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Variational calculations on the helium isoelectronic sequence

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We have performed variational calculations on the helium isoelectronic sequence for values of the nuclear charge Z ranging from 1 to 10. The basis used is a modification of that employed by Frankowski and Pekeris in 1966, whose calculation has not been superseded before now. Using 230-term wave functions, we obtain for $Z=2$ through 10 variational energies accurate to better than a few parts in 10^{13} . Our results illustrate the importance of using basis functions which have the same analytic structure as the exact wave function being approximated.

During the 40 years after the birth of wave mechanics, the ground state of the helium atom was the subject of progressively more accurate variational calculations.¹⁻¹⁴ The relative simplicity of a system composed of a nucleus and only two electrons made it possible to do far more accurate calculations on helium than were computationally feasible on more complicated systems. In studying the helium atom, important lessons applicable to larger systems were learned about how to select basis functions which would yield rapidly convergent variational energies. The pioneering work of Hylleraas in 1929 demonstrated the importance of including basis functions which explicitly depend on the interelectronic separation to take account of electron correlation, and in 1966 the impressive calculation by Frankowski and Pekeris¹⁴ helped to confirm the existence of the logarithmic terms in the series expansion for many-electron wave functions derived by Fock.¹⁵ Frankowski and Pekeris's calculation, which involved obtaining the lowest eigenvalue of non-sparse 246×246 matrix, was performed on the computer GOLEM using 19 decimal digits in single precision [sic], and to this day their calculation has not been superseded.

Our own efforts to duplicate the calculation of Frankowski and Pekeris led to the discovery that a somewhat different algorithm for selecting the basis functions yielded a considerable improvement in the rate of convergence of the variational calculation. Specifically, for the helium isoelectronic sequence with $Z=2$ through $Z=10$, we have found that the inclusion of basis functions which are tailored to describe electron correlation is more important than the incorporation of those which are concentrated far from the nucleus, as measured on a length scale of a_0/Z , where a_0 is the Bohr radius. For $Z=2$ through 10, our basis with 230 functions yields variational energies lower than the extrapolated values obtained by Frankowski and Pekeris, who steadily increased their basis dimensions up to a maximum value of 246. In other words, we have found that our algorithm for selecting basis functions yields a 230-term variational wave function whose energy is not only below that of the 246-term wave function of Frankowski and Pekeris, but

also is lower than their extrapolated value for the energy. The key to this significant improvement was our inclusion of basis functions whose use is suggested by Fock's expansion for helium eigenfunctions. Thus our results demonstrate the importance, when doing a variational calculation, of choosing basis functions with the same analytic structure as the exact eigenfunction being approximated.

In their study of the 1^1S ground states of the helium isoelectronic sequence, Frankowski and Pekeris used basis functions of the form $\phi_{n,l,m,i,j}(2Zks, 2Zkt, 2Zku)$, where Z is the nuclear charge, k is a flexible scaling parameter, and

$$\phi_{n,l,m,i,j}(s,t,u) = s^n t^l u^m (s^2 + t^2)^{i/2} (\ln s)^j e^{(-1/2)s}, \quad (1)$$

where s , t , and u are the Hylleraas coordinates

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

and the integers i , j , l , m , and n obey the constraints

$$i = 0 \text{ or } 1, \quad 0 \leq l, \quad 0 \leq m, \quad 0 \leq j \leq \frac{1}{2}(l + m + n + i). \quad (3)$$

For singlet states l is even and for triplet states it is odd. Frankowski and Pekeris allowed n to be negative only if

$$i + l + m + n \geq 1, \quad (4)$$

and both i and j equal 0. To order the basis functions, Frankowski and Pekeris introduced an index ω given by

$$\omega = i + j + l + m + \max(0, n). \quad (5)$$

The basis was steadily enlarged by progressively increasing the maximum allowed value of ω .¹⁶

We found that a number of changes in the algorithm for ordering the basis functions produced a significant increase in the rate of convergence of the calculation as the basis was enlarged.

(i) It was found numerically that the coefficients of all the terms with $i=1$ were relatively smaller (by factors of 10^{-2} or more) than those of comparable terms with the same

value of $(i + l + m + n)$. Hence we decided to drop all the terms with $i = 1$. This had two beneficial effects: we could include more terms of different types, and the numerical stability of the Cholesky decomposition we used in finding the lowest eigenvalue was greatly enhanced.

