

Energies of the Ground States of He, Li⁺, and O⁶⁺

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A complete 14-parameter calculation for the ground state of He and similar 10-parameter calculations for the ground states of Li⁺ and O⁶⁺ have been carried out. In addition, using the four most important of eleven terms, which were tried individually as fifteenth parameters, an 18-parameter calculation for He has been carried out but without minimizing against the scale parameter k . Similar 12-parameter calculations were carried out for Li⁺ and O⁶⁺ using the two most important terms beyond the tenth in the He calculation. As a result, the 18-parameter nonrelativistic ionization potential of He is found to be 198311.4 cm⁻¹. The series of 6, 10, 14, 18 parameter values appears to converge to 198312.3 cm⁻¹ with an error of less than 2 cm⁻¹. Adding the relativistic corrections yields 198310.4 cm⁻¹ which agrees to 0.1 cm⁻¹ with the latest experimental value. Considering the uncertainties of the theoretical and experimental values, the magnitude of the Lamb shift of the ground state of He (compared to He⁺) must be less than 3 cm⁻¹ which does not contradict present theoretical estimates. Similar agreements but within wider limits of error are found for the 12-parameter energy values of the ground states of Li⁺ and O⁶⁺.

A. INTRODUCTION

HYLLERAAS' well-known method of obtaining the energy of the ground state of helium has recently been carried to a higher (tenth) approximation than previously available.¹ This work showed that Hylleraas' earlier eighth approximation energy contained an error² and that the agreement between theory and experiment is not as good as previously believed. By assuming the mass polarization and relativistic corrections of Bethe³ and Eriksson⁴ respectively, a difference between observed and theoretical ionization potential of He of 25 cm⁻¹ was found. It was suggested that this discrepancy might be due to an electromagnetic shift (opposite in direction to the Lamb shift) or to incomplete mass polarization or relativistic corrections or to a failure of the tenth approximation in approaching the correct nonrelativistic value. Since the publication of our previous paper, the relativistic corrections have been studied by Sucher and Foley.⁵ They found that a term that may be interpreted as a spin-spin interaction had been neglected in the earlier treatments. It amounts to 4 cm⁻¹ but is of such a sign that the discrepancy between theory and experiment is increased rather than decreased, i.e., is 29 rather than 25 cm⁻¹. The question of the mass polarization has been studied anew by Wilets⁶ who obtained a slightly smaller correction than given by Bethe.³

Even before the new relativistic correction was known, work was started to carry the nonrelativistic Hylleraas calculation to still higher orders. When the preliminary results of these calculations were presented

at the Rydberg Centennial Symposium at Lund, we learned that Hylleraas² had independently carried out similar calculations arriving at very similar results. In view of the importance of the subject and the ever-present possibility of numerical mistakes in the extensive calculations, it appeared worth while to complete and publish our calculations independently of Hylleraas' new work.

B. HYLLERAAS FUNCTIONS AND CORRESPONDING ENERGIES OF THE GROUND STATE OF He

The Hylleraas type of wave function is of the form

$$\psi = \mathfrak{N} e^{-\frac{1}{2}ks} \sum c_{lmn} k^{l+m+n} s^l t^m u^n, \quad (1)$$

where s , t , and u are related to the distances r_1 , r_2 , and r_{12} (measured in atomic units) of the two electrons from the nucleus and from each other, respectively, by

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

\mathfrak{N} is a normalization constant and k and the c_{lmn} are constants which are to be adjusted so that the energy

TABLE I. Constants of 14-parameter wave function (14) for the ground state of He.

	3.85	3.75
k (input)	3.85	3.75
E (input)	-2.90370	-2.90370
k from (8)	3.8499301	3.7500555
E from (8)	-2.90370063	-2.90370089
β	+0.39836744	+0.39601198
γ	+0.17742685	+0.17483693
δ	+0.011878857	-0.041079523
ϵ	+0.020414801	+0.024913648
ζ	-0.11994054	-0.11315715
χ_6	+0.077281607	+0.054080045
χ_7	-0.084952179	-0.074771058
χ_8	+0.022483449	+0.021974359
χ_9	+0.014528286	+0.012947629
χ_{10}	+0.042902881	+0.030114033
χ_{11}	+0.0012248967	-0.0012596415
χ_{12}	-0.00010041525	-0.00010267038
χ_{13}	-0.0020615103	-0.0020306527
\mathfrak{N}	1.3617172	1.3633714

¹ Chandrasekhar, Elbert, and Herzberg, *Phys. Rev.* **91**, 1172 (1953), henceforth referred to as I.

