Optimal Kinoshita wave functions with half-integer powers

Optimal Kinoshita wave functions with half-integer powers

Toshikatsu Koga

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

Kinoshita wave functions for helium and helium-like atoms have been generalized by using half-integer powers for constituent terms. An extensive optimization has been performed for these powers as well as the exponent and mixing coefficients. The optimal functions have been constructed for the number of terms $N = 10, 20, 30, 50, 100$ and the atomic number $Z = 1$ $(H^-) - 10$ (Ne^{8+}). It is demonstrated that the use of half-integer powers dramatically improves the accuracy of the Kinoshita function: In the case of He, for example, the optimal 100-term function gives $-2.903\,724\,377\,033$ hartrees, which is only 1×10^{-12} hartrees higher than the most accurate literature value. The high accuracy of the optimal Kinoshita functions with half-integer powers has been also confirmed for the first two excited states of the helium atom. © *1996 American Institute of Physics.* [S0021-9606(96)01215-5]

I. INTRODUCTION

In the early days of quantum mechanics, Hylleraas[1-5] succeeded to obtain accurate wave functions for helium and helium-like atoms. For S states, Hylleraas proposed an expansion,

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

where

$$s = |\mathbf{r}_1| + |\mathbf{r}_2|, \quad t = |\mathbf{r}_1| - |\mathbf{r}_2|, \quad u = |\mathbf{r}_1 - \mathbf{r}_2|.$$

In the Hylleraas wave function (1), exponent ζ, mixing coefficients $\{c_i\}$, and a set of non-negative integers $\{l_i, m_i, n_i\}$ are parameters, where $\{m_i\}$ must be even for ^1S states and odd for ^3S states. Accurate variational determinations of these parameters were reported in Refs. 6–10.

In 1957, Kinoshita[11,12] discussed (see also Scherr[13]) that the Hylleraas expansion (1) cannot be a formal series solution of the Schrödinger equation for two-electron atoms and proposed an alternative expansion,

$$\Psi_N = \exp(-\zeta s) \sum_{i=1}^{N} c_i s^{l_i} \left(\frac{t}{u}\right)^{m_i} \left(\frac{u}{s}\right)^{n_i}, \tag{2}$$

which generalizes the Hylleraas expansion through negative powers of the variables s and u. To our knowledge, actual applications of the Kinoshita expansion have been very limited: Only for the ground-state He atom, Kinoshita[11,12] reported 10-, 22-, 34-, 38-, 39-, and 80-term functions, and Davidson[14] constructed 34- and 44-term functions. Some of these functions were improved[8] by the reoptimization of the parameters ζ and $\{c_i\}$. Very recently,[15] an extensive optimization has been performed for the composition of N terms, as well as ζ and $\{c_i\}$, of the Kinoshita expansion (2). The results for $N = 1 - 100$ and $Z = 1 - 10$ showed[15] that the optimal term selection (i.e., optimization of the powers $\{l_i, m_i, n_i\}$) drastically improves the accuracy of the Kinoshita function.

In the present paper, we show that a generalization of the powers from integers to half-integers, followed by the varia-

tional optimization of these powers, improves much dramatically the accuracy of the Kinoshita expansion. Namely, our generalized Kinoshita expansion is

$$\Psi_N = \exp(-\zeta s) \sum_{i=1}^{N} c_i s^{l_i/2} \left(\frac{t}{u}\right)^{m_i} \left(\frac{u}{s}\right)^{n_i/2}. \tag{3}$$

It is important that the extension from integer to half-integer values of the powers little loses the simplicity of the original Kinoshita expansion (2) and yet does not cause any new complexity in the evaluation of the Hamiltonian and overlap matrix elements (see Sec. II). For the Hylleraas expansion (1), the use of half-integer powers was studied by Schwartz[16-18] and Schwartz[19] with definite success. However, the essential difference of our approach from theirs is the variational determination of optimal combination of these powers. The exponent ζ and the mixing coefficients $\{c_i\}$ have been optimized as well. The resultant optimal Kinoshita functions with half-integer powers are reported here for $N = 10, 20, 30, 50, 100$ and for $Z = 1$ (H^-) through 10 (Ne^{8+}) in their ground state. The present best He energy from the optimal 100-term function is $-2.903\,724\,377\,033$ hartrees which is only 1×10^{-12} hartrees above the most accurate literature value obtained by using more than 200 terms with more complicated forms. Examination of the first $(1s2s, 2\ ^3S)$ and second $(1s2s, 2\ ^1S)$ excited states of He

TABLE I. Optimal Kinoshita energies for the He atom in the ground $(1\ ^1S)$ state.

