.079 658	0.098 824	0.118 349	0.138 249	0.158 533	0.179 204
c_5	− 0.008 958	− 0.066 731	− 0.096 594	− 0.126 471	− 0.156 343	− 0.186 207	− 0.216 066	− 0.245 919	− 0.275 769

$$\Psi_3 = \exp(-\zeta s)(1 + c_1 u + c_2 t^2). \quad (3c)$$

As another test of our program, we have also performed variational calculations for the trial functions (3a)–(3c) using the same program package. The results have agreed with those in the literature,[1–6,14] though the literature data have been found to be less accurate.

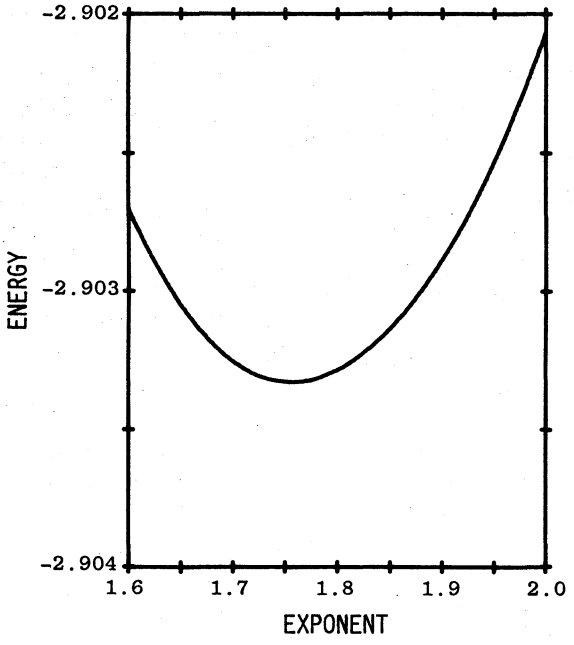

FIG. 1. The Hylleraas six-term energy for He as a function of the exponent ζ. All the linear coefficients in Eq. (2) are optimized for a given value of ζ.

After these various examinations, we conclude that the energy and parameters for the wave function (2) given in the literature are not accurate. The Hylleraas six-term wave function associates an energy much lower than the energy hitherto given in the literature. When we input the parameters given by Slater (see Table I), we have the energy − 2.903 237 797 for He. Therefore, the energy and the parameters given in the literature appear consistent. Comparison of the present and literature parameters (Table I) shows that the essential origin of the present energy lowering lies in the value of the exponent ζ. Figure 1 depicts the energy of the Hylleraas six-term wave function for the helium atom as a function of the exponent ζ. Sufficient optimization of the nonlinear parameter ζ is suggested to be crucial for the accurate determination of the energy. The Hylleraas six-term wave functions for several two-electron atomic ions are summarized in Table II.

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