Ritz-Hylleraas Solutions of the Ground State of Two-Electron Atoms Involving Fractional Powers*

H. M. Schwartz

Department of Physics, University of Arkansas, Fayetteville, Arkansas

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Earlier work on the inclusion of half-integral powers in the Ritz-Hylleraas ground-state solutions of the nonrelativistic wave equation for the helium atom is extended through functions involving 18 parameters. Energies that are lower than those found with other published comparable functions are obtained in all cases. Preliminary results are also given of calculations involving more general fractional powers, Z values different from 2, and half-integral-power solutions for which the expectation value of the square of the Hamiltonian is finite. With the latter type of expansions one obtains, at least at an early stage, an additional improvement in the approximation. Thus, with 11 parameters one finds the energy -2.903704 atomic units, which differs by only 0.0007% from the 80-parameter solution of Kinoshita. The initial results found for $Z=8$ indicate an improvement in convergence over that obtained for $Z=2$; the energy -59.156560 atomic units, which was obtained with a 12-parameter function, was only 0.00006% larger than the energy obtained by Pekeris with his 210-term function. The computed mass polarization corrections give also satisfactory results as judged by the similar results obtained with the most extensive solutions available.

1. INTRODUCTION

IN a previous note[1] there were presented initial results on the use of Hylleraas functions with half-integral exponents, i.e., expansions of the form

$$\psi = e^{-ks/2} \sum c_{lmn} s^{l/2} t^{2m} u^{n/2},$$

$$(s = r_1 + r_2, \; t = r_2 - r_1, \; u = r_{12}),$$

$$l, m, n = 0, 1 \cdots \quad (1)$$

as Ritz approximants to the ground-state solution of the nonrelativistic Schrödinger equation for the helium atom,

$$H\psi \equiv \left[-\frac{1}{2\mu}(\nabla_1^2 + \nabla_2^2) - 2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \right]\psi = E\psi;$$

$$\mu = \frac{M}{1+M}, \quad (2)$$

where M is the nuclear mass and all quantities are in atomic units. At the time of writing of that note, the accuracy of the published results on this solution[2] was still pretty much of an open question, there existing no certain way of ascertaining the rapidity of convergence of the computed Ritz-Hylleraas sequence.[2] The introduction of half-integral exponents in the Hylleraas expansion tended to considerably improve this convergence as shown by the initial results presented in Table I of I. This provided the stimulus for further calculations of this type through functions involving 18 parameters, the limit on the number of parameters being in part imposed by the limitations of desk

calculator work. The results are given in Table I (Sec. 2), which includes also a correction to the 13-parameter function of I.

A comparison (Table III, Sec. 2) of the energy results with those in reference 2 as well as with those of Hart and Herzberg[3] and of Kinoshita,[4] shows that the functions of type (1) give invariably closer energies for trial functions of the same number of parameters. On the other hand, this superiority of functions (1) ultimately begins to decrease with the increase in the number of parameters. This decrease is of course to be expected. What is perhaps still an open question is whether the advantage shown by functions (1) will subsist or will be completely washed out as the number of parameters becomes comparable with the highest number employed by Kinoshita.[4] In what concerns the finding of a sufficiently precise value for the lowest eigenvalue of (2), this question may well have already lost its practical significance, inasmuch as it is quite likely that the very extensive solutions found by Kinoshita[4] and by Pekeris[5] do already give this eigenvalue to the required accuracy. The uncertainty which still exists in this regard derives from the insufficiency of the presently available theoretical estimates of the error which attaches to the energy values computed by the Ritz method.[6] Another related difficulty is the meagerness of our present knowledge of the analytical properties of the exact ground-state solution of (2). For these reasons, at least, the study of various types of solutions of (2) appears to be still justified.

The functions of Table I of I as well as those of Table I of this paper do not give a finite result for the mean

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[1] H. M. Schwartz, Phys. Rev. **103**, 110 (1956). This paper will be referred to as I.

[2] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[3] J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).

[4] T. Kinoshita, Phys. Rev. **105**, 1490 (1957); **115**, 366 (1959).

[5] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[6] Nevertheless it can in fact be shown by a reasoning which while not completely certain admits of a high degree of probability, that the limits of error on the values of Kinoshita and of Pekeris are already very close to those imposed by present experimental uncertainties.