N	Optimal Kinoshita with half-integer powers	Optimal Kinoshita with integer powers
5	$-2.903\,569\,904\,286$	$-2.903\,384\,915\,45$
10	$-2.903\,721\,712\,458$	$-2.903\,707\,688\,14$
20	$-2.903\,724\,228\,359$	$-2.903\,723\,608\,39$
30	$-2.903\,724\,361\,888$	$-2.903\,724\,249\,24$
40		$-2.903\,724\,359\,34$
50	$-2.903\,724\,376\,757$	$-2.903\,724\,372\,40$
100	$-2.903\,724\,377\,033$	$-2.903\,724\,376\,95$

TABLE II. Optimal structure of some N-term Kinoshita functions for the ground-state He atom. Powers (l_i, m_i, n_i) of Eq. (3) are shown together with the exponent ζ.

$N = 5$ $\zeta = 1.834\,382\,779$ $(E = -2.903\,569\,904\,286)$
  (0,0,0)(1,0,2)(2,0,3)(3,0,2)(4,2,3)

$N = 10$ $\zeta = 1.721\,032\,471$ $(E = -2.903\,721\,712\,458)$
  (0,0,0)(0,0,2)(1,0,0)(1,0,2)(2,0,2)(2,0,3)(3,2,1)(3,2,3)(5,2,4)(11,4,11)

$N = 20$ $\zeta = 1.995\,225\,276$ $(E = -2.903\,724\,228\,359)$
  (0,0,0)(0,0,5)(2,0,2)(2,0,4)(3,0,0)(3,0,3)(3,0,7)(5,0,2)(7,0,3)(8,0,0)
  (9,0,2)(2,2,4)(4,2,4)(4,2,5)(4,2,6)(8,2,4)(12,2,3)(6,4,6)(7,4,9)(15,4,8)

$N = 30$ $\zeta = 1.717\,086\,327$ $(E = -2.903\,724\,361\,888)$
  (0,0,0)(0,0,1)(1,0,0)(1,0,4)(2,0,0)(2,0,2)(2,0,4)(3,0,0)(3,0,2)(3,0,3)
  (3,0,6)(3,0,8)(4,0,0)(4,0,3)(4,0,4)(5,0,0)(5,0,3)(7,0,2)(0,2,1)(1,2,2)
  (2,2,6)(3,2,4)(3,2,5)(4,2,7)(5,2,8)(6,2,5)(3,4,7)(4,4,5)(8,4,10)(10,6,7)

$N = 50$ $\zeta = 1.952\,310\,118$ $(E = -2.903\,724\,376\,757)$
  (0,0,0)(0,0,3)(1,0,2)(1,0,3)(2,0,0)(2,0,2)(3,0,0)(3,0,4)(3,0,5)(3,0,9)
  (4,0,0)(4,0,3)(4,0,5)(4,0,7)(4,0,14)(5,0,0)(5,0,2)(5,0,5)(7,0,4)(8,0,6)
  (9,0,2)(11,0,0)(11,0,7)(15,0,8)(0,2,5)(1,2,4)(2,2,4)(2,2,6)(3,2,7)(4,2,4)
  (4,2,6)(4,2,7)(4,2,8)(5,2,5)(5,2,7)(6,2,7)(8,2,4)(9,2,4)(9,2,8)(13,2,4)
  (3,4,10)(4,4,9)(6,4,5)(6,4,6)(7,4,8)(13,4,9)(6,6,15)(8,6,7)(16,6,8)(16,8,5)

---

shows that the present generalization and optimization of the Kinoshita function also work for excited states. Hartree atomic units are used throughout this paper.

II. COMPUTATIONAL DETAILS

The generalized Kinoshita wave function (3) includes linear parameters $\{c_i\}$ and nonlinear parameters ζ and $\{l_i, m_i, n_i\}$.

