a more coherent picture of these low-energy cross sections.

With the electron–rare gas atom scattering lengths apparently well known, it is tempting to offer a simple model from which they would follow. In a model previously suggested by Kivel,[45] the effect of the closed electron shells on the scattering was taken to vanish exactly, with the scattering length being determined entirely by the polarization potential. This potential was further assumed to start at a very large distance from the atom. This picture is clearly too simple since it predicts a negative scattering length for all the rare gases, in contradiction to the He and Ne results. (At finite energies it is also inconsistent with the Ramsauer-Townsend effect.) However, if the model is modified so that there is a small positive scattering length of magnitude 1 to $\frac{3}{2}$ a_0 contributed by the closed shells in

each case, while the polarization potential begins at a distance of 3 to 4 a_0 (as it does effectively for hydrogen), then all the scattering lengths are predicted accurately. The contribution from the closed shells might then be interpreted as an effectively repulsive core, whose small radius may be thought of as an effective atomic radius.

Finally, there are a number of things which have been left undone, such as a more serious analysis of the drift velocity data, and a detailed study of the differential cross sections.

ACKNOWLEDGMENTS

[45] B. Kivel, Phys. Rev. **116**, 1484 (1959).

Further Results Concerning Half-Integral Hylleraas Expansions*

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Previous calculations concerning the ground state of two-electron atoms, involving Ritz–Hylleraas expansions with half-integral powers, are continued through expansions involving 31 parameters. As far as can be judged from a comparison of the energies with those obtained with other expansions, the results continue to be favorable. Thus, already with 18 parameters, the computed energies for He and O vii differ from the best published values by 2 and 0.3 parts per million, respectively. Even better results are obtained for He with expansions involving both half-integral and negative powers. A few initial results of calculations for the excited state 2 ^1S are also presented.

1. INTRODUCTION

THE ground-state solution of the nonrelativistic Schrödinger equation for two-electron atoms has recently received considerable attention. Two problems are of immediate interest: the determination of the energy eigenvalue (of the nonrelativistic Hamiltonian for helium) with an accuracy of better than one part per million (ppm), and the determination of the analytic behavior of the corresponding eigenfunction near the singularities of the wave equation.

The significance of having a solution of the first problem, in view of the recent very careful relevant measurements of Herzberg,[1] is well known.[2] In all likeli-

hood, the recent very extensive calculational results[3] already provide the requisite solution. There still remains a shadow of doubt because the rigorously calculated lower bound of the energy falls short of providing together with the more precise upper bounds, limits of the desired accuracy.[4]

The second problem is of interest both in connection with the first problem (quite obviously so), and also in connection with the search for practically tractable and reliable approximations to the ground-state eigenfunctions of two-electron atoms that can serve as standards of comparison in the current attempts to

[1] G. Herzberg, Proc. Roy. Soc. (London) A248, 309 (1958).

[2] For its bearing on the important question of a confirmation of the computed first-order radiative corrections in this two-body problem, see, e.g., reference 1.

[3] T. Kinoshita, Phys. Rev. **105**, 1490 (1957); **115**, 366 (1959); C. L. Pekeris, *ibid.* **112**, 1649 (1958); **115**, 1216 (1959); W. Kolos, C. C. J. Rothaan, and R. A. Sack, Rev. Mod. Phys. **32**, 178 (1960); G. Munschy and P. Pluvinage, J. Phys. Radium **23**, 184 (1962); C. Schwartz, Phys. Rev. **128**, 1146 (1962).

[4] It is possible, though, to arrive at an adequate lower bound on the basis of reasoning, which, while falling short of absolute rigor, can be taken to possess a high degree of credibility [Bull. Am. Phys. Soc. **5**, 65 (1960)].

find methods of atomic wave function approximation for the two-electron case admitting of extension to atoms with many electrons.[5] Rigorous analytic results on this problem have been slow in forthcoming. Interesting attempts have been made long ago by Bartlett[6] and more recently by Pluvinage[7] and by Fock.[8] The analysis in these publications is however only of a formal character. An important beginning, though, in a rigorous analytic approach has been made recently by Kato.[9] His results are, however, as yet of limited scope.