TABLE I. Nonrelativistic wave functions of Hylleraas type with half-integral exponents for the He ground state, for which $\langle H^2 \rangle$ diverges. The energy is in atomic units; the coefficient c_{lmn} as given in Eq. (1).[a] The functions are normalized.

k } input[b]	3.5	3.51	3.5	3.5
$-E$ }	2.903714	2.903714	2.9037168	2.9037190
k } output[b]	3.500063	3.510051	3.500018	3.500015
$-E$ }	2.903714	2.903714	2.9037174	2.9037186
lmn				
000	1.396891	1.396267	1.3998363	1.3715826
001	0.176230	0.176456	0.1539403	0.1156624
010	0.329918	0.330492	0.4119643	0.4551549
002	0.518531	0.520100	0.5560845	0.6159175
100	−0.232072	−0.229571	−0.2307628	−0.1153529
200	0.007720	0.012139	0.0071788	−0.1146762
101	−0.173014	−0.176040	−0.1726858	−0.1672808
011	−0.255171	−0.258750	−0.4367977	−0.5735045
004	0.023654	0.024203	0.0291609	0.0751512
012	0.066024	0.066989	0.1956241	0.3497075
003	−0.244199	−0.248732	−0.2686550	−0.3649887
102	0.136041	0.143005	0.1357688	0.1820912
110	0.030952	0.033774	0.0307856	0.0314524
013			−0.0297931	−0.1046422
202				−0.0195603
300				0.0389373
005				−0.0073613
014				0.0132067

[a] The notation in Eq. (1) relative to the designation of the coefficients is slightly different from that employed in Table I of I.
[b] This terminology is explained in footnote 11.

value $\langle H^2 \rangle$ of the square of our Hamiltonian operator. This failure need not prevent the sequence of energies computed from such Ritz approximating functions to converge to the true energy value (Sec. 2). However, while the existence of $\langle H^2 \rangle$ is not required for the calculation of the nonrelativistic energy, this expression enters in the relativistic correction, and for this reason, a recalculation was made with functions of type (1) but with omission of the terms in $u^{\frac{1}{3}}$ and $s^{\frac{1}{2}}u^{\frac{1}{3}}$ which are responsible for a logarithmic singularity in the integral of $\langle H^2 \rangle$.[7] The results are shown in Table II and are discussed in Sec. 2.

In order to have an additional check on the goodness of our functions, the mass polarization corrections were computed with these functions. The results are discussed in Sec. 3.

The motivation, largely empirical, in the introduction of the semi-integral exponents in (1), leads to the question raised in I as to the further improvement that may be possible with the use of more general fractional exponents. Preliminary work on this question (Sec. 4) is not particularly encouraging, but this work is of too limited a scope to be conclusive. On another question raised in I, the dependence upon the nuclear charge Z of the advantage of using fractional exponents in the problem under discussion, preliminary results (Sec. 4) are more definite, and point to an additional relative

improvement in the energy eigenvalue for nuclear charge larger than two.

2. SOLUTIONS INVOLVING HALF-INTEGRAL POWERS

As stated in the introduction, the choice of half-integral exponents in (1) was dictated mainly by empirical considerations. It was suggested in the first place by an examination of the relative distribution in size of the coefficients in the approximating functions computed by Chandrasekhar and Herzberg.[2] Another consideration was the purely practical one of ease of computation. The matrix elements entering in our Ritz variational problem[8] involve only integrals of the form

$$\int_0^\infty ds \int_0^s du \int^u dt\, e^{-s} s^a t^b u^c$$

$$= \Gamma(a+b+c+3)/(b+1)(b+c+2). \quad (3)$$

It is seen that fractional values of a and of c do not lead to any significant complication. On the other hand, the introduction of terms involving log s, which is a related procedure, does introduce some computational complication, inasmuch as in place of (3) we also get expressions which involve derivatives of the gamma function. Such terms have in fact been used by Hylleraas and Midtal[9] and to very good advantage.[10]

TABLE II. Nonrelativistic wave functions of Hylleraas type with half-integral exponents for the He ground state, for which $\langle H^2 \rangle$ is finite. The energy is in atomic units; the coefficients c_{lmn} as given in Eq. (1).[a] The functions are normalized.

