

1 ¹S, 2 ¹S, and 2 ³S States of H⁻ and of He[†]

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(Received January 12, 1962)

The ionization energy J , including mass-polarization and relativistic corrections but not the Lamb shift correction, was evaluated for the 1 ¹S state of the negative-hydrogen ion using determinants up to order $n=444$. We get $J(444)=6083.0943$ cm⁻¹, and, by extrapolation, $J(\infty)=6083.0958$ cm⁻¹. A search for bound states 2 ¹S and 2 ³S of H⁻ led to negative results. In the case of helium, an *upper* bound to the nonrelativistic energy eigenvalue ν for the 1 ¹S state was evaluated at $n=1078$ to be $\nu_+=198317.866$ cm⁻¹, as against the previously determined *lower* bound of $\nu_-(1078)=198317.374$ cm⁻¹. For the 2 ³S state this gap is already completely closed at $n=715$, with $\nu_+(715)=38453.1299$ cm⁻¹ and $\nu_-(715)=38453.1292$ cm⁻¹. At $n=1078$, $J=38454.827375$ cm⁻¹, and the electron charge density at the nucleus $D(0)$ comes out 33.18414092, in agreement with previously extrapolated values. This substantiates a disagreement of the order of one part in 10⁶ between theory and experiment in the hyperfine structure of the 2 ³S state of He³ which was established by White, Chow, Drake, and Hughes. With Suh and Zaidi's value for the Lamb shift of -0.109 ± 0.009 cm⁻¹, the ionization energy of the 2 ³S state comes out 38454.718 ± 0.009 cm⁻¹, as against Herzberg's experimental value of 38454.73 ± 0.05 cm⁻¹. For the 2 ¹S state we get $J(615)=32033.318$ cm⁻¹, which with a Lamb shift of -0.104 ± 0.014 cm⁻¹ evaluated by Suh and Zaidi, leads to an ionization energy of 32033.214 ± 0.014 cm⁻¹. The experimental value is, according to Herzberg, equal to 32033.26 ± 0.03 cm⁻¹ or, at worst, ±0.05 cm⁻¹. A summary is given of the verification to date of the Lamb shift in two-electron atoms.

1. INTRODUCTION

THE solutions of the wave equation for two-electron atoms presented here were obtained by method *B*, which is based on the method *A*^{1,2} described previously, except that instead of the *iteration* procedure followed there, the energy eigenvalue ϵ was obtained by evaluating the determinant first for two initial values ϵ_1 and ϵ_2 and then proceeding to the root by Newton's method, followed by parabolic extrapolation. The calculations were carried out on WEIZAC by double-precision floating arithmetic, and in most cases ϵ_1 could be guessed sufficiently well, for a given order n of the determinant, so as to lead to an agreement between ϵ_3 and ϵ_4 to within 1 or 2 units in the 18th place. With this accuracy in ϵ , the corresponding wave function ψ_n for each order n can probably be relied on to within one part in 10⁹.

2. THE 1 ¹S STATE OF H⁻

According to the theory of Wildt³ the principal process responsible for the opacity of the solar photosphere is the continuous absorption by the negative hydrogen ion. The work of Chandrasekhar *et al.*⁴ has by now firmly established this theory. However, in the infrared region, the theoretical results are not in agreement with recent laboratory experiments carried out by Burch and Smith.⁵ The problem of the solution of the two-electron wave equation for the continuum, without resorting to the one-electron approximation, is still an open one. The absorption coefficient in the continuum is proportional

to the oscillator strength f_{0n} given by

$$f_{0n} = \frac{1}{3}(E_0 - E_n)|\psi_0(\mathbf{r}_1 + \mathbf{r}_2)\psi_n|^2, \quad (1)$$

where E_0 and E_n denote the energies in the initial and continuum states, and ψ_0 and ψ_n the corresponding wave functions. Pending the availability of a solution for the continuum wave function ψ_n which will be accurate to within any prescribed limits, we have evaluated the ground-state wave function ψ_0 by solving determinants of orders $n=308$ and 444 , for eventual use in (1). The results are shown in Table I, together with those for $n=125$ and 203 reported previously.¹ The difference between the energy eigenvalue $\epsilon^2(444)$ at $n=444$ and the extrapolated value $\epsilon^2(\infty)$ is two parts in 10⁸, so that the wave function $\psi(444)$ is probably dependable to within one part in 10⁴. More accurate wave functions for the 1 ¹S state can readily be obtained, should that prove desirable.

3. DOES THE NEGATIVE HYDROGEN ION HAVE MORE THAN ONE BOUND STATE?

This question is of importance to stellar opacity theory, and has also arisen in connection with current scattering-length theories.⁶ We have searched for bound states 2 ¹S and 2 ³S and found none. Since similar investigations have no doubt been made by others, we present here our results in order to avoid repetition in the future. In the case of $Z=1$ a state is bound if the energy eigenvalue

$$\epsilon^2 = -E > 0.5. \quad (2)$$

Table II shows eigenvalues ϵ^2 obtained by solving determinants of increasing order n . It is seen that for a given n , ϵ^2 is less for the 2 ¹S state than for the 2 ³S state.