For given values of ζ and $\{l_i, m_i, n_i\}$, the linear parameters $\{c_i\}$ were variationally determined by solving a generalized eigenvalue equation $\mathbf{HC} = \mathbf{SC}E$, where all the Hamiltonian H_{ij} and overlap S_{ij} matrix elements are expressed in terms of a basic integral

$$\int_0^\infty ds \int_0^s dt \int_t^s du \; \exp(-2\zeta s) s^i t^j u^k$$

$$= \frac{\Gamma(i+j+k+2)}{(j+1)(j+k+2)(2\zeta)^{i+j+k+3}}. \tag{4}$$

Since $i + j + k$ is either integer or half-integer for the wave function (3), the required gamma function can be precisely calculated by

$$\Gamma(n+1) = n!, \tag{5a}$$

$$\Gamma(n+\tfrac{1}{2}) = \frac{(2n-1)!!}{2^n} \sqrt{\pi}. \tag{5b}$$

The nonlinear parameter ζ was determined by the scaling procedure (see, e.g., Ref. 20) so that the virial theorem is satisfied, i.e., $V = -2T$ or $E = -V^2/4T$ holds, where T and V are the kinetic and potential energies, respectively. Since the optimal values for ζ and $\{c_i\}$ are mutually dependent, the determinations of ζ and $\{c_i\}$, for a given set of $\{l_i, m_i, n_i\}$, were repeated alternately until our convergence threshold $|V/2T + 1| \leq 1 \times 10^{-12}$ is satisfied.

The determination of the best set of powers $\{l_i, m_i, n_i\}$ $(i = 1, \ldots, N)$ is not simple. After various examinations, we have employed in the present study an iterative local optimization which is outlined as follows.

(1) For a given N, we choose a set of powers $\{l_i, m_i, n_i\}$ $(i = 1, \ldots, N)$ as an initial value. (2) We locally optimize the powers (l_j, m_j, n_j) for the jth term, keeping the remaining powers $\{l_i, m_i, n_i\}$ $(i \neq j)$ fixed. The exponent ζ and the coefficients $\{c_i\}$ are always optimized by the methods described earlier. (3) The local optimization of powers is applied to all the N terms in turn to complete one cycle of power optimizations. (4) Such a cycle is iterated until no further improvement is obtained within one cycle of the local power optimization.

All the aforementioned procedures (1)–(4) are repeated starting from many different initial sets of powers in order to find a best composition of powers for the N terms. We finally obtain the optimal N-term Kinoshita function specified by

---

TABLE III. Comparison of some very accurate energies E and the numbers N of used terms for the He atom.

N	E	Remarks	Reference
1078	$-2.903\,724\,375$	Perimetric variables	21
1648	$-2.903\,724\,376\,707$	Gaussian geminals	22
50	$-2.903\,724\,376\,757$	Optimal Kinoshita with half-integer powers	Present
100	$-2.903\,724\,377\,033$	Optimal Kinoshita with half-integer powers	Present
230	$-2.903\,724\,377\,034\,0$	Hylleraas with log terms	23
616	$-2.903\,724\,377\,034\,073$	Hylleraas with double exponents plus hydrogenic	24
308	$-2.903\,724\,377\,034\,114\,4$	Kinoshita with fractional powers	25

TABLE IV. Optimal Kinoshita energies for the H^- ion.

N	Optimal Kinoshita with half-integer powers	Literature
10	−0.527 743 228 813 1	
20	−0.527 750 451 864 8	
30	−0.527 750 960 781 8	
44		−0.527 750 736 888 1[a]
50	−0.527 751 014 652 5	
68		−0.527 750 974 243 2[a]
100	−0.527 751 016 522 7	−0.527 751 009 126 5[a]
230		−0.527 751 015 3[b]
455		−0.527 751 016 544 240[c]
616		−0.527 751 016 544 203[a]

[a]Reference 24.
[b]Reference 23.
[c]Reference 25.

the best parameter values of ζ, $\{c_i\}$, and $\{l_i, m_i, n_i\}$ for a given Z.

III. RESULTS AND DISCUSSION

Table I summarizes the energies E of the optimal N-term Kinoshita functions ($N = 5 - 100$) with half-integer powers for the helium atom. The corresponding results obtained[15] with integer powers are also given there for comparison. The accelerated energy convergence with increasing N is clear for the use of half-integer powers. The 50-term energy from half-integer powers compares well with the 100-term energy from integer powers. In Table II, the detailed structures of the optimal functions are exemplified for He. We find that the optimal composition of N terms is not regular when N is increased: The terms appeared in the optimal N-term function do not always appear in the optimal N'-term function ($N' > N$). This makes the empirical determination of the optimal structure difficult, but at the same time makes significant contribution to the energy improvement when the number of constituent terms is increased.

TABLE V. Optimal 100-term Kinoshita energies for Li^+ ($Z = 3$) through Ne^{8+} ($Z = 10$). "Limit" shows the most accurate literature value taken from Ref. 25.