k } input	3.5	3.5	3.5
$-E$ }	2.903666	2.903704	2.903711
k } output	3.500100	3.499909	3.500151
$-E$ }	2.903666	2.903704	2.903711
lmn			
000	1.477574	1.456080	1.447247
002	0.535292	0.659123	0.679155
010	0.465583	0.408421	0.421906
100	−0.294954	−0.286999	−0.274295
011	−0.527949	−0.436981	−0.465458
003	−0.161543	−0.316917	−0.259914
102	0.051240	0.040603	−0.047367
012	0.237770	0.194866	0.216767
013	−0.033982	−0.030215	−0.035105
110	0.031565	0.035130	0.033076
004		0.057239	0.037792
202			0.028654

[a] The notation is the same as in Table I.

[8] See, for instance, H. A. Bethe and E. E. Salpeter, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1957), Vol. 35, Sec. 32.
[9] E. A. Hylleraas and J. Midtal, Phys. Rev. **103**, 829 (1956); **109**, 1013 (1958). The second paper corrects a numerical error contained in the first.
[10] As the authors give only the final energy result for a function involving 24 parameters, it is not at present possible to compare their results with those presented here. Neither is there as yet available a discussion of the analytical motivation, if such exists, for the inclusion of their particular logarithmic term.

[7] A preliminary result was given in J. phys. radium **19**, 505 (1958).

TABLE III. Comparison of the energy results derived from Ritz approximations employing half-integral powers with those derived from integral-power expansions. Entries are the absolute values of the energy in atomic units.

Number of parameters	10	11	13	14	18	20	22
Positive-integral-power expansions	2.903603[a]			2.903701[b]	2.903715[c]	2.903718[d]	
Integral-power expansions[e]	2.903626						2.903714
Half-integral-power expansions[f]	2.903666	2.903704	2.903714	2.903717	2.903719		

[a] S. Chandrasekhar, D. Elbert, and G. Herzberg, Phys. Rev. **91**, 1172 (1953).
[b] See reference 2.
[c] This value is a closer approximation for the 18-parameter function of reference 2, as given in reference 4.
[d] See reference 3.
[e] See reference 4.
[f] The first two entries in this row are from Table II, the others from Table I.

The new solutions are presented in Table I. Included is also a 13-term function, which represents a correction of a small numerical error that crept into the earlier work for this function.[1] This error was detected when it was realized that the difference between the values -2.9037190 atomic units (a.u.) for the "output" energy[11] and -2.9037135 atomic units for the "input" energy was in excess of what could be reasonably expected.[12] As a test for the stability of the solution with respect to small variations in the parameter k [which appears in the exponential factor in Eq. (1)] and as an additional check on the computation, the same function was recalculated for $k=3.51$ and is also included in Table I.

The motivation for the calculation of the functions presented in Table II was given in the introduction. It is seen that for these three functions there is in fact an appreciable improvement over the corresponding older functions[13] as judged by the energy values. This improvement would seem to disappear, however, with the 13-term function, as judged by the following results:

13th exponent-triplet: $\frac{3}{2},0,0$ $1,0,0$ $0,0,3$ $2,0,0$

$-E$ (in atomic units): 2.9037119 2.9037119 2.903713 2.903712

In this connection, it should be noted that with the exception of the above case the experimentation that was done with respect to an optimum choice of exponents has been quite limited in all cases, especially for the functions with the higher number of parameters.

The choice of the value 3.5 for the parameter k was made after a number of trials with the 6-parameter function of Table I of I. It has been retained for the functions involving more parameters in the belief that the choice of an optimum value for k becomes less critical as the number of parameters increases. In order

to check this, several k values were tried for the 10-term function of Table II, with the following results:

$k=$	3.7	3.55	3.5	3.45
$-E$ (in at. units)=	2.90364	2.903662	2.903666	2.903659

An additional indication that the chosen value for k is not too far from the best value is provided by the closeness of the output and input[11] E and k in all cases investigated.

The comparison of the results presented here with similar results that have been published,[2–4] given in Table III, does not include any functions with logarithmic terms[9] because, as stated earlier, no functions of this character involving a smaller number of parameters than 24 have as yet been published. From the point of view of constructing the best wave function (best, as judged by the corresponding energy eigenvalue) for a given and reasonably small number of parameters, it would seem to be of interest to investigate further expansions involving logarithmic and fractional-exponent terms.