It is owing to the present status of the two problems in question that further exploration of a purely computational character in this field appears to be still justified. It is this consideration which prompted a resumption of the computational work involving Hylleraas expansions with half-integral exponents.[10] If such expansions continue to be relatively successful as the number of terms is increased, they may possibly lead to improved convergence in the high-precision approximations.[11] At the same time, these investigations could be of some suggestive value in the purely theoretical analysis of our problem. A possible illustration of this point is provided by our results with expansions involving mixed negative and half-integral exponents (Sec. 3). It appeared of some interest to examine also the effectiveness of the suggested expansions in determining the energies for the excited state $2\,^1S$. Initial results for He and Li II are discussed in Sec. 5.

2. EXPANSIONS INVOLVING POSITIVE HALF-INTEGRAL POWERS. $Z=2$

The new results involving half-integral exponents are presented in Table I. These were obtained with the aid of a double-precision program for computing determinants on the IBM 650. Since the eigenvalues are already closely known, a small number of linear interpolations is sufficient to insure the desired accuracy in the solution. The computational cost in determining the energies is thus relatively small. Finding the associated eigenfunctions, however, entails an added computer program and increased cost, and the work was therefore not undertaken at this time.

[5] See, e.g., L. C. Green, S. Matsushima, C. Stephens, et al., Phys. Rev. 112, 1187 (1958); C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. 32, 194 (1960); A. W. Weiss, Phys. Rev. 122, 1826 (1961); and the references given in these papers.

[6] J. H. Bartlett, Phys. Rev. 51, 661 (1937). This work is based on earlier investigations of T. H. Gronwall, Ann. Math. 33, 279 (1932); Phys. Rev. 51, 655 (1937).

[7] P. Pluvinage, J. Phys. Radium 16, 675 (1955). Much of this work has been done in collaboration with G. Munschy. See, e.g., Munschy, thesis, University of Strasbourg, 1958 (unpublished) and the references contained in it. For a detailed discussion of the correlation between the theoretical ideas (including the rigorous results of Kato, reference 9) and calculational results, see Munschy and Pluvinage, reference 3.

[8] V. Fock, Izv. Akad. Nauk S.S.S.R., Ser. Fiz. 18, 161 (1954).

[9] T. Kato, Comm. Pure Appl. Math. 10, 151 (1957).

[10] H. M. Schwartz, Phys. Rev. 120, 483 (1960). This paper will be referred to as A.

[11] Such expectation appears to be now confirmed, at least in part, by the published results of C. Schwartz (reference 3).

TABLE I. Energies corresponding to approximate solutions of the nonrelativistic Schrödinger equation for He, of the form $e^{-k(r_1+r_2)/2} \sum C_{lmn}(r_1+r_2)^{l/2}(r_1-r_2)^{2m}r_{12}^{n/2}$ with non-negative integral l, m, n.

Item	Number of parameters	(l,m,n) set[a]	k	$-E$ (a.u.)
1	18	1	3.5	2.9037148
2	18	1	3.7	2.9037187
3	18	1	3.75	2.9037190
4	18	1	3.8	2.9037189
5	18	2	3.75	2.9037194
6	24	3	3.5	2.9037192
7	24	3	3.75	2.9037204
8	24	4	3.75	2.9037206
9	31	5	3.75	2.90372159
10	31	6	3.75	2.90372158
11	31	6	3.7	2.90372144

[a] Set 1: $\begin{cases} l = 0\ 0\ 0\ 1\ 0\ 1\ 0\ 0\ 0\ 0\ 2\ 3\ 4\ 1\ 2\ 2\ 4 \\ m = 0\ 0\ 1\ 0\ 1\ 1\ 0\ 0\ 1\ 1\ 0\ 0\ 0\ 0\ 0\ 1\ 0. \\ n = 0\ 2\ 0\ 0\ 1\ 0\ 3\ 4\ 2\ 3\ 6\ 0\ 0\ 0\ 2\ 2\ 0\ 2 \end{cases}$

Set 2 = set 1 with the exponent triplet $(l,m,n) = (1,0,0)$ replaced by $(6,0,0)$. Set 3 = set 1 together with the triplets $(0,0,5)$, $(2,0,3)$, $(0,1,4)$, $(1,0,4)$, $(0,0,8)$, $(2,1,4)$. Set 4 = set 2 together with the triplets $(3,1,0)$, $(0,1,4)$, $(0,0,8)$, $(2,0,6)$, $(4,0,4)$, $(2,0,8)$. Set 5 = set 3 together with the triplets $(3,1,0)$, $(3,0,2)$, $(4,1,2)$, $(6,0,0)$, $(4,0,4)$, $(2,0,6)$, $(2,0,8)$. Set 6 = set 5 with $(1,0,0)$ replaced by $(0,1,6)$.