² See also E. Hylleraas, Proc. Rydberg Centennial Conference, Lund, Sweden, July, 1954, p. 83.

³ H. A. Bethe in Geiger-Scheel's *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, Part 1.

⁴ M. A. S. Eriksson, *Z. Physik* **109**, 762 (1938).

⁵ J. Sucher and H. M. Foley, *Phys. Rev.* **95**, 966 (1954).

⁶ L. Wilets (private communication).

is minimized. In order to be minimized with regard to the c_{lmn} , the energy E must fulfill the determinantal equation (see Bethe³):

$$|k^2 M_{ij} - k L_{ij} - E N_{ij}| = 0. \quad (3)$$

Here i and j stand each for a set of numbers, $l_i m_i n_i$ and $l_j m_j n_j$ respectively, and M_{ij} , L_{ij} , and N_{ij} are the following sums of integrals:

$$\begin{aligned} M_{ij} = & (l_i l_j - m_i m_j + l_i n_j + n_i l_j - m_i n_j - n_i m_j) \times [l_i + l_j, m_i + m_j, n_i + n_j + 1] \\ & - 0.5(l_i + l_j + n_i + n_j) \times [l_i + l_j + 1, m_i + m_j, n_i + n_j + 1] \\ & - (n_i n_j + l_i n_j + n_i l_j) \times [l_i + l_j, m_i + m_j + 2, n_i + n_j - 1] \\ & + (n_i n_j + m_i n_j + n_i m_j) \times [l_i + l_j + 2, m_i + m_j, n_i + n_j - 1] \\ & + 0.5(l_i + l_j) \times [l_i + l_j - 1, m_i + m_j + 2, n_i + n_j + 1] \\ & + 0.5(n_i + n_j) \times [l_i + l_j + 1, m_i + m_j + 2, n_i + n_j - 1] \\ & - l_i l_j \times [l_i + l_j - 2, m_i + m_j + 2, n_i + n_j + 1] \\ & + m_i m_j \times [l_i + l_j + 2, m_i + m_j - 2, n_i + n_j + 1] \\ & + 0.25 \times [l_i + l_j + 2, m_i + m_j, n_i + n_j + 1] \\ & - 0.25 \times [l_i + l_j, m_i + m_j + 2, n_i + n_j + 1], \end{aligned} \quad (4)$$

$$N_{ij} = [l_i + l_j + 2, m_i + m_j, n_i + n_j + 1] - [l_i + l_j, m_i + m_j + 2, n_i + n_j + 1], \quad (5)$$

$$L_{ij} = 4Z[l_i + l_j + 1, m_i + m_j, n_i + n_j + 1] - [l_i + l_j + 2, m_i + m_j, n_i + n_j] \\ + [l_i + l_j, m_i + m_j + 2, n_i + n_j], \quad (6)$$

where Z is the nuclear charge ($=2$ for He). The brackets $[a, b, c]$ stand for the integrals

$$[a, b, c] = \int \int \int e^{-s^a t^b u^c} ds dt du = \frac{(a+b+c+2)!}{(b+1)(c+2)}. \quad (7)$$

The determinantal equation (3) must be solved for several values of k until E is minimized against k also. A check on the correctness of k and E is obtained from the formulas

$$k = L/2M, \quad E = L^2/4MN, \quad (8)$$

where

$$L = 2 \sum_{i,j} c_i c_j L_{ij}, \quad M = 2 \sum_{i,j} c_i c_j M_{ij}, \quad N = 2 \sum_{i,j} c_i c_j N_{ij}. \quad (9)$$

Here the c_i , c_j are the coefficients c_{lmn} derived from the secular determinant with the best E .