[†] Research supported by the Air Force Office of Scientific Research through the European Office of the Office of Aerospace Research.

¹ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

² C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

³ R. Wildt, Astrophys. J. **190**, 611 (1939).

⁴ S. Chandrasekhar, Astrophys. J. **128**, 114 (1958).

⁵ S. J. Smith and D. S. Burch (to be published).

⁶ L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **119**, 164 (1960); T. Ohmura, J. Math. Phys. **1**, 27 (1960); *ibid.*, **1**, 35 (1960); S. Geltman, Phys. Rev. **119**, 1283 (1960).

TABLE I. The 1¹S state of H⁻. Values of the nonrelativistic energy $-\epsilon^2$, the mass-polarization correction (ϵ^2/AN) or $-\epsilon_M$, and the relativistic correction E_j . J denotes the theoretical ionization potential, excluding the Lamb shift correction. ω is the degree of the polynomial used, n the order of the corresponding determinant.

n	125	203	308	444	Extrapolated	Units
ω	10	12	14	16		
ϵ^2	0.5277506102525	0.5277509355954	0.5277509908056	0.5277510062954	0.527751014	au
$\epsilon^2(A/N)$	0.0328812134	0.0328798705	0.0328797785	0.0328797771	0.0328797771	au
$\langle p_1^4 \rangle$	2.462483	2.462574	2.462581	2.462577		au
$\langle \delta(r_2) \rangle$	0.164488398	0.164529224	0.164542335	0.164547396	0.1645510	au
$\langle \delta(r_{12}) \rangle$	0.002748758	0.002743964	0.002741536	0.002740206	0.0027385	au
$-(2/\alpha^2)E_2$	0.017765150	0.017756631	0.017753316	0.017751807		$\alpha^2\text{ry}$
$(2\epsilon^2-1)R_H$	6087.2394	6087.3108	6087.3229	6087.3263	6087.3279	cm^{-1}
$-\epsilon_M$	-3.928102	-3.927941	-3.927930	-3.927930	-3.927930	cm^{-1}
E_j	-0.30239	-0.30349	-0.30388	-0.30404	-0.30416	cm^{-1}
J	6083.0089	6083.0793	6083.0910	6083.0943	6083.0958	cm^{-1}
$\langle r_1 \rangle$	2.70988116	2.71014948	2.71017604	2.71017831	2.71017853	au
$\langle r_{12} \rangle$	4.41211529	4.41263790	4.41269000	4.41269452	4.41269492	au
$\langle r_1^2 \rangle$	11.905735	11.912774	11.913603	11.913692	11.913702	au
$\langle r_{12}^2 \rangle$	25.186148	25.200181	25.201833	25.202010	25.202031	au

On the basis of the results obtained for $n=95, 125, 161$, and 203, ϵ^2 extrapolates to 0.4981 for the 2¹S state and to 0.4987 for the 2³S state. Further solution of determinants of orders 444 and 1078 in the case of the 2³S state led to an extrapolated value of 0.4993, still unbound. One gets the impression that for both states ϵ^2 tends to the value 0.5 as $n \rightarrow \infty$. We consider the results presented in Table II as evidence *against* the existence of a second bound state of the negative hydrogen ion.

4. LOWER BOUNDS TO THE ENERGY LEVELS OF THE 1¹S AND 2³S STATES OF HELIUM

In spite of the manifest convergence of the computed energy eigenvalues to an upper bound, there is still room for argument that this indicated limit may be different from the exact eigenvalue. The issue would be settled if the eigenvalue could be bracketed between theoretical upper and lower bounds separated by a gap which is less than the experimental error in the term value. The difficulty with the lower bound has been⁷⁻¹⁰ that, for a given order of determinant n , the distance between it and the experimental value is many times greater than the distance between the latter and the upper bound. In Temple's¹¹ method, the lower bound $-\epsilon_+^2$ to the energy E_1 in the 1¹S state is given by

$$\epsilon_+^2 = \epsilon_-^2 + \Delta, \quad \Delta = \frac{\sigma}{(\epsilon_-^2 + E_2)}, \quad (3)$$

where E_2 is the exact eigenvalue for the 2¹S state, $-\epsilon_-^2$ is the upper bound $(\psi, H\psi)$, H the Hamiltonian of the system, and

$$\sigma = [(H\psi, H\psi) - (\psi, H\psi)^2]. \quad (4)$$

⁷ T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

⁸ T. Kinoshita, Phys. Rev. **115**, 366 (1959).

⁹ N. W. Bazley and D. W. Fox, Phys. Rev. **124**, 483 (1961).