All the expansions included in Tables I, II, and III correspond to functions which yield a finite value of $\langle H^2 \rangle$, the expectation value of the square of our Hamiltonian. Comparison of the items 1–4 of Table I with the energy results discussed in Sec. 2 of A, confirms the expectation that the initial advantage shown by expansions associated with finite $\langle H^2 \rangle$ over corresponding expansions for which $\langle H^2 \rangle$ diverges, does not persist as the number of terms increases. All the functions considered in A and some of the expansions referred to here, contain a term with the factor $(r_1+r_2)^{1/2}$ which would lead therefore to a singularity in derivatives at $r_1=r_2=0$. This singularity does not prevent of course the expansions from serving as proper Ritz functions for the approximate determination of the energy eigenvalue. But, as in the case of the nonconvergence of the integral $\langle H^2 \rangle$, the question arises if the possession of this singularity has an effect on the rapidity of convergence of the Ritz sequence as judged by the associated energy eigenvalues. Comparison of the results in entries 3 and 5 as well as 9 and 10 of Table I does not disclose any such effect.

It had been conjectured in A that small variation in the scaling factor k would have negligible effect on the energy eigenvalues as the number of terms in the expansions becomes relatively large. But a test of this conjecture proved it not wholly tenable, as is shown by the results in entries 1–4, 6–7, and 10–11 of Table I. The value $k=3.75$ appears to be definitely better, even if only to a small extent, than the value $k=3.5$ adopted in A.

Because of the absence of any unambiguous strictly analytic criteria for the choice of the exponents in the expansions, it is not possible to be sure if the one made is to any degree an optimum one. In order to have some indication on this question, two different sets of expo-

nents were used for a 24-term expansion, with results shown in entries 7 and 8 of Table I.

3. EXPANSIONS INCLUDING NEGATIVE POWERS

In order to be able to judge if the fractional-power expansions still retain any superiority as the number of parameters increases through 31, it is necessary to have suitable comparison functions. No published results appear to be available for 31 parameters. However, there exists one function involving nonnegative integral exponents and 29 parameters,[12] and the associated energy value, -2.9037201 a.u. (atomic units), compares with the 24-parameter value listed in item 7 of Table I. It appeared, therefore, of interest to find the energies yielded by optimum 31-parameter expansions of the Kinoshita type,[3] using the ratios of the coefficients of the expansions as computed by Kinoshita as a partial criterion in the selection of the exponents. The results are given in entries 1 and 2 of Table II. When these are

TABLE II. Energies corresponding to approximate solutions of the nonrelativistic Schrödinger equation for He, of the form $e^{-k(r_1+r_2)/2} \sum C_{lmn}(r_1+r_2)^{l/2}(r_1-r_2)^{2m}r_{12}^{n/2}$ with integral l, m, n (positive and negative).

Item	Number of parameters	(l,m,n) set[a]	k	$-E$ (a.u.)
1	31	1	3.71	2.90372128
2	31	2	3.71	2.90372127
3	28	3	3.75	2.9037214
4	31	4	3.75	2.9037220
5	31	5	3.75	2.90372214
6	31	5	3.7	2.90372216
7	31	6	3.7	2.90372217
8	31	6	3.6	2.90372216

a Set 1: $\begin{cases} l=0\ 2\ 0\ 4\ 2\ 0\ 0\ 6\ 4\ 2\ 0\ 2\ 0\ 0\ 0\ 4\ 4\ 0\ 8\ \ 0 \\ m=0\ 0\ 0\ 0\ 0\ 1\ 0\ 0\ 0\ 0\ 1\ 1\ 0\ 1\ 0\ 1\ 2\ 0\ \ 0 \\ n=0\ 0\ 2\ 0\ 2\ 4\ 0\ 0\ 2\ 4\ 6\ 0\ 2\ 8\ 4\ 4\ 0\ 0\ 0\ 10 \end{cases}$