In I, the ten-parameter function

$$\psi = \mathfrak{N} e^{-\frac{1}{2}ks} (1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 s u \\ + \chi_7 t^2 u + \chi_8 u^3 + \chi_9 t^2 u^2) \quad (10)$$

was used and an energy value for the ground state of He of

$$E = -2.903603 \text{ atomic units} \quad (11)$$

with $k=3.51$ was obtained.⁷

By adding the four terms

$$\chi_{10} t^4 + \chi_{11} t^6 + \chi_{12} t^4 u^2 + \chi_{13} t^2 u^4 \quad (12)$$

to the bracket in (10), i.e., using a 14-parameter function and minimizing, an energy value of

$$E = -2.903629 \text{ atomic units} \quad (13)$$

⁷ The values for the normalization constant \mathfrak{N} given in the last column of Table I of I are erroneous and should be replaced by 1.359625, 1.359841, and 1.360462.

was obtained. Here $k=3.53$ was assumed and no minimizing with regard to k was attempted (see, however, below).

In view of the smallness of the decrease of the energy in adding the terms (12), an attempt was made to ascertain whether perhaps other terms might have a larger effect. For this purpose, a fifteenth column was added to the secular determinant in turn corresponding to a term in u^4 , or s^3 , or $t^2 u^3$, or $t^2 s$ and each time the energy was evaluated. The difference of the resulting E values from the value (13) indicated the relative importance of the terms considered. Similarly, the importance of the various terms (12) was ascertained by dropping the particular column of the secular determinant and finding the effect on the energy. In this way, it was found that the contributions of the terms in t^4 , t^6 , $t^4 u^2$ are small⁸ compared to those in $t^2 u^4$, u^4 , s^3 , and $t^2 s$. Therefore, the following 14-parameter function was finally chosen:

$$\psi = \mathfrak{N} e^{-\frac{1}{2}ks} (1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 s u + \chi_7 t^2 u \\ + \chi_8 t^2 u^3 + \chi_9 t^2 u^2 + \chi_{10} s t^2 + \chi_{11} s^3 + \chi_{12} t^2 u^4 + \chi_{13} u^4). \quad (14)$$

With $k=3.53$, this gave an energy value of

$$E = -2.903690 \text{ atomic units.} \quad (15)$$

The test of relation (8) showed that the assumed k value was not yet correct and several further (14×14) determinantal equations with different k values had to be solved. In Table I the coefficients, normalization constants and k and E values obtained from (8) are given for two sets of input values E and k near the

⁸ The term $t^2 u^3$ was also found to be of little importance at this stage. However, later on it was found that a numerical error had occurred in the calculation for $t^2 u^3$ and that actually $t^2 u^3$ is more important than $t^2 u^4$ as shown by the 18-parameter function given below.

TABLE II. Effect of adding various parameters to the 14-parameter Hylleraas function (14) with $k=3.85$.

Term added	E atomic units	ΔE 10^{-6} atomic units
...	-2.9037007	0
s^2u	-2.9037011	-0.4
su^2	-2.9037010	-0.3
s^4	-2.9037076	-6.9
s^2t^2	-2.9037036	-2.9
s^2u^2	-2.9037032	-2.5
t^4	-2.9037015	-0.8
t^2u^3	-2.9037070	-6.3
u^5	-2.9037076	-6.9
t^6	-2.9037014	-0.7
t^4u^2	-2.9037013	-0.6
$s^{-1}u$	-2.9037025	-1.8
$t^2u^3+u^5$	-2.9037098	-9.1
$s^4+s^2t^2+t^2u^3+u^5$	-2.9037162	-15.5

minimum. By interpolation from the corresponding values of the determinant (3), one obtains for the minimum:

$$k=3.80, \quad E=-2.903701 \text{ atomic units.} \quad (16)$$

By comparing with (15), it is seen that the effect on the energy of minimizing with respect to k is small.

In order to see what influence on the energy the addition of still higher terms in the series (1) might have, various trial terms were again added in turn to the 14-parameter function (14) as a fifteenth term and the energy determined in each case for $k=3.85$. This involved only the addition of a single column to the Gaussian algorithm by means of which the 14×14 determinants had been solved for $E=-2.90370$ and $E=-2.90371$. The results are shown in Table II. Only five terms give a noticeably different energy: u^5 , s^4 , t^2u^3 , s^2t^2 , and st^2u (in order of decreasing importance). The term $s^{-1}u$ was tried at the suggestion of Professor H. M. James (Purdue University) since he had found it of importance in a low-order approximation; but this term turned out to be unimportant in a 15-parameter function (see Table II).