¹⁰ For a discussion of the various methods for obtaining lower bounds of eigenvalues see G. L. Caldow and C. A. Coulson, Proc. Cambridge Phil. Soc. **57**, 341 (1961).

¹¹ G. Temple, Proc. Roy. Soc. (London) **A119**, 276 (1928).

With a 39-term variational wave function ψ , Kinoshita⁷ obtained the values $\epsilon_-^2 = 2.9037225$, $\epsilon_+^2 = 2.9038737$, giving a gap between the upper and lower bound of 33 cm^{-1} , as against the experimental accuracy¹² of $\pm 0.15 \text{ cm}^{-1}$. He then used⁸ the more complicated method of Stevenson and Crawford¹³ in which an eigenvalue ζ is first determined from a solution of the variational problem

$$-2\zeta(\psi, H\psi) + (H\psi, H\psi) = \text{minimum}, \quad (5)$$

and then ϵ_+^2 is obtained from

$$\epsilon_+^2 = -\zeta + [\zeta^2 - 2\zeta(\psi, H\psi) + (H\psi, H\psi)]^{1/2}. \quad (6)$$

Kinoshita introduced a modification of this method designed to minimize also $(\psi, H\psi)$. For the 39-term solution he gets $\epsilon_-^2 = 2.9037200$, $\epsilon_+^2 = 2.9037906$, giving a gap of 15 cm^{-1} . With an 80-term solution his values are $\epsilon_-^2 = 2.9037237$, $\epsilon_+^2 = 2.9037467$, and the gap is reduced to 5 cm^{-1} .

We have evaluated $\langle H^2 \rangle$ for the 1¹S and 2³S states of helium using the wave functions obtained previously by our method.^{1,2} In the results for the 1¹S state shown in Table III, which are based on Temple's equation (3),

TABLE II. Values of the energy eigenvalue ϵ^2 (in au) for the 2¹S and 2³S states of H⁻. A state is bound if $\epsilon^2 > 0.5$.

n	ω	2 ¹ S	2 ³ S
95	8	0.489466	0.493766
125	9	0.491720	0.494863
161	10	0.493330	0.495694
203	11	0.494517	0.496337
Extrapolated		0.4981	0.4987
444	15		0.497867
1078	21		0.498838
Extrapolated			0.4993

¹² G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958).

¹³ A. F. Stevenson and M. F. Crawford, Phys. Rev. **54**, 375 (1938).

TABLE III. Upper and lower bounds $-\epsilon_-^2$ and $-\epsilon_+^2$ to the energy E_1 of the 1^1S state of helium. $\sigma = [(H\psi, H\psi) - (\psi, H\psi)^2]$. The energy E_2 of the 2^1S state is -2.14597404 . $\nu_- = (2\epsilon_-^2 - 4)R_{\text{He}^4}$, $\nu_+ = (2\epsilon_+^2 - 4)R_{\text{He}^4}$.

n	ϵ_-^2 (au)	σ	ϵ_+^2 (au)	ν_- (cm $^{-1}$)	ν_+ (cm $^{-1}$)
252	2.903724290	0.000025076	2.903757383	198317.3558	198324.6177
444	2.903724356	0.000008623	2.903735736	198317.3702	198319.8674
715	2.903724370	0.000003861	2.903729466	198317.3734	198318.4916
1078	2.903724375	0.000001698	2.903726615	198317.3743	198317.8659
Extrapolated	2.903724376			198317.3747	

the gap has been reduced to 0.5 cm^{-1} at a determinant of order $n=1078$. Extrapolation to $n \rightarrow \infty$ is difficult in this case because the ratios of the differences do not approach constancy. The gap between the upper and lower bounds for the level of the ground state of helium thus stands now at about three times the experimental error of 0.15 cm^{-1} .

For the 2^3S state, the results given in Table IV show that for a determinant of order $n=715$ the gap has been reduced to 0.0006 cm^{-1} , with an indicated rate of decrease by a factor of 50 for each step. It was therefore not considered worthwhile to compute $\langle H^2 \rangle$ for $n=1078$, especially since the present experimental error¹⁴ in the 2^3S term value is 0.05 cm^{-1} . To the author's knowledge this is the first instance of a complete merging of the upper and lower bounds in an eigenvalue problem. An upper bound ν_+ to the 2^1S state of helium is given in Table VII.

