

## Twenty-Parameter Eigenfunctions and Energy Values of the Ground States of He and He-Like Ions

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The nonrelativistic energies of the ground states of  $H^-$ , He,  $Li^+$ ,  $B^{+++}$ ,  $O^{6+}$ ,  $Ne^{8+}$ ,  $Mg^{10+}$  have been calculated by using 20-parameter Hylleraas functions. The coefficients of these functions are listed. The correction due to the motion of the nucleus (mass polarization correction) has been calculated on the basis of these 20-parameter functions. Except for He this correction is found to be quite different from earlier values in the literature. The present status of the problem of the Lamb shift of the ground state of He is briefly discussed.

### A. INTRODUCTION

IN order to obtain experimental values for the Lamb shift of the ground states of two-electron systems, it is necessary to have not only accurate experimental energy values of these ground states, but also reliable theoretical values based on the Dirac theory so that, by taking the difference, the shift produced by electrodynamic and other terms not included in the Dirac theory can be determined. For this reason, an attempt to obtain improved Dirac values of the energies of He,  $Li^+$ , and  $O^{6+}$  had been made in two previous papers by Chandrasekhar, Elbert, and one of us.<sup>1</sup> The main problem is to obtain a sufficiently high approximation to the Schrödinger (i.e., nonrelativistic) energy values; a secondary problem is to find the relativistic corrections.

In I a ten-parameter (nonrelativistic) solution for He was obtained. The resulting energy value was appreciably higher than the old Hylleraas value while one would have expected it to be lower since, in addition to Hylleraas terms, two additional terms had been introduced into the wave function. This indicated a slight error in the original Hylleraas solution, which has since been confirmed by Hylleraas.

In view of the comparatively large discrepancy between the observed and the ten-parameter energy value, further parameters up to 18 were introduced into the wave function, as reported in II. In this way, the gap between observation and calculation was very much reduced and almost closed.

All the calculations in I and II were carried out by desk calculators. It appeared of interest to check and extend these calculations by the use of FERUT, the electronic digital computer, at the University of Toronto. Up to now, 20-parameter calculations have been carried out for He and the He-like ions,  $H^-$ ,  $Li^+$ ,  $B^{+++}$ ,  $O^{6+}$ ,  $Ne^{8+}$ , and  $Mg^{10+}$ . When it became known to us that independently Hylleraas and Midtdal<sup>2</sup> at the University of Oslo and Kinoshita<sup>3</sup> at Cornell University

had carried out similar calculations using additional and somewhat unconventional terms, we decided not to proceed to higher orders of approximation in our calculations, as originally intended, but rather to present our calculations at the 20-parameter stage. We have direct calculations for a number of ions not considered by Hylleraas and Kinoshita. Moreover, we trust that our results present welcome checks in those cases where the other investigators have carried out higher order calculations. In addition, the wave functions given here may be of use for a calculation of the relativistic corrections about which there still appears to be some uncertainty.

### B. METHOD OF CALCULATION

The form of the 20-parameter eigenfunction used in our calculations of the energy of the ground states of two-electron systems was the following:

$$\begin{aligned} \psi = \mathfrak{N}e^{-\frac{1}{2}ks} & (1 + \chi_1 u + \chi_2 l^2 + \chi_3 s + \chi_4 s^2 + \chi_5 u^2 \\ & + \chi_6 s u + \chi_7 l^2 u + \chi_8 u^3 + \chi_9 l^2 u^2 + \chi_{10} s l^2 + \chi_{11} s^3 \\ & + \chi_{12} l^2 u^4 + \chi_{13} u^4 + \chi_{14} u^5 + \chi_{15} l^2 u^3 + \chi_{16} s^2 l^2 + \chi_{17} s^4 \\ & + \chi_{18} s l^2 u + \chi_{19} l^4), \end{aligned} \quad (1)$$

where, as usual,

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad \text{and} \quad u = r_{12}.$$

Except for the last two terms, the function (1) agrees with that used in II. The two additional terms are those which, according to Table II of II, give the next largest contribution when added independently to a 14-parameter solution. None of the other terms tried in II and not included in (1) give a change of an energy by more than  $7 \times 10^{-7}$  atomic unit (or  $0.15 \text{ cm}^{-1}$ ).