Z	Ion	Optimal Kinoshita	Limit
3	Li^+	−7.279 913 412 668	−7.279 913 412 669
4	Be^{2+}	−13.655 566 238 42	−13.655 566 238 42
5	B^{3+}	−22.030 971 580 24	−22.030 971 580 24
6	C^{4+}	−32.406 246 601 89	−32.406 246 601 90
7	N^{5+}	−44.781 445 148 77	−44.781 445 148 77
8	O^{6+}	−59.156 595 122 75	−59.156 595 122 76
9	F^{7+}	−75.531 712 363 95	−75.531 712 363 96
10	Ne^{8+}	−93.906 806 515 03	−93.906 806 515 04

In Table III we collect some of very accurate He energies from the literature[21-25] and compare them with the present best results from the optimal 50- and 100-term Kinoshita functions with half-integer powers. If the employed numbers of expansion terms are taken into account, we see the efficiency of the optimal Kinoshita function. In particular, the present 50-term energy is already lower than the famous Pekeris value[21] obtained with 1078 terms. Moreover, the present 100-term energy is only 1×10^{-12} hartrees higher than the most accurate value[25] in spite of the smallness of the present expansion.

The hydrogen anion ($Z = 1$) is known[23] to be very difficult compared to the other two-electron atoms. Several optimal Kinoshita energies for the H^- ion are listed in Table IV. A few literature values[23-25] are also included there for comparison. The present Kinoshita functions composed of the optimally selected terms are found to be also effective for H^-: The optimal 100-term energy, for example, is much better than the 230-term energy reported by Freund et al.[23] It was also clarified[9] that for H^- ($Z = 1$), the radial correlation (represented mainly by the variables s and t) is more important as opposed to the angular correlation (represented mainly by the variable u) significant for $Z \geq 2$. Although we omit the details, comparison of the optimal structures for

TABLE VI. Optimal Kinoshita energies with half-integer powers for the He atom in the first excited ($1s2s, 2\,^3S$) state.

N	Optimal Kinoshita (Present)	Pekeris (Ref. 21)	Thakkar-Smith (Ref. 26)	Drake (Ref. 24)
10	−2.175 222 991 807			
20	−2.175 229 239 802		−2.175 229 193	
30	−2.175 229 368 131		−2.175 229 343	
40			−2.175 229 363	
44				−2.175 229 368 965 6
50	−2.175 229 377 902			
55			−2.175 229 376	
68	−2.175 229 378 225			−2.175 229 376 678 8
100	−2.175 229 378 225			−2.175 229 378 076 9
125		−2.175 220 979 61		
190				−2.175 229 378 234 5
254		−2.175 229 258 88		
444		−2.175 229 376 80		
616				−2.175 229 378 236 790 7
1078		−2.175 229 378 237		

TABLE VII. Optimal Kinoshita energies with half-integer powers for the He atom in the second excited $(1s2s,2\ ^1S)$ state.

N	Optimal Kinoshita (Present)	Pekeris (Ref. 21)	Thakkar-Smith (Ref. 26)	Drake (Ref. 24)
10	−2.145 859 283 017			
20	−2.145 969 552 619		−2.145 966 060	
30	−2.145 973 300 682		−2.145 971 291	
40			−2.145 972 811	
44				−2.145 973 621 073 9
50	−2.145 974 036 113			
55			−2.145 973 824	
68				−2.145 973 998 274 1
100	−2.145 974 045 971			−2.145 974 036 279 9
190				−2.145 974 045 808 9
203		−2.145 958 989		
308		−2.145 972 779		
406				−2.145 974 046 051 233
444		−2.145 973 945		
615		−2.145 974 037		
616				−2.145 974 046 054 143

$Z=1-10$ has indeed shown that terms with $m_i \neq 0$ (i.e., the radial correlation through the variable t) appear more frequently for $Z=1$ than for the other cases. This is also a reason that in the literature, applications of a single (and empirical) selection rule for constituent terms to all Z values yielded rather poor results for $Z=1$.

For the two-electron cations Li^+ through Ne^{8+}, the optimal Kinoshita functions are again efficient, and the convergence of the corresponding energies with increasing N is as fast as it is for He and H^-. In Table V, the present optimal 100-term Kinoshita energies are summarized. For the cations Be^{2+}, B^{3+}, and N^{5+}, the present results coincide with the most accurate literature value[25] to the given decimal places. For the other cations, the deviations are 1×10^{-12} hartrees (Li^+) and 1×10^{-11} hartrees (C^{4+}, O^{6+}, F^{7+}, and Ne^{8+}).