Set 1: $\begin{cases} l=\ \ 0\ \ \ 2\ \ -2\ -2\ -2\ -4\ -2\ -4\ -2\ -2\ -2 \\ m=\ \ 1\ \ \ 1\ \ \ 0\ \ \ 1\ \ \ 0\ \ \ 0\ \ \ 1\ \ \ 1\ \ \ 0\ \ \ 1\ \ \ 0. \\ n=-2\ -2\ \ \ 4\ \ \ 0\ \ \ 6\ \ \ 8\ \ \ 2\ \ \ 4\ \ \ 8\ \ \ 4\ \ 10 \end{cases}$

Set 2 =set 1 with the exponential triplets $(l,m,n)=(0, 1, -2)$, $(2, 1, -2)$ replaced by $(0,1,6)$, $(-2, 0, 12)$. Set 3 =set 3 of Table I together with $(-2, 0, 4)$, $(-2, 1, 2)$, $(-2, 1, 0)$, $(-2, 0, 6)$. Set 4 =set 3 together with $(3,1,0)$, $(6,0,0)$, $(0,1,6)$. Set 5 =set 4 with $(0,0,5)$, $(2,1,4)$ replaced by $(-4, 0, 8)$, $(-4, 1, 4)$. Set 6 =set 4 with the triplets $(1,0,0)$, $(2,0,3)$, $(2,1,4)$, $(0,1,6)$ replaced by $(-4, 0, 8)$, $(-4, 1, 4)$, $(0,0,7)$, $(4,1,0)$.

compared with the energies in entries 9 or 10 of Table I, it is seen that although the latter energies are indeed smaller than the former, the difference is relatively small, and no definite conclusion can be drawn from this comparison.[13]

Taking into consideration the formal theoretical results of Bartlett[6] and of Fock,[7] as well as the computational results of Hylleraas and Midtdal,[14] it suggested itself to explore the inclusion of negative exponents in our expansions. The results of a few trial computations are given in items 3–8 of Table II. The effectiveness of

[12] U. N. Demkov, M. G. Neigauz, and R. V. Seniukov, Opt. i Spectroscopiya 4, 709 (1958).

[13] However, cf. footnote 11.

[14] E. A. Hylleraas and J. Midtdal, Phys. Rev. 109, 1013 (1958).

such expansions appears to be clearly demonstrated by these results.

4 RESULTS FOR ATOMIC NUMBER $Z>2$

Initial results of calculations for $Z>2$, as discussed in Sec. 4 of A, appeared to indicate that with increasing Z there is also some enhancement in the relative superiority, as far as the associated energy eigenvalues are concerned, of expansions involving fractional powers as compared with other expansions with the same number of terms. The interest in this question lies partly in the possibility that a clear indication on the above behavior relative to Z might have some suggestive value for the purely analytical theory of the behavior of the ground-state eigenfunctions of our Hamiltonian. But, of course, these results have also independent interest.

The entries in Table III represent only a small number of results on this topic, so that only limited conclusions can be drawn at this time. Nevertheless, they do appear to uphold the indication noted in Sec. 4 of A. Thus, the energy value in the third entry of Table III for $Z=3$, associated with a Ritz-Hylleraas expansion involving only 24 parameters, differs from the corresponding 203-parameter value of Pekeris,[3] -7.2799133 a.u., by less than 2 ppm; and for $Z=8$, already the 18-parameter value given in entry 7 differs from the corresponding best value of Pekeris, -59.156595 a.u., by only about 0.3 ppm.

Comparing the results given in entries 11 and 12 of Table III, we see that in this case there is little indication of any sensible effect in the inclusion of negative exponents in the expansion. Further calculational experimentation on this point for $Z>2$ would, therefore, be worth doing only when there is a need for approximations to the wave functions in question which are of sufficiently high precision (as judged by the associated energies) while involving a relatively moderate number of parameters. On the other hand, the results of Table

TABLE III. Energies corresponding to approximate solutions of the nonrelativistic Schrödinger equation for Li II and O VII, of the form $e^{-k(r_1+r_2)/2} \sum C_{lmn}(r_1+r_2)^{l/2}(r_1-r_2)^{2m}r_{12}^{n/2}$.