5. THE 2^3S STATE OF HELIUM

The 2^3S state of helium was treated previously² by method *A*, where it was found that for a determinant of order $n=715$ the nonrelativistic energy eigenvalue converged to an accuracy of about 0.001 cm^{-1} . Since this is considerably better than the present uncertainty of 0.05 cm^{-1} in the experimental¹⁴ term value, it was felt that there was no need to go to the next step of $n=1078$. One of the results, the electron density at the nucleus, $D(0)$, defined by

$$D(0) = 8\pi \langle \delta(\mathbf{r}_2) \rangle = 8\pi \int d^3x_1 \psi^2(\mathbf{r}_1, 0), \quad (7)$$

came out 33.18416 at $n=715$, with an extrapolated value of 33.18414 , indicating an accuracy of six parts in

10^7 . $D(0)$ is equal to $32(1+\epsilon)$, where $(1+\epsilon)$ is the correction to the Fermi formula for hyperfine splitting. Recently, White *et al.*¹⁵ have measured the hyperfine splitting of the 2^3S state of He^3 , and achieved an accuracy of two parts in 10^7 . Using our value of $D(0)$, they found a disagreement of one part in 10^5 with the hyperfine-structure theory of Sessler and Foley.¹⁶ It was therefore of interest to substantiate further the value of $D(0)$, and for this purpose we took up a suggestion by V. W. Hughes to go one step further by solving a determinant of order $n=1078$. Table V shows that up to $n=715$ the first two values of the ratio of differences x of $D(0)$ are very close to -0.10 , so that the previous extrapolated value of 33.18414 was well founded. The new result for 1078 verifies this, and the new extrapolated value of 33.1841426 is probably reliable to within five parts in 10^8 . The discrepancy between theory and experiment calls for a re-examination of the theory of hyperfine structure of the 2^3S state of He^3 .

In Table VI are shown the new results for the 2^3S state obtained from the determinant of order $n=1078$. The convergence for this state is so rapid that the previously extrapolated values, based on $n=125, 252, 444$, and 715 , are in close agreement with the values for 1078 . Taking the new value of the Lamb shift obtained by Suh and Zaidi¹⁷ of $-0.109 \pm 0.009 \text{ cm}^{-1}$ we get for the ionization potential of the 2^3S state

$$38454.8274 - 0.109 = 38454.718 \pm 0.009 \text{ cm}^{-1}, \quad (8)$$

in good agreement with the experimental value which Herzberg¹⁴ estimates to be $38454.73 \pm 0.05 \text{ cm}^{-1}$.

6. THE 2^1S STATE OF HELIUM

In treating the first singlet excited state 2^1S we can follow the same method *B* used for the ground state,

TABLE IV. Upper and lower bounds $-\epsilon_-^2$ and $-\epsilon_+^2$ to the energy E_2 of the 2^3S state of helium. $\sigma = [(H\psi, H\psi) - (\psi, H\psi)^2]$. The energy E_3 of the 3^3S state was taken as -2.06868898 . $\nu_- = (2\epsilon_-^2 - 4)R_{\text{He}^4}$, $\nu_+ = (2\epsilon_+^2 - 4)R_{\text{He}^4}$.

n	ϵ_-^2 (au)	σ	ϵ_+^2 (au)	ν_- (cm $^{-1}$)	ν_+ (cm $^{-1}$)
125	2.17522097961	0.000063736	2.175819259	38451.286218	38582.57536
252	2.17522925888	0.000001048	2.175239095	38453.103059	38455.26154
444	2.17522937680	0.00000001565	2.175229524	38453.128935	38453.16117
715	2.17522937822	0.00000000030	2.175229381	38453.129247	38453.12987
Extrapolated	2.17522937824		2.175229379	38453.129250	38453.12941

¹⁴ G. Herzberg (private communication).

¹⁵ J. A. White, L. Y. Chow, C. Drake, and V. W. Hughes, Phys. Rev. Letters **3**, 428 (1959).

¹⁶ A. M. Sessler and H. M. Foley, Phys. Rev. **98**, 6 (1955).

¹⁷ K. S. Suh and M. H. Zaidi (private communication).

except that we now consider the second root of the determinant. For a given order n of the determinant the condition of orthogonality to the 1¹S wave function is met¹⁸ by the orthogonality of the eigenvectors of the determinant. The analysis of the 2¹S state is thus based on the same recursion relation (22) and the resulting determinant (30) of reference 1. For $n=1$ there is no second root; for $n<9$ the second root gives an unbound state, with an energy eigenvalue $\epsilon^2<2$. For higher orders n , ϵ^2 becomes bound, and ultimately shows good convergence, as is seen from Table VII. For $n=615$, an accuracy in ϵ^2 of three parts in 10^9 seems to be indicated.

The Lamb shift correction to the ionization energy of the 2¹S state of He has recently been evaluated by Suh and Zaidi¹⁷ to be -0.104 ± 0.014 cm⁻¹. With the value of J at $n=615$ of 32033.3183, this leads to an ionization energy of 32033.214 ± 0.014 cm⁻¹, the uncertainty arising entirely from the Lamb shift correction. According to Herzberg¹⁴ the experimental ionization energy is 32033.26 ± 0.03 or, at worst, ±0.05 cm⁻¹.