If the four most important terms of Table II, *viz.*, u^5 , s^4 , t^2u^3 , s^2t^2 , are simultaneously added to the 14-

TABLE III. Constants of an 18-parameter wave function for the ground state of helium:

$$\psi = \mathcal{N}e^{-3k\sigma} (1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 s u + \chi_7 t^2 u + \chi_8 u^3 + \chi_9 t^2 u^2 + \chi_{10} s t^2 + \chi_{11} s^3 + \chi_{12} t^2 u^4 + \chi_{13} u^4 + \chi_{14} u^5 + \chi_{15} t^2 u^3 + \chi_{16} s^2 t^2 + \chi_{17} s^4).$$

k (input)	3.85	χ_8	+0.045441323
E (input)	2.90371	χ_9	+0.043516169
k from (8)	3.8499613	χ_{10}	+0.028227870
E from (8)	2.9037063	χ_{11}	+0.0071384413
β	+0.41389641	χ_{12}	+0.00050273143
γ	+0.21197114	χ_{13}	-0.0099342061
δ	+0.029010815	χ_{14}	+0.00093063179
ϵ	+0.0050395758	χ_{15}	-0.0075260852
ζ	-0.14909338	χ_{16}	+0.0030749706
χ_6	+0.079148647	χ_{17}	-0.00080572559
χ_7	-0.12587484	\mathcal{N}	1.3504631

parameter function (14), the following 18-parameter energy value is obtained:

$$E = -2.903716 \text{ atomic units.} \quad (17)$$

It should be noted that this value deviates from the 14-parameter value by much less than the sum of the four individual corrections taken from Table II (-15.5 against -23.0×10^{-6}). This gives one confidence that the other terms of Table II, if they were simultaneously added, would change the energy by less than the sum of the corrections of each term separately, that is, a 25-parameter value including all the terms in Table II would be between the value just given and

$$E = -2.903723 \text{ atomic units.} \quad (18)$$

It must be emphasized that the 18-parameter value (17) has been obtained with an assumed k -value, which is close to the minimum in the 14-parameter solution (16). From the change of E with k found there, it appears quite safe to conclude that minimizing of the 18-parameter value against k will change it by less than 0.000005. At the present stage, it did not seem worthwhile to carry through this minimizing process.

TABLE IV. Constants of 10-parameter wave functions (10) of Li^+ and O^{6+} .

	Li^+		O^{6+}	
k (input)	5.60	5.70	16.40	16.48
k from (8)	5.600055	5.699877	16.400023	16.479994
E (input)	7.279760	7.279770	59.15640	59.156405
E from (8)	7.2797624	7.2797596	59.156413	59.156422
β	+0.3598049	+0.3602588	+0.3771723	+0.3776096
γ	+0.2385639	+0.2569460	+0.6751016	+0.6935819
δ	-0.08864538	-0.04417829	+0.2922311	+0.3283520
ϵ	+0.01678235	+0.01818171	+0.1349207	+0.1569268
ζ	-0.1303588	-0.1370898	-0.5061933	-0.5152307
χ_6	+0.05504580	+0.07733141	+0.3317571	+0.3529975
χ_7	-0.09060980	-0.1066555	-0.7846255	-0.8396899
χ_8	+0.01606871	+0.01499941	+0.1682221	+0.1684930
χ_9	+0.01968222	+0.02688445	+0.4678856	+0.5306426
\mathcal{N}	5.750594	5.756579	141.2470	141.2869

The coefficients of the 18-parameter function nearest to the minimum are given in Table III. It should be noted that the k value from (8) is slightly less than the input value indicating that the best k value is less than 3.85.