We have also examined the accuracy of the Kinoshita function with half-integer powers for the first two excited states of the helium atom. To our knowledge, this is the first application of the Kinoshita expansion to excited states. Table VI summarizes the present results for the first excited $(1s2s,2\ ^3S)$ state and compares them with some literature results.[21,24,26] It is immediately seen that the optimal Kinoshita function is also efficient for the excited state: When we compare the energies from the same or similar number of expansion terms, the Kinoshita energy is always lowest. The present 100-term energy is much better than Pekeris' 444-term energy and close to Drake's 190-term energy. Similar accuracy of the Kinoshita expansion is found in Table VII for the second excited $(1s2s,2\ ^1S)$ state. For this state, the 100-term Kinoshita energy is lower than Pekeris' 615-term energy and Drake's 190-term energy.

IV. CONCLUDING REMARKS

We have generalized the Kinoshita expansion using half-integer powers and performed an extensive optimization of these powers as well as the exponent and the mixing coefficients. The results for $N=10-100$ and $Z=1-10$ in the

ground state demonstrate that the extension to half-integer powers combined with variational determination of their values substantially improves the accuracy of the Kinoshita function. For instance, the optimal 50-term Kinoshita energy is better than the Pekeris 1078-term energy for He. The same is also true for the first two excited states of He.[27]

The present success immediately suggests a further generalization of the powers from half-integers to quadrant integers (i.e., multiples of a quarter), for example. However, our pilot computations showed that energy improvement obtained did not appeal us compared to the complexity added by moving from half- to quadrant integers.

In the present study, we have restricted ourselves to the Kinoshita expansions with $N \leqslant 100$, but we expect a similar improvement for $N > 100$ by the optimal term selection. In our opinion, however, it would be most convenient if we could further improve the accuracy without increasing the number of terms. The present study shows that the variational selection of the powers of constituent terms replaces the use of complicated functional forms for the terms and/or the use of a huge number of the terms. We wish to continue our effort along this direction towards more accurate (yet concise) description of helium and heliumlike atoms.

ACKNOWLEDGMENTS

[1] E. A. Hylleraas, Z. Phys. **48**, 469 (1928).
[2] E. A. Hylleraas, Z. Phys. **54**, 347 (1929).
[3] E. A. Hylleraas, Z. Phys. **65**, 209 (1930).
[4] E. A. Hylleraas, Adv. Quant. Chem. **1**, 1 (1964).
[5] E. A. Hylleraas, Mathematical and Theoretical Physics, Vol. 2 (Wiley, New York, 1970), p. 416 ff.
[6] P. Jolly, Int. J. Quant. Chem. **16**, 1149 (1979).
[7] T. Koga, J. Chem. Phys. **93**, 3720 (1990).

[8] T. Koga, J. Chem. Phys. **94**, 5530 (1991).
[9] T. Koga, J. Chem. Phys. **96**, 1276 (1992).
[10] T. Koga and K. Matsui, Z. Phys. D **27**, 97 (1993).
[11] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).
[12] T. Kinoshita, Phys. Rev. **115**, 366 (1959).
[13] C. W. Scherr, Phys. Rev. A **19**, 469 (1979).
[14] E. R. Davidson, J. Chem. Phys. **39**, 875 (1963).
[15] T. Koga and S. Morishita, Z. Phys. D **34**, 71 (1995).
[16] H. M. Schwartz, Phys. Rev. **103**, 110 (1956).
[17] H. M. Schwartz, Phys. Rev. **120**, 483 (1960).
[18] H. M. Schwartz, Phys. Rev. **130**, 1029 (1963).
[19] C. Schwartz, Phys. Rev. **128**, 1146 (1962).

[20] P.-O. Löwdin, J. Mol. Spectrosc. **3**, 46 (1959).
[21] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959); **126**, 1470 (1962).
[22] K. B. Wenzel, Chem. Phys. Lett. **224**, 155 (1994).
[23] D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).
[24] G. W. F. Drake, Nuc. Inst. Meth. Phys. Res. B **31**, 7 (1988).
[25] A. J. Thakkar and T. Koga, Phys. Rev. A **50**, 854 (1994).
[26] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 16 (1977).
[27] Full details of all the present Kinoshita functions with the optimal half-integer powers are available upon request to the author at the internet address koga@muroran-it.ac.jp.