TABLE V. The electron density at the nucleus, $D(0)$, for the 2³S state of helium. Δ denotes the differences, and x the ratios of the differences.

n	$D(0)$	Δ	x	Extrapolated
125	33.165188			
252	33.1860652	0.020877		
444	33.1839485	-0.0021167	-0.10139	
715	33.18416103	0.0002125	-0.10039	
1078	33.18414092	-0.00002011	-0.09464	33.18414
				33.1841426

7. VERIFICATION OF THE LAMB SHIFT IN TWO-ELECTRON ATOMS

We have given in Table VIII a summary of the verifications to date of the Lamb shift in the S state of He and Li⁺. It should be noted that the Lamb shift correction to the *ionization* energy, which is the quantity observed, is the *difference* between the Lamb shift in

TABLE VI. The 2³S state of He. Values of the nonrelativistic energy $-\epsilon^2$, the mass-polarization correction (ϵ^2/AN) or $-\epsilon_M$, and the relativistic correction E_j . J denotes the theoretical ionization potential, excluding the Lamb shift correction.

n	715	Previous extrapolation	1078	Units
ϵ^2	2.17522937822	2.17522937824	2.175229378237	au
$\epsilon^2(A/N)$	0.00744213074	0.00744213071	0.007442130715	au
$\langle p_1^4 \rangle$	41.835544	41.835541	41.8355406	au
$\langle \delta(r_2) \rangle$	1.3203558	1.3203550	1.320355015	au
$-(2/\alpha^2)E_2$	0.003256860	0.003256860	0.00325686014	α^2 ry
$(2\epsilon^2-4)R_{He^4}$	38453.129247	38453.129250	38453.129250	cm ⁻¹
$-\epsilon_M$	-0.22388810	-0.22388810	-0.22388810	cm ⁻¹
E_j	1.92196	1.92201	1.922013	cm ⁻¹
J	38454.82732	38454.82737	38454.827375	cm ⁻¹

TABLE VII. The 2¹S state of helium. Values of the nonrelativistic energy $-\epsilon^2$, the mass-polarization correction (ϵ^2/AN) or $-\epsilon_M$, and the relativistic correction E_j . J denotes the theoretical ionization potential, excluding the Lamb shift correction, $\nu_+ = (2\epsilon_+^2-4)R_{He^4}$, where ϵ_+^2 is computed from (3) with E_2 replaced by $E_3 = -2.061271$.¹⁹

n	203	308	444	615	Extrapolated	Units
ω	12	14	16	18		
ϵ^2	2.145958989	2.145972779	2.145973945	2.145974037	2.145974044	au
$\epsilon^2(A/N)$	0.009527424	0.009506093	0.009504063	0.009503885	0.009503869	au
$\langle p_1^4 \rangle$	41.114986	41.117956	41.118548	41.118667	41.118697	au
$\langle \delta(r_2) \rangle$	1.308894	1.309310	1.309418	1.309447	1.309458	au
$\langle \delta(r_{12}) \rangle$	0.0086819	0.0086607	0.0086546	0.0086521	0.0086499	au
$-(2/\alpha^2)E_2$	0.0185402	0.0185138	0.0185091	0.0185076	0.0185068	α^2 ry
$(2\epsilon^2-4)R_{He^4}$	32029.9021	32032.9282	32033.1841	32033.2041	32033.2057	cm ⁻¹
ν_+	32321.68	32068.140	32040.309	32036.085	32035.238	cm ⁻¹
$-\epsilon_M$	-0.286622	-0.285980	-0.285919	-0.285914	-0.285913	cm ⁻¹
E_j	0.42908	0.40786	0.40180	0.40009	0.39942	cm ⁻¹
J	32030.0446	32033.0501	32033.3000	32033.3183	32033.3196	cm ⁻¹
$\langle r_1 \rangle$	2.969522	2.972631	2.973016	2.973057	2.973061	au
$\langle r_{12} \rangle$	5.262668	5.268842	5.269607	5.269688	5.269697	au
$\langle r_1^2 \rangle$	16.02381	16.08041	16.08822	16.08913	16.08924	au
$\langle r_{12}^2 \rangle$	32.17180	32.28477	32.30037	32.30218	32.30240	au

¹⁸ E. Hylleraas and B. Undheim, Z. Physik **65**, 759 (1930).

¹⁹ This is an extrapolated value, the last computed value being -2.061256 for $n=220$. See a forthcoming publication by the author. For a discussion of the problem of getting lower bounds to excited states see Per-Olov Löwdin, *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. II, p. 264.

TABLE VIII. Summary of the verification of the Lamb shift correction in He and Li⁺. J is the theoretical ionization energy, excluding the Lamb shift correction. The error Δ in J is taken as the difference between the value quoted for the given order n and the extrapolated value. $J_{\text{th}} = J + \text{Lamb shift}$.