The aim of the calculation is to vary the constants  $k$  and  $\chi_1, \chi_2, \dots, \chi_{19}$  until the energy is a minimum (see II and standard texts on wave mechanics). The computation problem reduces to the calculation of matrix elements and the subsequent solution of a matrix equation of order twenty. The elements of the energy determinant,

$$\Delta = |k^2 M_{ij} - k L_{ij} - E N_{ij}|, \quad (2)$$

were obtained from the formulas (4), (5), (6) of II by means of a program written for FERUT and the

<sup>1</sup> Chandrasekhar, Elbert, and Herzberg, Phys. Rev. **91**, 1172 (1953); S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955); henceforth referred to as I and II, respectively.

<sup>2</sup> E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).

<sup>3</sup> T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

TABLE I. Nonrelativistic energies of the ground states of He and He-like ions.

Ion	Energy without mass polarization		Mass polarization			Energy including mass polarization cm <sup>-1</sup>
	Atomic units	cm <sup>-1</sup>	$\epsilon(M/m)$	$\epsilon$ atomic units	cm <sup>-1</sup>	
H <sup>-</sup>	-0.0276446692	6064.00	0.0332072	1.80957×10 <sup>-5</sup>	-3.969	6060.03
He	-0.9037179	198316.0	0.159078	2.18088×10 <sup>-5</sup>	-4.786	198311.2
Li <sup>+</sup>	-2.779905382	610071.0	0.288964	2.25980×10 <sup>-5</sup>	-4.959	610066.0
B <sup>+++</sup>	-9.53095928	2091699	0.552818	2.75494×10 <sup>-5</sup>	-6.046	2091693
O <sup>6+</sup>	-27.156581537	5959976	0.951024	3.26202×10 <sup>-5</sup>	-7.159	5959969
Ne <sup>8+</sup>	-43.9067919	9636162	1.217055	3.33974×10 <sup>-5</sup>	-7.330	9636155
Mg <sup>10+</sup>	-64.6569328	14190231	1.483207	3.39258×10 <sup>-5</sup>	-7.446	14190224

matrices  $L_{ij}$ ,  $M_{ij}$ , and  $N_{ij}$  were made available on punched cards.

For a given value of  $k$ , the energy matrix equation has the form

$$(A - \lambda B)x = 0, \quad (3)$$

where  $x$  is a column vector and  $A$  and  $B$  are matrices. Initially  $B$  was inverted and the lowest eigenvalue obtained by a shift of origin and an iterative procedure involving high powers of the matrix  $B^{-1}A$ . However, the convergence was slow and errors crept in, primarily because of the use of fixed point arithmetic. The programming was finally done entirely in floating point and the secular determinant  $\Delta$  evaluated for specified values of  $E$  and  $k$ . Proceeding from an estimate of  $k$ , the determinant is evaluated for a sufficient number of  $E$  values to allow interpolation of  $E$  for  $\Delta=0$ . Thereupon  $k$  is revised until the lowest  $E$  is obtained.