(ii) The Fock expansion predicts that near the "triple-collision" point where $s = 0, t = 0, u = 0$, the wave function $\Psi(s, t, u)$ can be expanded as

$$\Psi(s, t, u) \sim 1 - Zs + \frac{1}{2}u + \dots, \quad (6)$$

where the ellipsis denotes higher-order terms, which have $l + m + n \geq 2$. This suggests that inequality (4) supra be modified so that n is allowed to be negative only if

$$l + m + n \geq 2, \quad (7)$$

taking account of our decision in (i) above to constrain i to be 0. In fact, it was found numerically that all the terms with n negative and $l + m + n = 1$ had very small coefficients, thereby reinforcing our decision to drop them from the variational wave function.

(iii) Whereas Frankowski and Pekeris used no terms involving both positive powers of $\ln s$ and negative powers of s , we found it advantageous to use such basis functions provided that $l + m + n \geq 2j + 2$. Our selection of such terms was motivated by the following considerations. Fock's work¹⁵ predicts that an expansion of the helium wave function about the hyperspherical origin should include terms of the form

$$F(s, t, u) \ln^2(s^2 + t^2), \quad (8)$$

where $F(s, t, u)$ is a homogeneous function of degree greater than or equal to 4. Since

$$\begin{aligned} \ln(s^2 + t^2) &= 2 \ln s + \ln(1 + t^2/s^2) \\ &= 2 \ln s + \sum_{p=1}^{\infty} \frac{(-1)^{p+1}}{p} \left(\frac{t^2}{s^2}\right)^p, \end{aligned} \quad (9)$$

it follows that

$$\begin{aligned} \ln^2(s^2 + t^2) &= 4 \ln^2 s + 4 \ln s \sum_{p=1}^{\infty} \frac{(-1)^{p+1}}{p} \left(\frac{t^2}{s^2}\right)^p \\ &\quad + \left[\sum_{p=1}^{\infty} \frac{(-1)^p}{p} \left(\frac{t^2}{s^2}\right)^p \right]^2. \end{aligned} \quad (10)$$

Hence for $j = 1$, one should include terms involving high powers of t^2/s^2 provided that $l + m + n \geq 4$, and similarly for the higher values of j .

(iv) The ordering scheme used by Frankowski and Pekeris, where the index

$$\omega = i + j + l + m + \max(0, n) \quad (11)$$

is progressively increased, emphasizes the inclusion of basis functions with large values of $l + m + n$. Such functions will tend to be concentrated at large distances from the nucleus; e.g., adopting the scale factor of $k = 0.91$ used by Frankowski and Pekeris in the helium calculation, the basis function $s^n e^{-Zks}$ has its maximum at $s = n/(2 \times 0.91) = n/1.82$. The 246-term wave function of Frankowski and Pekeris includes a basis function with $n = 7$; this will have a maximum at $s = 3.85$ a.u., which is rather large in comparison to the expectation value of s for the helium ground state, which is 1.86 a.u.¹² Hence this type of basis function will be primarily responsible for describing the exponentially decreasing "tail" of the wave function, which makes very little contribution to the total energy. It seemed to us to be more effective to include instead large powers of $u/s = r_{12}/(r_1 + r_2)$. A basis which includes many functions with high powers of this variable can be expected to do a better job of describing short- and moderate-range electron correlation, which will be more important to minimizing the variational energy.

Guided by these considerations, we selected basis functions of the form $\phi_{n,l,m,j}(2Zks, 2Zkt, 2Zku)$, where

$$\phi_{n,l,m,j}(s, t, u) = s^n t^l u^m (\ln s)^j e^{-(1/2)s}, \quad (12)$$

with $l_{\max} = 10, m_{\max} = 11, j_{\max} = 2$, and $(l + m + n)_{\max} = 5$. For $Z = 1, 2$, and 3 the scaling parameter k was optimized, and for the higher Z its value was preselected under the assumption that for large Z the optimal scaling parameter $k_{\text{opt}}(Z)$ approximately obeys the relation

$$k_{\text{opt}}(Z) \approx 1 - (\text{const})/Z. \quad (13)$$

In Table I are presented our results using a 230-term basis,

TABLE I. Comparison of the variational energies of Ref. 14 and this work. All energies are given in hartrees.

