

## Ground State of the Helium Atom\*

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Following a recent attempt to analyze the rate of convergence of Rayleigh-Ritz variational calculations on the ground state of helium, we were led to re-investigate the usefulness of inserting fractional powers of the variables into the conventional Hylleraas series. The results have been very successful: With a 164-term trial function containing half-powers of the variable  $s=r_1+r_2$ , we have matched the best eigenvalue obtained by Pekeris, who used 1078 terms of the conventional type. Our extrapolated value for the nonrelativistic eigenvalue is  $-2.9037243771$  a.u., with an estimated uncertainty of about  $1/10^{10}$ .

### INTRODUCTION

THE Rayleigh-Ritz variational method,

$$E \leq (\psi, H\psi) / (\psi, \psi), \quad (1)$$

was applied to the approximate solutions of the Schrödinger equation for helium,<sup>1</sup>

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 2/r_1 - 2/r_2 + 1/r_{12}, \quad (2)$$

by Hylleraas.<sup>2</sup> He used the trial function

$$\psi = \exp(-\frac{1}{2}ks) \sum_{l,m,n \geq 0} C_{lmn} s^l u^m t^n, \quad (3)$$

where  $s=r_1+r_2$ ,  $u=r_{12}$ ,  $t=r_2-r_1$ , and  $k$  is another adjustable parameter; and in the early years of work on this problem up to eight terms of the series (3) were used. More recently the availability of fast computing machines has led to the extension of this work by many people, the best results to date being those obtained by Pekeris,<sup>3</sup> who has used up to 1078 terms of (3).

In a recent publication<sup>4</sup> we have set up a crude, but useful, mathematical scheme for describing and predicting the rates at which the results of such calculations will converge as more terms are added to the series. In that analysis the Ritz procedure is likened to a least-squares fitting problem, and one can then calculate asymptotic formulas for the rate of decrease of the expansion coefficients  $C_N$ . The symbol  $N$  here stands for the polynomial order in the simple one-dimensional problems which one can solve; in describing the three-dimensional problem, Eq. (3), we take  $N=l+m+n$ . What we then seek to fit is the rate of decrease of increments of the energy eigenvalues calculated at each stage (for large  $N$ )

$$E(N) - E(N-1) \sim |C_N|^2. \quad (4)$$

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<sup>1</sup> We shall use throughout atomic units:  $e^2 = a_0 = 1$ .

<sup>2</sup> E. A. Hylleraas, *Z. Physik* **54**, 347 (1929).

<sup>3</sup> C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959).

<sup>4</sup> C. Schwartz, in *Computational Methods in the Physical Sciences* (Academic Press Inc., New York, 1962), Vol. 1.

It was really no great surprise to discover that, in general, this asymptotic convergence rate is governed by the behavior of the trial functions, as compared with that of the exact solution, near some singular point of the Hamiltonian. For the ground state of the two-electron atom, it was pointed out that the weak logarithmic singularity in the formal solution of Fock<sup>5</sup> was the controlling factor. This is a term of the form

$$R \ln R, \quad (5)$$

in a power series expansion of the solution of the wave equation, where  $R=r_1^2+r_2^2$  is small only when both electrons are near the nucleus simultaneously. We first considered putting such a term as (5) explicitly into the trial function, but then it seemed that this would be reasonable only if we could also include the next term; that is, we wanted to know the complete dependence of the logarithm on the other variables. The equations given by Fock proved to be just too complicated for us to solve, and so this approach was abandoned.

As an alternative, we sought another set of trial functions, larger than (3), which would give more freedom in the region where both  $r_1$  and  $r_2$  go to zero. Previously, Kinoshita<sup>6</sup> had allowed some negative values for the exponents  $l$  and  $m$ , and Schwartz<sup>7</sup> had included fractional values for these exponents. With a few half-power terms, Schwartz<sup>7</sup> obtained results slightly better than those from conventional series of the same size and this suggested the possibility of further study; but the total number of terms used was so small that one could not meaningfully speak of measuring the convergence rate.

Our analysis of model convergence problems<sup>4</sup> suggests that the use of fractional powers may be very helpful. Thus, the fitting of a function which near the origin behaves as

$$F \sim r^b \ln r,$$

in terms of polynomials of degree  $N$ ,  $u_N(r)$ , with a volume element  $r^a dr$ , gave expansion coefficients

<sup>5</sup> V. A. Fock, *Izv. Akad. Nauk SSSR Ser. Fiz.* **18**, 161 (1954).

<sup>6</sup> T. Kinoshita, *Phys. Rev.* **115**, 366 (1959).