C. HYLLERAAS FUNCTIONS AND CORRESPONDING ENERGIES OF THE GROUND STATES OF Li^+ AND O^{6+}

It appears of interest to carry through the Hylleraas calculation for some other two-electron systems. Li^+ and O^{6+} were chosen for this study and a 10-parameter calculation carried out similar to that for He in I. As may be seen from Eqs. (4)-(6), the quantities M_{ij} and N_{ij} in the determinantal equation (3) are the same as for He and only L_{ij} is different. Solving in the same way as for He, the sets of coefficients and corresponding energy values given in Table IV were found. By interpolation one obtains from the E and k values of Table IV and the values of 10×10 determinants

calculated for several other E values:

$$\begin{aligned} \text{For Li}^+: E &= -7.279763, \quad k = 5.63, \\ \text{For O}^{6+}: E &= -59.156404, \quad k = 16.48. \end{aligned} \quad (19)$$

The k value found for O⁶⁺ is remarkable since it is larger than $2Z$ which would be the k value in the absence of mutual interaction of the two electrons. It is also noteworthy that for high Z the coefficients $\beta, \gamma, \dots, \chi_9$ decrease much less rapidly than for low Z .

If the two most important terms beyond the tenth, s^{β^2} and s^3 , as judged from the He calculation, are added and a 12-parameter calculation carried out for Li⁺ with $k=5.60$ and for O⁶⁺ with 16.4, the following energy values are obtained:

$$\begin{aligned} \text{Li}^+: E &= -7.27982_5 \text{ atomic units}, \\ \text{O}^{6+}: E &= -59.15648_6 \text{ atomic units}. \end{aligned} \quad (20)$$

Since the energy depends only slightly on k (see Table IV), it would appear that minimizing against k will only very slightly lower the energy values (20) which may therefore be safely considered as 12-parameter values.

After completing these calculations, a paper by Eriksson⁹ came to our notice in which the author gives, as a 13-parameter value for Li⁺, $E = -7.27984_4$ which agrees most satisfactorily with our value. The terms in (1) used by Eriksson are the same as those used by us except that he has added u^4 . He does not give the coefficients in the eigenfunction.

D. DISCUSSION

In going from a Hylleraas wave function with 6 parameters to one with 10, 14, and finally 18 parameters, the nonrelativistic energy of the ground state of He changes from

$$\begin{aligned} &-2.90324_0 \text{ to } -2.903603 \text{ to } -2.903701 \\ &\text{to } -2.903716; \end{aligned} \quad (21)$$

that is, there is a fairly good convergence. It will be remembered that the last four terms added have the largest effect on the energy among a considerable number of terms that have been tried. None of the other terms that have been tried give a contribution greater than 0.000002₅ and most of them much less. To be sure, not all of the fifty terms which are possible up to sixth order have been tried, but only those have not been tried for which a similar *lower* order term gave a contribution of less than 0.00001 to the energy, e.g., since s^{β^2} gives only a contribution of 0.0000029, $s^{2\beta}$, s^{t^4} , \dots , and $s^{\beta t^2}$, s^{4t^2} , \dots were not tried since they would be expected to give a contribution much smaller than s^{β^2} . As shown previously, the resultant effect of a number of terms is less than additive. Since the terms that have not been used in the 18-parameter function give individual contributions less than 0.000002₅ and,

⁹ H. A. S. Eriksson, Arkiv. Mat. Astron. Fysik B30, No. 6 (1944).

with one exception, less than 0.0000008, it appears probable, as is also suggested by the series of numbers (21), that the energy of the ground state of He converges to -2.90372 atomic units and is almost certainly not below -2.90373 . This assumes, of course, that the variation method does converge. Some doubt has been expressed with regard to this by various authors.¹⁰ Even if these doubts were justified, the value (18) still remains an upper limit to the energy.

The energy value obtained in this way refers to a fixed nucleus. The motion of the nucleus is largely taken into account by multiplying by $2R_{\text{He}}$ rather than by $2R_{\infty}$ when converting to wave number units. A small correction, the mass polarization, first discussed by Bethe, has recently been re-evaluated by Wilets⁶ to be $+4.1 \text{ cm}^{-1}$ (compared to Bethe's 5.2 cm^{-1}). In this way, subtracting the energy of the ground state of He⁺, one obtains from (18) the following *lower* limit for the nonrelativistic ionization potential of He:

$$\text{I.P.}_{\text{n.r.}} \geq 198311.4 \text{ cm}^{-1}. \quad (22)$$

This number is 25.9 cm^{-1} higher than the previous lower limit based on the 10-parameter approximation and the old mass polarization.