### C. RESULTS

Calculations as described above have been carried through for the ground states of H<sup>-</sup>, He, Li<sup>+</sup>, B<sup>+++</sup>, O<sup>6+</sup>, Ne<sup>8+</sup>, Mg<sup>10+</sup>. The energy values in atomic units (2 rydbergs) obtained in this way are listed in the second column of Table I. The values given are net energies referred to the ground states of the corresponding one-electron systems, that is, are the total energies obtained from (1) less  $\frac{1}{2}Z^2$ . The coefficients  $\chi_i$  of the corresponding eigenfunctions are given in Table II. They have been obtained by FERUT from the secular determinants using the final  $E$  and  $k$  values. The quantities  $L$ ,  $M$ , and  $N$  of Eq. (9) of II, as well as the values of  $k$  and  $E$  and the normalization factor  $\mathcal{N}[=k^3/\pi(2N)^{1/2}]$  are also included in Table II. It may be recalled that a check on the correctness of the calculations is obtained by ascertaining whether the relations

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

are fulfilled. Substitution of the values of Table II gives indeed a very satisfactory check, namely to better than 1 part in 10<sup>6</sup> for  $k$  and 1 part in 10<sup>7</sup> for  $E$ , except for H<sup>-</sup> for which the corresponding numbers are  $2 \times 10^6$  and  $2 \times 10^6$ .

The energy values of Table I must still be corrected for the motion of the nucleus. As is well known, part of this correction is taken into account by using the Ryd-

berg constant for the particular ion rather than that for infinite mass when converting to wave number units. The resulting ionization potentials in cm<sup>-1</sup> are given in the third column of Table I.

The remaining correction for the motion of the nucleus, the so-called mass polarization correction first discussed by Bethe,<sup>4</sup> depends in a rather complicated way on the eigenfunctions. Wilets and Cherry<sup>5</sup> have recently given explicit expressions for this mass polarization  $\epsilon$  in terms of the coefficients of the eigenfunctions used. They showed that  $\epsilon$  (in atomic units) is given by

$$\epsilon = \frac{2\pi^2 \mathcal{N}^2 m}{k^4 M} \sum_{\substack{lmn \\ l'm'n'}} c_{lmn} c_{l'm'n'} \left\{ \begin{matrix} lmn \\ l'm'n' \end{matrix} \right\}, \quad (4)$$

where the  $c_{lmn}$  are related to the coefficient  $\chi_i$  (see II) by

$$\chi_i = k^{l+m+n} c_{lmn}, \quad (5)$$

$m$  and  $M$  are the masses of the electron and the nucleus, and  $\left\{ \begin{matrix} lmn \\ l'm'n' \end{matrix} \right\}$  are certain integrals given explicitly in terms of  $l$ ,  $m$ ,  $n$ ,  $l'$ ,  $m'$ ,  $n'$  by Eq. (18) of Wilets and Cherry's paper.<sup>6</sup> The quantities  $\left\{ \begin{matrix} lmn \\ l'm'n' \end{matrix} \right\}$  and the sums in (4) were evaluated by FERUT using the coefficients of Table II. The resulting values of  $\epsilon M/m$  are given in the fourth column of Table I, while the fifth and sixth columns give the mass polarizations in atomic units and in cm<sup>-1</sup> for the principal isotopes of the ions considered. Adding these to the ionization potentials of column 3 gives the final 20-parameter nonrelativistic ionization potentials of the last column. These numbers represent the principal result of the present paper.

It may be noted that the reduced mass polarizations  $\epsilon M/m$  vary almost linearly with the atomic number. This makes it readily possible to interpolate and extrapolate the mass polarization for ions for which they have not been calculated here.

<sup>4</sup> H. A. Bethe, *Handbuch der Physik* (Verlag J. Springer, Berlin, 1933), second edition, Vol. 24, Part I, p. 375 ff.

<sup>5</sup> L. Wilets and I. J. Cherry, *Phys. Rev.* **103**, 112 (1956).

<sup>6</sup> In this equation the factor  $4(\sigma+3)!$  should be replaced by  $2(\sigma+3)!$  as was pointed out to us by Dr. Wilets.

TABLE II. Coefficients of 20-parameter wave functions, normalization constants, etc., for the ground states of H<sup>-</sup>, He, and He-like ions.