<sup>7</sup> H. M. Schwartz, *Phys. Rev.* **120**, 483 (1960).

$$C_N = \int r^a dr r^b \ln r u_N(r) / \left[ \int r^a dr u_N^2(r) \right]^{\frac{1}{2}} \quad (6)$$

$$\underset{N \rightarrow \infty}{\sim} 1/N^{\frac{1}{2}a+b+1}.$$

If we were now to use instead polynomials of degree  $N$  in the variable  $r^{\frac{1}{2}}$ , a simple change of variables in (6) shows that one will get a much faster rate of decrease of the coefficients:

$$C_N' \underset{N \rightarrow \infty}{\sim} 1/N^{a+2b+\frac{3}{2}}. \quad (7)$$

This line of reasoning led us to expect that we might improve on Pekeris' results simply by inserting half-powers of the variable  $s$  into the series (3). Of the three variables,  $s$ ,  $t$ ,  $u$ , this is the one which goes to zero only when both electrons approach the origin; but the reduction from the complete three-variable problem to the simple one-dimensional model is not at all clearly understood. Thus, one could imagine that the correct terms to add were half-powers of some more complicated combination of the coordinates, such as  $r_1+r_2+r_{12}$  (the perimeter), or  $(r_1^2+r_2^2)^{\frac{1}{2}}$ , etc. We, therefore, consider that we were, in part, very fortunate in finding the very successful results, reported below, with such a simple device.

### RESULTS

The trial functions used were of the form (3) with  $l=0, \frac{1}{2}, 1, \frac{3}{2}$ , etc.;  $m=0, 1, 2$ , etc.;  $n=0, 2, 4$ , etc.; and terms were grouped in order of increasing  $N=l+m+n$ . The single term with  $l=\frac{1}{2}, m=n=0$  was omitted in order to avoid any singularity in the first derivative of the wave function. The parameter  $k$  was fixed at the value 3.5.<sup>7</sup> For each value of  $N$ , the eigenvalue of the corresponding matrix was found, and the results are collected in Table I. The computations were carried out on an IBM 704 computer using arithmetic accurate to about 20 decimal places. For each given matrix, a good estimate of the eigenvalue was inserted, and the corresponding approximate eigenvector was found by solving the inhomogeneous simultaneous linear equation system by the method of Gaussian elimination. With this given vector  $V$ , we then computed the scalar product.

$$V \cdot (E-H) \cdot V, \quad (8)$$

and using this as an error indicator we could rapidly interpolate to the correct eigenvalue. For the larger matrices, it was more economical to use the inverse matrix calculated at the first guessed  $E$  value for producing the eigenvectors, by iteration, at all other stages of the process. The total machine time required for our largest matrix (dimension 189) was about 2 h.

Pekeris' best result, obtained with 1078 parameters, was  $E=-2.903724375$ , and we have reached this value with only 164 terms of the expanded series. The

TABLE I. Ground-state energy of the helium atom as computed with the extended Hylleraas series containing half-powers of  $r_1+r_2$ .

$N$	Number of terms	Energy (in atomic units)	Differences	Ratios of successive differences
1.0	3	-2.890 992 6		
1.5	5	-2.891 502 4	0.0005098	23.5
2.0	9	-2.903 464 3	0.0119619	0.0084
2.5	13	-2.903 564 9	0.0001006	1.08
3.0	19	-2.903 673 6	0.0001087	0.329
3.5	25	-2.903 709 409 041	0.0000358	0.295
4.0	34	-2.903 719 965 865	0.00001056	0.276
4.5	43	-2.903 722 878 593	0.000002913	0.331
5.0	55	-2.903 723 842 484	0.0000009639	0.344
5.5	67	-2.903 724 173 169	0.0000003307	0.397
6.0	83	-2.903 724 304 348	0.0000001312	0.339
6.5	99	-2.903 724 348 846	0.000000445	0.379
7.0	119	-2.903 724 365 724	0.0000001688	0.393
7.5	139	-2.903 724 372 358	0.0000000663	0.407
8.0	164	-2.903 724 375 05	0.0000000269	0.412
8.5	189	-2.903 724 376 16	0.0000000111	
Extrapolated		-2.903 724 377 1 ±1		

quantitative rate of convergence of Pekeris' results was found to be described by the formula

$$E(N) - E(N-1) \sim 1/N^p, \quad (9)$$

where  $p$  lies between 7 and 8. Our earlier analysis,<sup>4</sup> which was not certain about the values of the parameters  $a$  and  $b$  to be used in Eq. (6), predicted  $p$  between 5.5 and 10. From Eqs. (4), (6), and (7) we would expect our new calculations to show that

$$E'(N) - E'(N-1) \sim 1/N^{p'}, \quad (10)$$

where  $p'=2p-1$ . The ratios of successive differences of the entries in Table I do show a fair agreement with the law (10) with  $p'$  equal to 14 or 15. This is a very satisfying confirmation of our semiquantitative analysis of the convergence rate problem.