3. MASS POLARIZATION CORRECTION CALCULATIONS

The correction to the energy eigenvalue E of (2) arising from the finiteness of the mass of the nucleus and additional to the correction implicit in the replacement in (2) of the electronic mass by the reduced mass μ, the so-called mass polarization correction ϵ, is given by the expression[14]

$$\epsilon = \frac{1}{M} \int \nabla_1\psi \cdot \nabla_2\psi d\tau. \qquad (4)$$

The resulting matrix elements for the functions (1) have the same form as for the solutions involving integral powers,[15] with all factorials replaced by the corresponding gamma functions.

Results for the 13-term, 14-term, and 18-term functions of Table I and for the first three functions of Table II are given in Table IV. For comparison, published results for other functions are also included.

[11] The "output" E and k are given by the formulas obtained by variation with respect to the parameter k. See Eqs. (32–19) and (32–20) on p. 235 of reference 8.

[12] In reference 8 (p. 235) it is stated that the output energy represents a closer approximation to the true energy than the input value. However, when the number of parameters to be varied is sufficiently large and the choice of the scaling parameter k is sufficiently good, the difference between the input and output energies can be expected to be relatively small, and this is borne out by all the available results.

[13] Table I of I did not include a 12-parameter function. Such a function, obtained by adjoining a term with the exponent triplet $(\frac{1}{2},0,1)$ to the 11-term function of that table, yielded the energy value -2.902696 atomic units.

[14] See reference 8, Sec. 37.

[15] Equation (18) in L. Wiletz and I. J. Cherry, Phys. Rev. **103**, 112 (1956). The factor 4 in the formula should be replaced by 2.

Table IV. Values of the mass polarization correction, ϵ.

Reference	No. of parameters	ϵ (in atomic units)
Table II	10	2.182×10^{-5}
Table II	11	2.187×10^{-5}
Table II	12	2.183×10^{-5}
Table I	13	2.182×10^{-5}
Table I	14	2.182×10^{-5}
Table I	18	2.182×10^{-5}
a	10	2.187×10^{-5}
a	10	2.092×10^{-5}
a	18	2.182×10^{-5}
a	22	2.183×10^{-5}
	39	2.181×10^{-5}

a See reference 4 (first paper), Table III.

Presumably the value $\epsilon=2.181\times10^{-5}$ a.u. obtained by Kinoshita[4] and by Pekeris[5] is close to the exact value. It is then seen that with the exception of the 11-parameter function of Table II, the results yielded by the other functions both from Table I and from Table II are quite satisfactory. The exception shown by the 11-parameter function is strange, considering that in respect of the energy eigenvalue yielded by it, it is perhaps the best presently available for its number of parameters. Unless some error had crept into the work which had evaded detection, the high sensitivity of expression (4) to the type of wave function employed is worthy of note.

In this connection, it should be noted that it is entirely feasible to include the part of our Hamiltonian which gives rise to Eq. (4) in the Ritz-Hylleraas variational treatment, obviating in this manner the necessity of computing any correction for the nuclear motion.[16] The usual procedure was followed in order that the present results could be compared with those involving other types of wave functions.

4. PRELIMINARY CALCULATIONS FOR NUCLEAR CHARGE DIFFERENT FROM TWO AND FOR MORE GENERAL FRACTIONAL EXPONENTS

In order to check the efficacy of the fractional-exponent Ritz-Hylleraas wave functions for nuclear charge $Z\neq2$, a calculation was made for $Z=1$, $Z=3$, and $Z=8$ with the sets of exponents of the 10-parameter function of Table I of I and in the case of $Z=1$ also for the 6-parameter expansion of that table, this work having been completed before the newer functions shown in Table II have been considered. The result for the 12-term $Z=8$ function was obtained subsequently and for it the exponents of Table II were used. The results are shown in Table V. For comparison, corresponding results with positive-integral power expansions are also

[16] Using this method, we obtained with the 10-term function of Table II the value -2.903644 a.u. for the energy including the effect of mass polarization. This agrees with the result obtained with the conventional method employing the best value of the mass polarization correction.

Table V. Energy eigenvalues for the ground state of H⁻, Li II, and O VIII computed with half-integral-power Ritz-Hylleraas expansions. Values of the ratio R, given in Eq. (5), are included for comparison.