	H <sup>-</sup>	He	Li <sup>+</sup>	B <sup>+++</sup>	O <sup>6+</sup>	Ne <sup>8+</sup>	Mg <sup>10+</sup>
<i>k</i> (input)	1.35	3.87	6.20	10.40	17.60	22.20	27.00
<i>E</i>	0.5276446692	2.9037179	7.279905382	22.03095928	59.156581537	93.9067919	136.6569328
<i>x</i> <sub>1</sub>	+0.337294236	+0.417070598	+0.427894286	+0.434777444	+0.440607752	+0.442223704	+0.443411579
<i>x</i> <sub>2</sub>	+0.0808833954	+0.208366354	+0.320937389	+0.518229132	+0.868595114	+1.09042306	+1.32518519
<i>x</i> <sub>3</sub>	-0.213129754	-5.23482398 × 10 <sup>-3</sup>	+0.153723864	+0.253041238	+0.846501253	+1.14476659	+1.54137769
<i>x</i> <sub>4</sub>	+0.0200385445	+0.0409000245	+0.102493831	+0.194770903	+0.663489753	+1.05375129	+1.70039090
<i>x</i> <sub>5</sub>	-0.0287160073	-0.157224213	-0.291352815	-0.507177819	-0.948511149	-1.22002272	-1.52673508
<i>x</i> <sub>6</sub>	-0.0154381194	-0.0823275059	-0.178913186	-0.240745183	-0.601062578	-0.784059184	-1.03688038
<i>x</i> <sub>7</sub>	-9.21896695 × 10 <sup>-3</sup>	-0.125878664	-0.338922840	-0.987602064	-2.85014508	-4.55026849	-6.72746288
<i>x</i> <sub>8</sub>	+4.32904670 × 10 <sup>-3</sup>	+0.0476774784	+0.132405535	+0.398635198	+1.17774341	+1.90245817	+2.86604464
<i>x</i> <sub>9</sub>	+7.86976451 × 10 <sup>-4</sup>	+0.0407069233	+0.192820330	+0.969216519	+4.99873341	+10.1746072	+18.5924205
<i>x</i> <sub>10</sub>	-1.77558678 × 10 <sup>-3</sup>	+0.0319089519	+0.0934891553	+0.252556490	+0.807402893	+1.29379692	+1.93811653
<i>x</i> <sub>11</sub>	-7.40841223 × 10 <sup>-4</sup>	-9.49744884 × 10 <sup>-3</sup>	-0.0220645541	-0.0699871341	-0.0818249736	-0.0520134549	-0.124981910
<i>x</i> <sub>12</sub>	+1.63058368 × 10 <sup>-6</sup>	+5.12301157 × 10 <sup>-4</sup>	+5.22020228 × 10 <sup>-3</sup>	+0.0665530976	+0.923021496	+2.93948649	+7.84263832
<i>x</i> <sub>13</sub>	-2.73106176 × 10 <sup>-4</sup>	-9.22964704 × 10 <sup>-3</sup>	-0.0417113554	-0.214618312	-1.07667975	-2.20290557	-4.06329258
<i>x</i> <sub>14</sub>	+6.27409440 × 10 <sup>-6</sup>	+7.06572065 × 10 <sup>-4</sup>	+5.23645743 × 10 <sup>-3</sup>	+0.0444107350	+0.386667222	+1.00221902	+2.28140304
<i>x</i> <sub>15</sub>	-6.38293145 × 10 <sup>-5</sup>	-7.25137848 × 10 <sup>-3</sup>	-0.0484975747	-0.388582259	-3.16354776	-8.00936092	-17.5280675
<i>x</i> <sub>16</sub>	-1.84423133 × 10 <sup>-4</sup>	+2.30342328 × 10 <sup>-3</sup>	+0.0184000974	+0.0352818232	+0.553211466	+1.18983816	+2.56549714
<i>x</i> <sub>17</sub>	+1.55857013 × 10 <sup>-5</sup>	+1.36645365 × 10 <sup>-3</sup>	+6.95516177 × 10 <sup>-3</sup>	+0.0270144827	+0.227659768	+0.526835524	+1.24769787
<i>x</i> <sub>18</sub>	+6.48350632 × 10 <sup>-4</sup>	+1.60548903 × 10 <sup>-3</sup>	-0.0267015277	-0.147231569	-1.36483720	-2.95943701	-5.97143232
<i>x</i> <sub>19</sub>	+6.88602440 × 10 <sup>-4</sup>	+7.58736825 × 10 <sup>-4</sup>	-3.86042500 × 10 <sup>-3</sup>	-0.0289713347	-0.185285535	-0.388282536	-0.738207796
<i>L</i>	46.7052264	136.69594826	202.93034703	272.98892171	506.97889865	635.46304685	792.8473384
<i>M</i>	17.29733302	17.66098522	16.36537357	13.12444550	14.40281029	14.31223158	14.68236087
<i>N</i>	59.75173866	91.09236318	86.41364919	64.43408751	75.41703704	75.11319769	78.32341068
<i>g</i>	0.0716409212	1.36686946	5.77057414	31.5411342	141.298776	284.142323	500.588221

