Hylleraas wave functions revisited

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Hylleraas wave functions revisited

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Optimality of the combination of N terms used in the Hylleraas N-term wave function is examined for several two-electron atoms. It is pointed out that the N-term wave function given in the literature is not always the best N-term function for a fixed N. For example, the known Hylleraas six-term function

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

yields the energy of $-2.903\,329\,354$ a.u. for the helium atom, whereas a new six-term function

$$\Psi_{6,\mathrm{opt}} = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 u^2 + c_4 s^2 u + c_5 s^3 u)$$

gives a much lower energy of $-2.903\,452\,763$ a.u. It is also shown that the best combination of N terms depends largely on the nuclear charge.

I. INTRODUCTION

For the ground state of the helium and heliumlike atoms, Hylleraas proposed[1-3] an approximate wave function in the form of

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

where s, t, and u are the Hylleraas coordinates defined by

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}, \tag{2}$$

and where the exponent ζ and the mixing coefficients $\{c_i\}$ are variational parameters (see Refs. 4 and 5 for a review). The index N appearing in Eq. (1) specifies the number of terms involved in the spatial function Ψ_N. (The two-electron singlet spin function is implicit.) Numerical examinations with the trial functions such as

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

$$\Psi_3 = \exp(-\zeta s)(1 + c_1 u + c_2 t^2), \tag{3b}$$

$$\Psi_6 = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2), \tag{3c}$$

showed[1-8] that the Hylleraas wave function actually gives an accurate energy which compares well with the experimental one. Herzberg and co-workers[9-11] studied 10-, 14-, 18-, and 20-term wave functions for further improvement. The resultant Hylleraas wave functions have been often used[12-18] as parent functions to derive physical quantities of near exact accuracy. The Hylleraas wave function has constituted a very successful case of quantum theory from its early days and hence the function has been also introduced in several quantum chemistry books (see, e.g., Refs. 19–24).

In spite of their familiarity, it has been recently pointed out[25-27] that the known parameter values for several Hylleraas N-term wave functions are insufficiently accurate and accordingly the Hylleraas wave functions have energies lower than the values hitherto believed. Comparison of the new and literature parameters has shown[25-27] that the essential origin of the energy improvement lies in the value of the exponent ζ and sufficient optimization of this nonlinear parameter has been suggested to be crucial for the accurate determination of the wave function and the associated energy.

Once the explicit form of the Hylleraas function Ψ_N is fixed, i.e., the N constituent terms in Eq. (1) are specified by a set of nonnegative integers $\{l_i, m_i, n_i\}$, we now have[26,27] methods which determine the optimum parameters ζ and $\{c_i\}$ accurately. However, a question has emerged: How have the values $\{l_i, m_i, n_i\}$ been chosen to construct the N-term function? As long as we have examined, no literature has answered this question for $N \leqslant 6$. For $N = 10$–20, Herzberg and co-workers[9-11] have constructed their N-term function by adding $(N-6)$ terms to Ψ_6 [see Eq. (3c)] after partial examination of the relative energy improvement due to additional terms. However, their procedure is based essentially on intuition and furthermore it remains unverified whether the original six-term function is the best combination of six terms among available terms.

In the present paper, we study *systematically* a combination of constituent N terms which gives the "best" N-term function. In Sec. II, our method is described and the best Hylleraas N-term wave functions ($N \leqslant 20$) are reported for the helium atom. It is shown that except for the case of $N \leqslant 3$, the N-term functions given in the literature are not the optimum combinations of N terms. In Sec. III, the best N-term functions ($N \leqslant 6$) are studied for a few heliumlike atoms with nuclear charges $Z = 1$, 3, 5, and 10. We find that the optimum combination of N terms depends largely on Z, reflecting the different significance of the radial and angular correlations. Atomic units are used throughout this paper.

II. THE BEST HYLLERAAS *N*-TERM FUNCTIONS FOR HELIUM

Since the condition for $\{l_i, m_i, n_i\}$ is only that they must be nonnegative integers, there exists an infinite number of terms which are candidates for the Hylleraas N-term function. Therefore, we have imposed a restriction

$$l_i + 2m_i + n_i \leqslant \max \quad (i = 1,2,\ldots,N) \tag{4}$$

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in the search of the best combination of N terms. The constraint (4) would be consistent with the spirit of the series expansion (1). For $\max = 5$ and 7, the total numbers of available terms are 34 and 70, respectively.