Atom	State	J (cm ⁻¹)	Δ	n	Lamb shift	J_{th} (cm ⁻¹)	J_{exp} (cm ⁻¹)
He	1 ¹ S	198312.0258	0.0001	1078 ^a	-1.352±0.025 ^d -1.361±0.056 ^e -1.341±0.005 ^f	198310.674±0.025 198310.665±0.056 198310.685±0.005	198310.8±0.15 ^j
He	2 ¹ S	32033.318	0.001	615 ^b	-0.104±0.014 ^g	32033.214±0.014	32033.26±0.03[±0.05] ^k
He	2 ³ S	38454.8274	0.00001	1078 ^b	-0.109±0.009 ^g	38454.718±0.009	38454.73±0.05 ^k
Li ⁺	1 ¹ S	610087.449	0.004	444 ^c	-[7.83] ^b	610079.61	610079.4 ±5[±3] ^l
Li ⁺	2 ³ S	134045.2612	0.0001	308 ^c	-[1.14] ⁱ	134044.12	134044.19±0.10 ^l

^a See reference 2.

^b Present work.

^c C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

^d A. Dalgarno and A. L. Stewart, Proc. Phys. Soc. (London) **76**, 49 (1960).

^e See reference 21.

^f See reference 20.

^g See reference 17.

^h See reference 1.

ⁱ Based on an estimate by Dalgarno of a value of 168 for $\ln k_0$.

^j See reference 12.

^k See reference 14.

^l G. Herzberg and H. Moore, Can. J. Phys. **37**, 1293 (1959).

the level of the two-electron atom and in the ground state of the one-electron ion. The latter is 3.5 cm⁻¹ for He⁺ and 15.5 cm⁻¹ for Li⁺⁺. The best available theoretical Lamb shift correction is still the one for the ground state of He, where the accuracy claimed ranges from 0.4% in Schwartz's value²⁰ to 4% in the value derived by Salpeter and Zaidi.²¹ The experimental uncertainty in this level amounts, however, to 11% of the Lamb shift. It is desirable to bring up the experimental accuracy as well as the accuracy of the theoretical Lamb shift values to the precision of the J values, which is now of the order of 0.001 cm⁻¹.

ACKNOWLEDGMENTS

I am indebted to Professor Herzberg for experimental term values of the 2 ¹S and 2 ³S states of He, and to Professor Dalgarno for estimates of the value of $\ln k_0$ for the 2 ¹S and 2 ³S states of Li⁺. My thanks are also due to Professor Salpeter and to Dr. Suh and Dr. Zaidi for their values of the Lamb shift in the 1 ¹S, 2 ¹S and 2 ³S states of He. I am indebted to Yigal Accad for assistance in programming.

APPENDIX A. EVALUATION OF $(H\psi, H\psi)$ FOR S STATES

In the S states of two-electron atoms the non-relativistic wave function ψ is a function of the distances r_1 and r_2 of the electrons from the nucleus and of their mutual distance r_3 . The Hamiltonian is given by

$$\begin{aligned} \Pi\psi = r_1 r_2 r_3 H\psi = & -\frac{1}{2} r_1 r_2 r_3 (\partial^2 \psi / \partial r_1^2) - r_2 r_3 (\partial \psi / \partial r_1) \\ & -\frac{1}{2} r_1 r_2 r_3 (\partial^2 \psi / \partial r_2^2) - r_1 r_3 (\partial \psi / \partial r_2) \\ & - r_1 r_2 r_3 (\partial^2 \psi / \partial r_3^2) - 2 r_1 r_2 (\partial \psi / \partial r_3) \\ & -\frac{1}{2} r_2 (r_1^2 - r_2^2 + r_3^2) (\partial^2 \psi / \partial r_1 \partial r_3) \\ & -\frac{1}{2} r_1 (r_2^2 - r_1^2 + r_3^2) (\partial^2 \psi / \partial r_2 \partial r_3) \\ & + (-Z r_2 r_3 - Z r_1 r_3 + r_1 r_2) \psi. \end{aligned} \quad (\text{A1})$$

²⁰ C. Schwartz, Phys. Rev. **123**, 1700 (1961).

²¹ E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962).

In our method¹ we use instead of r_1 , r_2 , and r_3 the *perimetric* coordinates defined by

$$\begin{aligned} u &= \epsilon(r_2 + r_3 - r_1), \quad v = \epsilon(r_1 + r_3 - r_2), \\ w &= 2\epsilon(r_1 + r_2 - r_3), \end{aligned} \quad (\text{A2})$$

where the energy eigenvalue $E = -\epsilon^2$. Writing

$$\psi = e^{-\frac{1}{2}(u+v+w)} F(u, v, w), \quad (\text{A3})$$

we get from (A1)