D. DISCUSSION

The mass polarization correction was first calculated for He by Bethe who, using only a six-parameter eigenfunction, obtained a value 5.2 cm<sup>-1</sup> which does not deviate much from Wilets and Cherry's value (here confirmed) which is based on a 20-parameter function. The only other previously published mass polarization corrections are those of Robinson<sup>7</sup> who gave the values -4, -1, +2 for Li<sup>+</sup>, B<sup>+++</sup>, and O<sup>6+</sup>, respectively. These values do not agree at all with the values here calculated. Robinson himself expressed doubt in the reversal of the sign that he found.

For higher *Z* values, the mass polarization correction is clearly quite unimportant compared to the value of the ionization potentials (see Table I). It is relatively most important for H<sup>-</sup> for which apparently it had not previously been calculated.

In Table III, the nonrelativistic 20-parameter energy values here obtained are compared with previous ten-parameter values and the recent 24- and 39-parameter values of Hylleraas, Midtdal, and Kinoshita using the new mass polarizations throughout. It is apparent from this table that the relative change, by going to higher order approximations, becomes less with increasing *Z*. Presumably for *Z* > 3 the 20-parameter values are adequate even if an accuracy of 1 part per million is required.

The 18-parameter value of II (converted to the new value of the mass polarization) was 198310.7 cm<sup>-1</sup>. This value is so close to the 20-parameter value (see Table III) that if no other calculations were available, one would probably have been inclined to conclude that higher approximations could at best bring the energy up to 198312 cm<sup>-1</sup>. While Kinoshita's 39-parameter value is close to this extrapolation, Hylleraas and Midtdal's value is slightly beyond it. It is apparent that, by choosing rather unorthodox terms in the eigen-

functions, Hylleraas and Midtdal have succeeded in approaching the true eigenfunction much more closely than is possible by ordinary Hylleraas functions. One will have to conclude that with a given type of function, the convergence becomes very slow for large numbers of parameters.

Both Wilets and Cherry and Kinoshita have obtained lower bounds for the energy of the ground state of He. However, these lower bounds are still a considerable distance (~30 cm<sup>-1</sup>) from the upper bounds.

All energy values discussed thus far are nonrelativistic. In the past the magnitude of the relativistic correction has been subject to some uncertainty. Stimulated by the discrepancy between the 10-parameter energy value for He and the observed value (see I), Sucher and Foley<sup>8</sup> recalculated the relativistic corrections and found values of -1.9 and +3309 cm<sup>-1</sup> for He and O<sup>6+</sup> which were widely different from the earlier values of Bethe and Eriksson. Salpeter<sup>9</sup> obtained the corresponding value for Li<sup>+</sup> as +14.0 cm<sup>-1</sup>. However, these values were based on three-parameter wave functions. It was shown by Kinoshita<sup>3</sup> that the magnitude of the relativistic correction for He is very sensitive to the approximation used for the eigenfunction. He obtained with a 39-parameter function the value

TABLE III. Comparison of different approximations to the energy values of He and He-like ions.