In order to find a good N-term function, we first tried a method which chooses the N terms with largest mixing coefficients $|c_i|$ from an N'-term wave function $(N' > N)$. When this method was applied to the construction of a six-term function from the 34-term function (which results from $\max = 5$), we obtained

$$\Psi_6' = \exp(-\zeta s)(1 + c_1 u + c_2 u^2 + c_3 t^2 + c_4 su + c_5 s) \tag{5}$$

with the associated energy of $-2.903\,370\,418$ $(\zeta = 1.817\,945)$. Since the original six-term function Ψ_6 [see Eq. (3c)] has the energy of $-2.903\,329\,354$ $(\zeta = 1.755\,656)$, the new function Ψ_6' is certainly a better six-term function. However, Ψ_6' is not the best function as we see below and the above method is not appropriate to find the optimum N terms.

Our second method tries to find the best N-term function by adding a term which gives the largest energy improvement to the best $(N-1)$-term function. Starting from the single term function with $(l_1, m_1, n_1) = (0,0,0)$ and repeating the above procedure, we obtained an alternative six-term function

$$\Psi_6'' = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 s^3 + c_4 u^2 + c_5 s^2 u), \tag{6}$$

which has the energy $-2.903\,385\,680$ $(\zeta = 1.845\,689)$. A comparison of the energy values shows that Ψ_6'' is better than Ψ_6 and Ψ_6'.

To verify the optimality of the function Ψ_6'', we have third employed the most primitive method. Namely, all the possible combinations of six terms arising from the 34 terms have been examined keeping the first two terms to be 1 and u. Among ${}_{34-2}C_{6-2} = 35\,960$ combinations, we find that the best six-term function takes the form

$$\Psi_{6,\mathrm{opt}} = \exp(-\zeta s)(1 + c_1 u + c_2 t^2 + c_3 u^2 + c_4 s^2 u + c_5 s^3 u) \tag{7}$$

with the energy $-2.903\,452\,763$ $(\zeta = 1.858\,924)$, which is lower than the energy of the original function Ψ_6 by 0.000 123 409. The best function $\Psi_{6,\mathrm{opt}}$ does not coincide with either Ψ_6' or Ψ_6''. The best six-term function (7) has remained unchanged, even when we have examined ${}_{161-2}C_{6-2} = 25\,637\,001$ combinations resulting from $\max = 10$.

These experiences for the six-term function show that the perturbation theoretical methods are inappropriate for the search of the best Hylleraas N-term functions. Therefore, we have decided to use the most primitive method described above under the constraint $\max = 5$. For $2 \leqslant N \leqslant 4$, the first term has been fixed to be 1, while for $5 \leqslant N \leqslant 10$ the first two terms have been fixed to be 1 and u. For $12 \leqslant N \leqslant 20$, the terms which appear commonly in the preceding two calculations have been fixed in principle and the constraint $\max = 7$ has been applied. These restrictions have been introduced so as to reduce the number of possible combinations, but the maximum number of the examined combinations amounts to ${}_{34-2}C_{10-2} = 10\,518\,300$ for $N = 10$.

The best N-term functions obtained in the present study are summarized in Table I. Since we have imposed condition (4) (and the additional restriction described above) in our search of the optimum combination, we cannot assert that the present results represent the best N-term functions among *all* combinations of N terms, particularly for $N \geqslant 12$. However, we can claim at least that the N-term functions given in the literature are not the best possible functions except for $N \leqslant 3$. The energy improvement by the adoption of the best N terms is nontrivial. The maximum improvement is seen for $N = 6$. For $N \geqslant 10$, we find in the table that the energy associated with the literature N-term function is inferior to that associated with the present best $(N-2)$-term function. This means that we can reduce two or three terms in expansion (1) keeping the accuracy obtained in the literature. Such a reduction of the number of terms would considerably simplify the succeeding calculation of various physical quantities based on the Hylleraas wave function. We also notice that the terms appearing in the best N-term function do not always appear in the best N'-term function $(N' > N)$. This point prohibits the perturbation theoretical search of the optimum combination (as exemplified for the six-term case) and at the same time makes the significant contribution to the energy improvement when the number of the constituent terms is increased.

III. *Z* DEPENDENCE OF THE BEST HYLLERAAS *N*-TERM FUNCTION

We also had a question whether the N-term function, which is found to be best for the helium atom, is again the best function for heliumlike atoms. In order to clarify this point, we have examined the best N-term function $(2 \leqslant N \leqslant 6)$ for two-electron atoms with the nuclear charges $Z = 1$, 3, 5, and 10. The primitive search procedure has been employed with the constraint $\max = 7$ for $Z = 1$ and $\max = 5$ for $Z = 3$, 5, and 10.