$$\begin{aligned} -16\epsilon^2 \Pi\psi &= e^{-\frac{1}{2}(u+v+w)} \{ \epsilon [(4u^2v + 4uv^2 + 4u^2w + 4uvw + 2uw^2) F_{uu} \\ &+ (4u^2v + 4uv^2 + 4v^2w + 4uvw + 2vw^2) F_{vv} \\ &+ (8u^2w + 8v^2w + 4uw^2 + 4vw^2) F_{ww} \\ &- 4uw(2u+w) F_{uw} - 4vw(2v+w) F_{vw} \\ &+ (-4u^2 + 4v^2 + 2w^2 + 4uw + 4vw + 8uv \\ &- 4uvw - 4uv^2 - 4u^2v) F_u + (4u^2 - 4v^2 + 2w^2 \\ &+ 4uw + 4vw + 8uv - 4uvw - 4uv^2 - 4u^2v) F_v \\ &+ (8u^2 + 8v^2 - 4w^2 - 2uw^2 - 2vw^2 - 4u^2w - 4v^2w) F_w] \\ &+ [\epsilon/2(u+v)(2u+w)(2v+w) + (4Z-4\epsilon)(u+v) \\ &\times (u+v+w) - (2u+w)(2v+w)] F \}. \end{aligned} \quad (\text{A4})$$

The eigenvalue ϵ and the associated eigenvectors $A(l, m, n)$ and $F(a, b, c)$ in the truncated expansion

$$\begin{aligned} F &= \sum_{l, m, n=0}^k A(l, m, n) L_l(u) L_m(v) L_n(w) \\ &= \sum_{a, b, c=0}^k F(a, b, c) u^a v^b w^c \end{aligned} \quad (\text{A5})$$

are obtained by solving a determinant of order k . From (A4) we can express the coefficients $\Pi(l, m, n)$ in the expansion

$$-16\epsilon^2 \Pi\psi = e^{-\frac{1}{2}(u+v+w)} \sum \Pi(l, m, n) u^l v^m w^n \quad (\text{A6})$$

in terms of the $F(l, m, n)$ through the recursion relation

$$\begin{aligned} \Pi(l, m, n) = & \{4\epsilon[l(l+1) - (m-1)(2n+1) + n(n-1)]F(l, m-1, n) \\ & + 4\epsilon[m(m+1) - (l-1)(2n+1) + n(n-1)]F(l-1, m, n) + 4\epsilon(l+1)^2F(l+1, m-2, n) \\ & + 4\epsilon(m+1)^2F(l-2, m+1, n) + 4\epsilon(l+1)^2F(l+1, m-1, n-1) + 4\epsilon(m+1)^2F(l-1, m+1, n-1) \\ & + 4\epsilon[l^2 + m^2 - (n-1)(l+m+1)]F(l, m, n-1) + 2\epsilon(l+1)^2F(l+1, m, n-2) + 2\epsilon(m+1)^2F(l, m+1, n-2) \\ & + 8\epsilon(n+1)^2F(l-2, m, n+1) + 8\epsilon(n+1)^2F(l, m-2, n+1) + 4[-\epsilon(l+m) + 2Z-1]F(l-1, m-1, n) \\ & + 4[-\epsilon(l+n+1) + Z]F(l, m-2, n) + 4[-\epsilon(m+n+1) + Z]F(l-2, m, n) \\ & + 2[-\epsilon(2l+n+1) + 2Z-1]F(l, m-1, n-1) + 2[-\epsilon(2m+n+1) + 2Z-1]F(l-1, m, n-1) \\ & + 2\epsilon F(l-2, m-1, n) + 2\epsilon F(l-1, m-2, n) + 2\epsilon F(l-1, m-1, n-1) + \epsilon F(l, m-2, n-1) \\ & + \epsilon F(l-2, m, n-1) + \frac{1}{2}\epsilon F(l-1, m, n-2) + \frac{1}{2}\epsilon F(l, m-1, n-2) - F(l, m, n-2)\}. \quad (A7) \end{aligned}$$

With the $\Pi(l, m, n)$ known, we get directly

$$(H\psi, H\psi) = (4\epsilon^2/N) \sum \Pi(l, m, n) \times \Pi(l', m', n') \Omega(l+l', m+m', n+n'), \quad (A8)$$

where

$$\begin{aligned} \Omega(a, b, c) = & \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \int_0^\infty e^{-w} dw \\ & \times u^a v^b w^c / [(u+v)(2u+w)(2v+w)], \quad (A9) \end{aligned}$$

and N is the normalization constant

$$\begin{aligned} N = & \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \\ & \times \int_0^\infty e^{-w} dw (u+v)(2u+w)(2v+w) F^2. \quad (A10) \end{aligned}$$

Because of symmetry in the two electrons, the function needed in (A9) is

$$\begin{aligned} W(a, b, c) = & \Omega(a, b, c) + \Omega(b, a, c) \\ = & \int_0^\infty e^{-u} du \int_0^\infty e^{-v} dv \int_0^\infty e^{-w} dw (u^a v^b + u^b v^a) w^c / \\ & [(u+v)(2u+w)(2v+w)]. \quad (A11) \end{aligned}$$