Our analysis of convergence rates is not rigorous, but it is certainly more than an empirical fitting to the numerical outputs of a computer. Our uncertainty figure of  $1/10^{10}$  for  $E$  is empirically arrived at (see Table I), but the confidence to be placed on this figure depends on how convincing our theory<sup>4</sup> may appear, especially in the light of the results discussed above. A rigorous statement of the accuracy could be obtained by computing a lower bound for the energy. However,

all such calculations that have been carried out for this problem in the past have proved to be very unrewarding: at the most recent attempt<sup>8</sup> the lower bounds came out about two or three orders of magnitude farther away from the apparent convergence point than did the upper bounds. This situation may be understood qualitatively as follows. The convergence rate of the upper bound is determined by the ability of the given trial functions to represent the effects of the singularities in the Hamiltonian  $H$ . The lower-bound calculations involve the average value of  $H^2$ , and here the singularities are made more severe; thus the convergence rate will be much slower.

We have not computed any properties of the helium ground state other than the energy, since it appears that the work already published by Pekeris is suffi-

<sup>8</sup> C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).

ciently accurate to cope with all practical needs of the present and near future. The work reported here was undertaken merely to investigate whether the insertion of half-powers in the Hylleraas series did achieve the vast improvement hoped for. We are presently applying this technique to a calculation of the fine structure of the lowest  $^3P$  state in helium, since we have already found that the conventional basis does not there converge rapidly enough to allow a determination of the fine-structure constant to the new anticipated accuracy of  $1/10^6$ .

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## Measurement of Total Cross Sections for the Scattering of Low-Energy Electrons by Lithium, Sodium, and Potassium\*†

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The atomic beam recoil technique has been used to measure the total cross sections for the scattering of electrons by lithium in the energy range of about 1 to 10 eV. In this method, the atom beam is crossfired by a modulated electron beam. Recoil results in a scattering out of the atom beam at the modulation frequency. A phase-sensitive lock-in amplifier is used to detect the atom-scattering signal, which is obtained here from a continuously oxygenated surface ionization detector. The angular resolution of the apparatus at 1 eV for lithium and potassium is approximately  $9^\circ$  and  $14^\circ$ , respectively, in the electron polar scattering angle.

The lithium data were normalized to potassium at each energy at which measurements were made, by the use of two simultaneously operating ovens. As a check on the method, total cross-section measurements in the same energy range were made for sodium. These are in good agreement with the results of Brode, as are some absolute determinations made on sodium, potassium, and cesium at several energies. The general shape of the lithium curve is quite similar to that of the potassium curve over the ranges studied. The lithium cross section values vary from about 50 to 70% of the potassium values in the 1- to 10-eV region. There is the appearance of a resonance at about the same energy (1.5 eV) as those observed in the other alkalis.

### I. INTRODUCTION

**B**Y means of a modified Ramsauer technique, Brode performed a series of experiments in which he measured the total cross sections for the scattering of low-energy electrons by all of the alkali metal vapors except lithium, as well as some other metal vapors and gases.<sup>1</sup> His results revealed, first, that the absolute

values of the alkali cross sections were extremely large (over  $10^{-14}$  cm<sup>2</sup> in the entire low-energy range), and second, that the relative shapes of all the alkali curves were similar, particularly with regard to a strong resonance at energies of a few electron volts. Lithium was not studied because of the experimental difficulties associated with the high temperature necessary to obtain sufficient lithium vapor pressure, and the particularly serious corrosive action of hot lithium vapor.<sup>2</sup>

Early calculations of Allis and Morse predicted a very flat elastic cross section vs energy curve for lithium as well as quite small ( $\sim 10^{-15}$  cm<sup>2</sup>) absolute values, but they did not take either polarization or exchange into account.<sup>3</sup> Furthermore, the resonance

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<sup>1</sup> R. B. Brode, Phys. Rev. **25**, 636 (1925); **34**, 673 (1929); **35**, 504 (1930); **37**, 570 (1931).

<sup>2</sup> R. B. Brode (private communication).

<sup>3</sup> W. P. Allis and P. M. Morse, Z. Physik **70**, 567 (1931).