Z	No. of parameters	Absolute value of energy in atomic units	R [given in Eq. (5)]
1	6	0.526541	0.06ᵃ
	10	0.526967	−3.1ᵇ
3	10	7.279817	0.36ᶜ
8	10	59.15647	0.35ᶜ
8	12	59.156560 [Pekerisᵈ=59.156595]	
2	6	2.903381	0.29ᵉ
	10	2.903639	0.31ᶠ

a Compared with the value given by R. E. Williamson, Astrophys. J. 96, 438 (1942).
b Compared with the value given by L. R. Henrich, Astrophys. J. 99, 59 (1944). Henrich's function consists of 11 terms.
c Compared with the values in reference 2.
d See reference 5.
e Compared with the value given by E. A. Hylleraas, Z. Physik 54, 347 (1929).
f Compared with the value given by S. Chandrasekhar, D. Elbert, and G. Herzberg, Phys. Rev. 91, 1172 (1953). Our value from Table I of I is used rather than that from Table II for the sake of more valid comparison with the R values for $Z\neq2$.

included, as well as those of Pekeris,[5] which can be expected to be of very high accuracy. In order to compare the results with those for $Z=2$, we consider the ratio

$$R\equiv(E_{int}-E_{fract})/(E_{fract}-E), \qquad (5)$$

where $E_{int}(E_{fract})$ is the energy eigenvalue obtained with the integral (fractional) power expansions, and E represents the energy obtained by Pekeris. The values of this ratio, R, are entered in the last column of Table V with a corresponding entry also for $Z=2$. It is seen that with the exception of the 10-term function for the negative hydrogen ion, there is indeed an improvement in energy resulting from the use of fractional-exponent expansions. The 10-term function for $Z=1$ could be compared only with the 11-term function of Henrich,[17] but, even so, it is apparent that at least for the choice of powers that was made, there is little, if any, advantage to be gained by using fractional powers. On the other hand, as judged by the ratio R of Eq. (4), it is seen that the advantageous feature of the half-integral-powers expansions does indeed increase for higher Z values.

Table VI. Energy eigenvalues for the ground state of He computed with fractional-power Ritz-Hylleraas expansions. Corresponding values for half-integral-powers expansions are included for comparison.

Wave functions	k^a	$-E$ (in atomic units)
Involving the exponent triplets $(l,m,n)^a$: (0,0,0), (0,0,½), (0,1,0), (0,0,1)	3.6	2.90254
4-parameter function of Table I of I	3.614	2.90277
Involving the exponent triplets: (0,0,0), (0,0,1), (0,1,0), (0,0,³⁄₂), (0,0,2), (1,0,0)	3.44	2.90345
6-parameter function of Table I of I	3.5	2.90338

a See Eq. (1).

[17] L. R. Henrich, Astrophys. J. 99, 59 (1944).

Considering the improvement in energy obtained with the half-integral Hylleraas expansions for the case $Z=2$, it seemed of interest to see if any further improvement could be obtained by employing more general fractional powers. Without any precise analytical guide for selecting the powers, it did not seem worthwhile at this time to undertake any extensive investigation of possibilities. Only functions involving 4 and 6 parameters were considered, and for quite a small selection of powers. The results are presented in Table VI. The energies for corresponding half-integral-power functions are also shown for comparison.

5. CONCLUSIONS

The results so far obtained with the use of fractional powers in the Ritz-Hylleraas method of solution for the ground state of two-electron atomic systems, indicate that at least for functions involving less than about 20 parameters, and as far as the energy eigenvalue is concerned, such use is advantageous. It would be desirable, however, in this connection, to have also some detailed information on the effect of including logarithmic terms in the Hylleraas expansions.

Although, as stated in the introduction, the search for a determination of the lowest eigenvalue of the Hamiltonian in Eq. (2) with a precision consistent with present experimental accuracy may well have already been successfully completed, it would still be of some interest to find out if more rapid convergence, than has so far been obtained, could be produced by an extension of the present results to functions involving considerably more parameters. It is, of course, possible that as soon as the number of parameters becomes sufficiently large, all expansions of Hylleraas type show approximately the same behavior. However, pending a strict theoretical analysis of the properties of the exact solution in question, further calculational experimentation may not be amiss.

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