Item	Z	Number of parameters	(l,m,n) set[a]	k	$-E$ (a.u.)
1	3	18	1	5	7.2798874
2	3	24	2	4.7	7.2798963
3	3	24	2	5	7.2799020
4	3	31	3	4.7	7.2799020
5	3	31	3	5	7.2799055
6	8	18	4	15.5	59.1655772
7	8	18	4	16	59.1565789
8	8	18	4	16.5	59.1565780
9	8	24	5	16	59.1565794
10	8	31	6	15.5	59.1565798
11	8	31	6	16	59.1565803
12	8	31	7	15.5	59.1565809

a Set 1 =set 1 of Table I. Set 2 =set 3 of Table I. Set 3 =set 5 of Table I. Set 4 =set 1 of Table I with $(1,0,0)$ replaced by $(0,1,6)$. Set 5 =set 3 of Table I with $(1,0,0)$ replaced by $(0,1,6)$. Set 6 =set 6 of Table I. Set 7 =set 5 of Table II.

III do point to a small but sensible effect resulting from the choice of k. But in this case, too, attempts to arrive at an optimum choice, cannot be considered to be sufficiently warranted at present.

5 SOME RESULTS FOR THE EXCITED STATE 2 ^1S

In principle, it is a very simple matter to find approximations to the nonrelativistic energies for the first excited singlet S states of two-electron atomic systems with the aid of the same computer program and by the same method as employed for finding their ground-state energies. In practice, as is well known, such a method can be expected to be relatively inefficient on both physical and mathematical grounds. It may nevertheless be of possible interest to have at least some initial indication as to how the fractional-power expansions compare with the integral-power expansions, also with respect to the evaluation of the first excited singlet S state. The following few results were obtained with this possibility in mind.

The computations were made only through expansions with 18 parameters and only for $Z=2$ and $Z=3$, where comparison could be made with available calculations of high precision.[15] For $Z=2$, the expansion 2 of Table I was employed with the following results.

$k=$	3.5	3	2.75
$-E$ (in atomic units) $=$	2.078	2.092	2.075

By comparison, an 18-parameter expansion involving positive integral powers gave for $k=3$ the value $E=-2.066$ a.u. For $Z=3$, and 18 parameters, the eigenvalues obtained for a set of k ranging from 4 to 5 showed little variation. The lowest value, -4.95 a.u., was obtained for $k=4.7$. This differs by about 2% from the best available calculational result,[15] compared to the corresponding difference for $Z=2$ of about 3%.

In order to obtain some indication of the rate of convergence at this stage of our process, the energy for $Z=3$ was computed also with 11 parameters, employing the expansion given in Table II of A and taking $k=4.7$. The result, -4.88 a.u., is about 1% larger than the corresponding 18-parameter energy, so that at least in this case and at this stage the rate of convergence appears to be better than would be expected. However, preliminary work involving expansions with larger parameter numbers does seem to point to the expected eventual drastic slowing down in the rate of the convergence. This expectation is also confirmed by the relevant results in the recent paper of Munschy and Pluvinage.[3]

The above 11-parameter value can also serve as additional partial evidence that in the case of the excited 2 ^1S state as well, the use of the fractional-power expansions appears to be advantageous. This value differs by about 3% from the best available value,[15] compared with a corresponding difference of about 6% for the result in the case $Z=2$ obtained by Munschy and Pluvinage[3] with 13 parameters.

6. DISCUSSION

As stated in the introduction, a principal objective of the present results is to add to the computational data that could be useful in the study of the analytical problem relating to the structure of the exact wave functions in question. Presumably when that solution becomes available the means will be at hand for constructing good approximations with a minimum number of parameters and with minimum effort. But in the meantime the present cumbersome and costly approach seems unavoidable.

In this connection it is worth calling attention to the following instances in the presently available computational data which appear rather unexpected. The value, -2.9037223 a.u., which Kinoshita[3] obtains with his 34-parameter function is considerably larger, relatively speaking, than the '31-parameter values' given in items 1 and 2 of Table II. Such a relative increase, obtained with the addition of only three parameters at this stage of the approximation, appears surprising. For this reason, these calculations have been especially carefully checked and rechecked.[16] Even more surprising are the results of Munschy and Pluvinage[3] concerning their two 42-parameter functions with the remarkably separated associated energies, -2.90372311 and -2.90372421 a.u. In any possible further numerical study of the kind reported here it may be worth examining the question raised by these instances.

[15] C. L. Pekeris, Phys. Rev. **126**, 143, 1470 (1962).

[16] Nevertheless, the possibility of error can perhaps never be completely ruled out in the absence of a reliable independent check. Such a check was available for the results presented in A in the "output" energy values (which can be computed when the associated eigenfunctions are known).