Z	Frankowski and Pekeris		This work	k
	246 terms	Extrapolated	230 terms	
1	-0.527 751 016 35	-0.527 751 016 38	-0.527 751 015 3	0.39
2	-2.903 724 377 032 6	-2.903 724 377 033 3	-2.903 724 377 034 0	0.80
3	-7.279 913 412 666 0	-7.279 913 412 667 8	-7.279 913 412 669 2	0.94
4	-13.655 566 238 418	-13.655 566 238 421	-13.655 566 238 423 5	0.96
5	-22.030 971 580 235	-22.030 971 580 239	-22.030 971 580 242 7	0.97
6	-32.406 246 601 889	-32.406 246 601 894	-32.406 246 601 898 4	0.98
7	-44.781 445 148 763	-44.781 445 148 768	-44.781 445 148 772 6	0.99
8	-59.156 595 122 749	-59.156 595 122 755	-59.156 595 122 757 8	1.00
9	-75.531 712 363 950	-75.531 712 363 957	-75.531 712 363 959 4	1.00
10	-93.906 806 515 025	-93.906 806 515 031	-93.906 806 515 037 4	1.00

along with the energies determined by Frankowski and Pekeris with their 246-term basis and their extrapolated values. It is seen that for $Z=2$ through 10 our variational energies obtained with a 230-term basis are better than even the extrapolated values of Frankowski and Pekeris. For $Z=1$ our variational energy is inferior to that determined by Frankowski and Pekeris because the wave function for H^- is so diffuse that it is more advantageous, at this level of approximation, to describe the long-range tail of the wave function than to include all the details of electron correlation at short and intermediate distances.

These calculations were performed on a Burroughs B7700 computer, which has about 22 decimal digits in double precision. The lowest eigenvalue and the corresponding eigenfunction of the Hamiltonian were found using subroutines from the EISPACK matrix eigenvalue library. To test the numerical stability of our matrix element generation and diagonalization algorithms, the five quantities $K(1,j)$ ($j=0$ through 4) defined in the Appendix to the article of Frankowski and Pekeris, which are used to calculate recursively the matrix elements, were changed first individually and then collectively by about 1 part in 10^{21} . All six variations yielded energies which changed only in the 21st digit. Hence we conclude that our calculation does not suffer from accumulating round-off error.

In our view, it would be unwise to attempt to determine our own extrapolated eigenvalues when past experience shows that such an extrapolation almost always overestimates the exact energies. However, in an attempt to estimate the effect of using additional basis functions, we added 26 extra functions, 16 with $j=0$ and $l+m+n=6$ and 10 with $j=3$ and $l+m+n=6$ to our original 230-term basis. For $Z=2$ the variational energy was lowered by less than 1 part in 10^{14} , and for $Z=10$ the change was less than 1 part in 10^{16} . Hence we believe that for $Z=2$ through 10 our variational energies exceed the exact energies by at most a few units in the last digit reported in Table I. Thus we think that for $Z=2$ through 10 our variational energies obtained with 230-term wave functions are more accurate by at least a factor of 2 than those obtained with 246-term wave functions by Frankowski and Pekeris.

The results of our work have a number of implications:

(i) This calculation, together with the earlier work of

Frankowski and Pekeris, demonstrates the advantage of using basis functions which have the same analytic structure at many-particle cusps as the exact eigenfunction. We estimate that our 230-term wave functions yield variational energies at least a factor of 10^3 more accurate than could be obtained with a basis which did not include logarithmic terms.

(ii) Now that we have highly accurate variational wave functions, we can redetermine theoretically the energy of the "real" helium atom, including mass-polarization and relativistic effects. We hope to reduce the uncertainty in the best previous theoretical estimate¹⁷ by about an order of magnitude, calculating if necessary the second-order mass polarization correction.

(iii) Calculations such as ours are feasible on any main-frame computer which has sufficient word length. A typical run on the University of Delaware's Burroughs B7700 computer, which has about 22 decimal digits in double precision, took about 12 min of CPU (central processing unit) time. Running time on a front-line computer such as a Cray would be significantly less. Thus *ab initio* calculations on few-electron systems taking full account of correlation effects, provided that the basis functions are selected carefully, should be well within the reach of almost any research group.

(iv) A numerical redetermination of the radius of convergence of the $1/Z$ expansion for the ground state of a two-electron atom, about which there has been some controversy regarding the accuracy of previous calculations done with a basis of Hylleraas functions,¹⁸⁻²² can be undertaken using our basis functions, if necessary introducing the "split-shell" exponential used in a subsequent calculation by Frankowski on excited states of the helium isoelectronic sequence.²³

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¹⁶The conditions as stated here, which we believe are correct, differ slightly from those given on pp. 47 and 48 of Ref. 14. We have also observed two misprints in Ref. 14: In Eq. (15) for "du" read "u du", and in Eq. (A13) for "(-)^j(1-S_{j+1})" read "(-)^j!(1-S_{j+1}).". Neither point affects any of the numerical results of Ref. 14.

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