The results are summarized in Table II together with the associated energies. It is very clear that the best combination of N terms depends largely on the nuclear charge Z. Particularly for $Z = 1$, the best combination differs from the others even for $N = 2$. For $Z = 2$–10, the best two- and three-term functions have exactly the same structure, but one or two terms are different when $N \geqslant 4$. The optimum combination for $Z = 5$ and 10 are found to be same for all N examined and we anticipate that the terms in the best functions may be common for $Z \geqslant 5$.

From the results given in Table II, we cannot find any definite rule about the Z dependence of the best Hylleraas N-term function. However, we may be able to refer to the different significance of the radial and angular correlations. By the definition of the Hylleraas variables [Eq. (2)], we may interpret that the terms involving s and t contribute mainly to the radial correlation, while the terms involving u contribute mainly to the angular correlation. We observe in the table that for $Z = 1$, the terms including the variables s and t appear more frequently than for a larger Z case. Therefore, we

TABLE I. The Hylleraas N-term wave functions. The present results show the optimum combinations of N terms when the conditions max = 5 and 7 are imposed on, respectively, for $2\leqslant N\leqslant 10$ and $12\leqslant N\leqslant 20$. The underlined terms are fixed during the search of the optimum combination.

	Literature			Present	
N	Terms	Energy	Reference	Terms	Energy
2	$1,u$	$-2.891\,120\,717$[a]	7	The same as the literature	
3	$1,u,t^2$	$-2.902\,432\,029$[a]	2	The same as the literature	
4	⋯	⋯	⋯	$\underline{1},u,t^2,s^3$	$-2.902\,772\,273$
5	⋯	⋯	⋯	$\underline{1},\underline{u},t^2,u^2,s^2u$	$-2.903\,384\,915$
6	$1,u,t^2,u^2,s,s^2$	$-2.903\,329\,354$	2, 25, 26	$\underline{1},\underline{u},t^2,u^2,s^2u,s^3u$	$-2.903\,452\,763$
7	⋯	⋯	⋯	$\underline{1},\underline{u},t^2,u^2,su,t^2u, st^2u$	$-2.903\,541\,538$
8	⋯	⋯	⋯	$\underline{1},\underline{u},t^2,u^2,su,t^2u,s^2, st^2u$	$-2.903\,610\,262$
9	⋯	⋯	⋯	$\underline{1},\underline{u},t^2,u^2,su,t^2u,s^2, u^3,s^2t^2$	$-2.903\,665\,621$
10	$1,u,t^2,u^2,su,t^2u,s^2, u^3,s,t^2u^2$	$-2.903\,602\,729$	9, 10, 27	$\underline{1},\underline{u},t^2,u^2,su,t^2u,s^2, u^3,st^2,t^2u^2$	$-2.903\,686\,386$
12	⋯	⋯	⋯	$\underline{1},\underline{u},\underline{t^2},\underline{u^2},\underline{su},\underline{t^2u},\underline{s^2}, \underline{u^3},st^2,t^2u^2,u^4,s^2u^4$	$-2.903\,706\,348$
14	$1,u,t^2,u^2,su,t^2u,s^2, u^3,st^2,t^2u^2,u^4,s,s^3, t^2u^4$	$-2.903\,701\,491$	10, 27	$\underline{1},\underline{u},\underline{t^2},\underline{u^2},\underline{su},\underline{t^2u},\underline{s^2}, \underline{u^3},\underline{st^2},\underline{t^2u^2},u^4,t^2u^3, su^5,s^3t^4$	$-2.903\,713\,385$
16	⋯	⋯	⋯	$\underline{1},\underline{u},\underline{t^2},\underline{u^2},\underline{su},\underline{t^2u},\underline{s^2}, \underline{u^3},\underline{st^2},\underline{t^2u^2},\underline{u^4},t^2u^3, u^5,u^6,t^4u^3,s^4t^2u$	$-2.903\,717\,166$
18	$1,u,t^2,u^2,su,t^2u,s^2, u^3,st^2,t^2u^2,u^4,t^2u^3, u^5,s,s^3,s^4,s^2t^2,t^2u^4$	$-2.903\,716\,636$	10, 27	$\underline{1},\underline{u},\underline{t^2},\underline{u^2},\underline{su},\underline{t^2u},\underline{s^2}, \underline{u^3},\underline{st^2},\underline{t^2u^2},\underline{u^4},\underline{t^2u^3}, \underline{u^5},s^4u^2,t^4u^3,s,s^4t^2,s^4u$	$-2.903\,720\,915$
20	$1,u,t^2,u^2,su,t^2u,s^2, u^3,st^2,t^2u^2,u^4,t^2u^3, u^5,s,s^3,s^4,t^4,s^2t^2, t^2u^4,st^2u$	$-2.903\,717\,754$	11, 27	$\underline{1},\underline{u},\underline{t^2},\underline{u^2},\underline{su},\underline{t^2u},\underline{s^2}, \underline{u^3},\underline{st^2},\underline{t^2u^2},\underline{u^4},\underline{t^2u^3}, \underline{u^5},\underline{u^6},\underline{t^4u^3},s,s^4t^2,s^3u, s^2u^2,s^5$	$-2.903\,722\,007$