Assuming the extrapolated convergence suggested above, the energy value would be

$$\text{I.P.}_{\text{n.r.}}(\text{extrapol.}) = 198312.3 \text{ cm}^{-1}, \quad (23)$$

with an error probably not greater than $\pm 2 \text{ cm}^{-1}$ and more likely positive than negative.

If one were to use the old relativity correction of Eriksson, i.e., $+2.2 \text{ cm}^{-1}$, one would obtain Eriksson:

$$\begin{aligned} \text{I.P.}_{\text{rel}}(\text{He}) &\geq 198313.6 \text{ cm}^{-1}, \\ \text{I.P.}_{\text{rel}}(\text{extrapol.}) (\text{He}) &= 198314.5 \pm 2 \text{ cm}^{-1}. \end{aligned} \quad (24)$$

However, if Sucher and Foley's relativistic correction is used, i.e., -1.9 cm^{-1} , one obtains¹¹ Sucher-Foley:

$$\begin{aligned} \text{I.P.}_{\text{rel}}(\text{He}) &\geq 198309.5 \text{ cm}^{-1}, \\ \text{I.P.}_{\text{rel}}(\text{extrapol.}) (\text{He}) &= 198310.4 \pm 2 \text{ cm}^{-1}. \end{aligned} \quad (25)$$

A provisional experimental value obtained by Zbinden and one of us¹² is

$$\text{I.P.}_{\text{exp}}(\text{He}) = 198310.5 \pm 1 \text{ cm}^{-1}. \quad (26)$$

¹⁰ See, for example, Bartlett, Gibbons, and Dunn, Phys. Rev. 47, 679 (1935); also V. A. Fock, Izvest. Akad. Nauk. S. S. S. R Ser. Fiz. 18(2), 161 (1954). The objections of Bartlett *et al.* have been refuted by Coolidge and James [Phys. Rev. 51, 855 (1937)] who have shown that the Hylleraas method does converge to the correct energy value. However, according to Kato [Trans. Am. Math. Soc. 70, 212 (1951)], Coolidge and James' proof "is not complete from a mathematical standpoint." Kato has established the convergence of the variation method. He considers it as "highly plausible" but not as proven that it converges to the correct energy value.

¹¹ Here account has been taken of the note added in proof in Sucher and Foley's paper in which one part of the correction (E_g') is doubled.

¹² G. Herzberg and R. Zbinden (unpublished).

TABLE V. Ionization potentials and Lamb shifts of He and He-like ions.

	Ionization potential (cm ⁻¹)			Lamb shift (cm ⁻¹)	
	nonrelativistic	relativistic	observed	obs	calc
He	198312. ₃	198310. ₄	198310. ₅	+0.1±3	-1.4
Li ⁺	610049	610087	610079	-8±25	-8.5
O ⁶⁺	5959957	5963266	5963000	-266±600	-460

The agreement between the experimental value and the extrapolated theoretical value using the Sucher-Foley relativistic correction is surprisingly close, much closer than one would have expected from the combined uncertainty of the theoretical and experimental values. At any rate, the large discrepancy found in I is entirely due to poor convergence of the tenth approximation.

Since the theoretical value (25) is based on the Dirac theory, the difference between the observed and the calculated value would represent an observed value for the electrodynamic (Lamb) shift of the ground state of He beyond that of He⁺. This shift comes out to be

$$-4.0 \pm 3 \text{ cm}^{-1} \quad \text{and} \quad +0.1 \pm 3 \text{ cm}^{-1}$$

for the extrapolated values (24) and (25) based on the Eriksson and Sucher-Foley corrections, respectively. There appears to be general agreement that the Sucher-Foley correction is the correct one. Thus, we conclude that the Lamb shift of the ground state of He lies very probably between +3 cm⁻¹ and -3 cm⁻¹. Günther¹³ and Håkansson¹⁴ have made rough theoretical estimates of the Lamb shift of He, obtaining -1.6 and -1.2 cm⁻¹, respectively. It is seen that these values are entirely compatible with the observed value. Conversely, if one considers the theoretical Lamb shift as correct, it would indicate that in extrapolating the convergence of the various approximations to the nonrelativistic energy of the He ground state, the effect of the neglected terms has been slightly underestimated (i.e., by 1.5 cm⁻¹ or 0.000007 atomic units), which does not seem unreasonable. The extreme limit suggested above (-2.90373 atomic units) would give an "observed" Lamb shift of -2.1 cm⁻¹, that is, the predicted Lamb shift is well bracketed by the observed values following from the extrapolated and the extreme nonrelativistic energies.