Ion	10 parameters cm <sup>-1</sup>	20 parameters cm <sup>-1</sup>	24 parameters Hylleraas- Midtdal cm <sup>-1</sup>	39 parameters Kinoshita cm <sup>-1</sup>
H <sup>-</sup>	6041.4	6060.03	6077.8	
He	198286.0	198311.2	198313.5	198312.2
Li <sup>+</sup>	610035	610066.0	610066.8	
O <sup>6+</sup>	5959929	5959969	5959972	

<sup>8</sup> J. Sucher and H. M. Foley, Phys. Rev. **95**, 966 (1954).  
<sup>9</sup> E. E. Salpeter, quoted in II.

<sup>7</sup> H. A. Robinson, Phys. Rev. **51**, 14 (1937).

$-0.57 \text{ cm}^{-1}$  which is likely to be the true value within  $0.01\text{--}0.02 \text{ cm}^{-1}$ . Values for  $\text{Li}^+$  and  $\text{O}^{6+}$  based on the 10-parameter functions of II were obtained by the Cornell group<sup>10</sup> and are  $19.6 \pm 3$  and  $3596 \pm 60 \text{ cm}^{-1}$ , respectively.

If Kinoshita's relativistic correction is accepted, one obtains the following relativistic, 20-, 24-, and 39-parameter energy values for He:

$$198310.6, \quad 198312.9, \quad \text{and} \quad 198311.6 \text{ cm}^{-1}.$$

A provisional experimental value due to Zbinden and one of us was quoted in II as  $198310.5 \pm 1 \text{ cm}^{-1}$ . This value when compared with the 24- and 39-parameter theoretical values leads to an observed Lamb shift of 2.4 and  $1.1 \text{ cm}^{-1}$ , respectively. The predicted Lamb shift (Håkansson,<sup>11</sup> Kabir and Salpeter<sup>12</sup>) is  $1.2 \pm 0.3 \text{ cm}^{-1}$ . Considering the present uncertainty of the experimental value and the uncertainty of the predicted Lamb shift one must conclude that there is agreement between experiment and the predictions of quantum electrodynamics. Experiments are in progress in this laboratory aimed at reducing the limit of error of the experimental value considerably.

<sup>10</sup> Salpeter, Peierls, and Nauenberg (private communication). The errors quoted are only estimates of the probable errors not rigorous limits.

<sup>11</sup> H. E. V. Håkansson, *Arkiv Fysik* **1**, 555 (1950).

<sup>12</sup> P. K. Kabir and E. E. Salpeter, *Bull. Am. Phys. Soc. Ser. II*, **1**, 46 (1956).

The new relativistic corrections for  $\text{Li}^+$  and  $\text{O}^{6+}$  added to the nonrelativistic values of Table I give the following relativistic ionization potentials:

$$\text{Li}^+: 610085.6, \quad \text{O}^{6+}: 5963565 \text{ cm}^{-1}.$$

The only experimental values are those of Robinson<sup>7</sup> and Tyrén<sup>13</sup>:

$$\text{Li}^+: 610079 \pm 25, \quad \text{O}^{6+}: 5963000 \pm 600 \text{ cm}^{-1}.$$

Thus the observed Lamb shifts are  $6.6 \pm 25$  and  $565 \pm 600 \text{ cm}^{-1}$ , respectively, which may be compared with Kabir and Salpeter's predicted shifts of 6 and  $360 \text{ cm}^{-1}$ . Work toward improving the experimental value for  $\text{Li}^+$  is in progress in this laboratory.

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<sup>13</sup> F. Tyrén, *Nova Acta Regiae Soc. Sci. Upsaliensis* **12**, 1 (1940).