[a] These energies have been recomputed in the present study.

suggest that the radial correlation is most important in the case of $Z=1$ or the H^- atom. When Z increases, the contribution of the angular correlation increases in a relative sense. For example, the variable u appears in the four terms of the six-term function of $Z=2$–10. Such a distinguished aspect of the electron correlation in the H^- atom has also been reported[28] in the study of the intracule or electron-pair density $h(r_{12})=h(u)$.

In summary, we have shown that the Hylleraas N-term functions given in the literature do not represent the best combination of N terms except for the cases $N=2$ and 3. We have reported better (possibly best in some cases) N-term functions ($N\leqslant 20$) for the helium atom. It has also been pointed out that the best combination of N terms depends on the nuclear charge of the two-electron atom under consideration. The Z dependence of the optimum combination has been suggested to be related with the different significance of the radial and angular correlations. Since the Hylleraas wave function provides us with a compact and accurate approximation, we hope that the improved N-term functions obtained in this paper will be of some help to the future study of the two-electron atomic systems.

TABLE II. Z dependence of the best Hylleraas N-term wave functions. The present results have been obtained under the conditions max = 7 and 5, respectively, for $Z=1$ and 2–10. The underlined terms are fixed during the search of the optimum combination. The associated energy is given in parentheses.

N	$Z=1$	$Z=2$	$Z=3$	$Z=5$	$Z=10$
2	$\underline{1},t^2$ $(-0.512\,293\,309)$	$\underline{1},u$ $(-2.891\,120\,717)$	$\underline{1},u$ $(-7.268\,157\,166)$	$\underline{1},u$ $(-22.019\,543\,675)$	$\underline{1},u$ $(-93.895\,416\,542)$
3	$\underline{1},u,st^2$ $(-0.525\,850\,518)$	$\underline{1},u,t^2$ $(-2.902\,432\,029)$	$\underline{1},u,t^2$ $(-7.278\,030\,333)$	$\underline{1},u,t^2$ $(-22.028\,353\,819)$	$\underline{1},u,t^2$ $(-93.903\,482\,023)$
4	$\underline{1},u,t^2,s^2t^4$ $(-0.526\,927\,442)$	$\underline{1},u,t^2,s^3$ $(-2.902\,772\,273)$	$\underline{1},u,t^2,t^2u$ $(-7.278\,505\,286)$	$\underline{1},u,t^2,u^2$ $(-22.029\,267\,558)$	$\underline{1},u,t^2,u^2$ $(-93.904\,865\,203)$
5	$\underline{1},\underline{u},t^2,s,st^4$ $(-0.527\,362\,212)$	$\underline{1},\underline{u},t^2,u^2,s^2u$ $(-2.903\,384\,915)$	$\underline{1},\underline{u},t^2,u^2,su$ $(-7.279\,446\,235)$	$\underline{1},\underline{u},t^2,u^2,su$ $(-22.030\,304\,830)$	$\underline{1},\underline{u},t^2,u^2,su$ $(-93.905\,927\,138)$
6	$\underline{1},\underline{u},t^2,s^2u,s^2t^2,s^2t^4$ $(-0.527\,569\,675)$	$\underline{1},\underline{u},t^2,u^2,s^2u,s^3u$ $(-2.903\,452\,763)$	$\underline{1},\underline{u},t^2,u^2,u^3,su$ $(-7.279\,566\,834)$	$\underline{1},\underline{u},t^2,u^2,s^2u,t^2u$ $(-22.030\,504\,023)$	$\underline{1},\underline{u},t^2,u^2,s^2u,t^2u$ $(-93.906\,250\,206)$

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