For Li⁺, the energy value (20) based on a 12-parameter Hylleraas function together with Bethe's mass polarization leads to a nonrelativistic ionization potential:

$$\text{I.P.}_{\text{n.r.}}(\text{Li}^+) \geq 610049 \text{ cm}^{-1}. \quad (27)$$

Sucher and Foley have not calculated the relativistic correction including the spin-spin interaction and we

¹³ M. Günther, *Physica* **15**, 675 (1949).

¹⁴ H. E. V. Håkansson, *Arkiv. Fysik* **1**, 555 (1950).

are dependent on Eriksson's old value¹⁵ of +38 cm⁻¹, yielding

$$\text{I.P.}_{\text{rel}}(\text{Li}^+) \geq 610087 \text{ cm}^{-1}. \quad (28)$$

This value agrees remarkably well with Robinson's¹⁶ experimental value of

$$\text{I.P.}_{\text{exp}}(\text{Li}^+) = 610079 \pm 25 \text{ cm}^{-1}. \quad (29)$$

The difference obs-calc of -8±25 cm⁻¹ would represent an observed value of the Lamb shift of Li⁺ (beyond that of Li²⁺). This value agrees with Håkansson's predicted value of -8.5 cm⁻¹ far better than the accuracy of the data warrants. If one uses Eriksson's¹⁰ 13-parameter value, the observed Lamb shift becomes -12±25 cm⁻¹.

For O⁶⁺, one finds from the 12-parameter energy value (20) the nonrelativistic ionization potential:

$$\text{I.P.}_{\text{n.r.}}(\text{O}^{6+}) \geq 5959957 \text{ cm}^{-1}. \quad (30)$$

In this case, Sucher and Foley⁵ have calculated their relativistic correction, obtaining +3309 cm⁻¹, which may be compared with Eriksson's +4110 cm⁻¹. Using the former yields

$$\text{I.P.}_{\text{rel}}(\text{O}^{6+}) \geq 5963266 \text{ cm}^{-1}. \quad (31)$$

The experimental value of Tyrén¹⁷ is

$$\text{I.P.}_{\text{exp}}(\text{O}^{6+}) = 5963000 \pm 600 \text{ cm}^{-1}. \quad (32)$$

From these two figures, an observed shift of -266±600 cm⁻¹ results which may be compared with Håkansson's predicted value of -460 cm⁻¹.

The results just presented are summarized in Table V. Neither the theoretical nor the experimental values for the ionization potentials of He, Li⁺, and O⁶⁺ are as yet sufficiently precise to obtain reliable values for the Lamb shifts of the ground states of these systems, but the precision is now approaching that required for such a determination. Preparations are being made for an attempt to increase the accuracy of both theoretical and experimental values still further so that a determination of the Lamb shift will become possible.

The extensive computations underlying the present work, all done by desk machines, were carried out by Miss Alma Marcus, Miss Cecile DeChantigny, and Mrs. Sarah Segall at the National Research Council of Canada. Preparatory computations were done by Miss Donna Elbert at the Yerkes Observatory. We are very much indebted to all of them for their care and perseverance in carrying out these long and tedious calculations.

¹⁵ Note added in proof.—According to E. E. Salpeter (private communication), the Sucher-Foley correction for Li⁺ amounts to +14 cm⁻¹ leading to $\text{I.P.}_{\text{rel}}(\text{Li}^+) \geq 610063 \text{ cm}^{-1}$.

¹⁶ H. A. Robinson, *Phys. Rev.* **51**, 14 (1937).

¹⁷ F. Tyrén, *Nova Acta Reg. Soc. Sci. Ups.* **12**, nr 1 (1940).