One representation of W is

$$\begin{aligned} W(a, b, c) = & (\tfrac{1}{2})^{a+b+c+1} (a+b+c+1)! c! \alpha! \\ & \times \sum_{m=0}^{\gamma} \binom{\beta}{2m} F(\lambda, c, m, \alpha), \quad (A12) \end{aligned}$$

$$\begin{aligned} F(\lambda, c, m, \alpha) = & \sum_{k=0}^{\infty} \{[k + \tfrac{1}{2}(\lambda+1)][k + \tfrac{1}{2}(\lambda+2)] \cdots \\ & \times [k + \tfrac{1}{2}(\lambda+c+1)][k + \tfrac{1}{2}(\lambda+c+2)] \cdots \\ & \times [k + \tfrac{1}{2}(\lambda+c+1) + \alpha]\}^{-1}, \quad (A13) \end{aligned}$$

$$\lambda = a+b, \quad \gamma = [\beta/2], \quad \alpha = \min(a, b), \quad \beta = |a-b|. \quad (A14)$$

The W 's were evaluated on the basis of the recursion

relations

$$\begin{aligned} 4W(a, b, c) = & 2[(a-1)!(b-1)!c!/(a+b-1)] \\ & - 2W(a, b-1, c+1) - 2W(a-1, b, c+1) \\ & - W(a-1, b-1, c+2), \quad (A15) \end{aligned}$$

$$\begin{aligned} W(a, b, c) = & (b-2)!f(a, c) + a!f(b-2, c) \\ & - W(a+2, b-2, c) + \tfrac{1}{2}W(a, b-2, c+2) \\ & - [a!(b-2)!c!/(a+b-1)], \quad (A16) \end{aligned}$$

where

$$\begin{aligned} f(a, c) = & \int_0^\infty e^{-u} du \int_0^\infty e^{-w} dw u^a w^c / (2u+w) \\ = & (a+c)! \sum_{n=0}^c \binom{c}{n} N(a+n), \quad (A17) \end{aligned}$$

$$N(a) = (-)^a \left[\ln 2 - 1 + \tfrac{1}{2} - \tfrac{1}{3} + \cdots + \frac{(-)^a}{a} \right]. \quad (A18)$$

With the aid of these relations one can determine all the W 's from a knowledge of

$$W(0, 0, c) = (\tfrac{1}{2})^{c+1} (c-1)! c! F(0, c, 0, 0) \quad (A19)$$

and

$$W(0, 1, c-1) = (\tfrac{1}{2})^{c+1} [(c-1)!]^2 F(1, c-1, 0, 0). \quad (A20)$$

These can be put in the form

$$W(0, 0, c) = \tfrac{1}{2} (c-1)! \sum_{\nu=0}^c (-)^{\nu} \binom{c}{\nu} F(\nu, 0, 0, 0), \quad (A21)$$

$$\begin{aligned} W(0, 1, c-1) = & \tfrac{1}{4} (c-1)! \\ & \times \sum_{\nu=0}^c (-)^{\nu} \binom{c-1}{\nu} F(1+\nu, 0, 0, 0), \quad (A22) \end{aligned}$$

by using the recursion relation

$$\begin{aligned} (c+1)F(\lambda, c+1, m, \alpha) = & 2F(\lambda, c, m, \alpha) \\ & - 2F(\lambda+1, c, m, \alpha). \quad (A23) \end{aligned}$$

The F 's required are given by

$$F(0, 0, 0, 0) = \pi^2/2 \quad (A24)$$

$$F(\lambda, 0, 0, 0) = (4/\lambda) [1 + \frac{1}{3} + \frac{1}{5} + \cdots + 1/(\lambda-1)],$$

$$\lambda \text{ even} \quad (\text{A25})$$

$$F(\lambda, 0, 0, 0) = (2/\lambda) [2 \ln 2 + 1 + \frac{1}{2} + \frac{1}{3} + \cdots + 2/(\lambda-1)],$$

$$\lambda \text{ odd.} \quad (\text{A26})$$

In the computations we aimed at 20-decimal accuracy for the W 's. For this purpose it was necessary to have an accuracy of 40 decimals in the auxiliary functions $f(a, c)$ and $F(\lambda, 0, 0, 0)$, an enterprise which resulted in the addition of a new subroutine of multiple precision arithmetic for WEIZAC.

APPENDIX B

In this series of papers on H^- , He , and Li^+ , the ionization potentials were first obtained in atomic units and then expressed in cm^{-1} . The values of the latter depend of course on the Rydberg constants used. Two other conversion factors occur, the factor a in the expression for the mass polarization ϵ_M ,

$$\epsilon_M = a(\epsilon^2 A/N) \text{ cm}^{-1}, \quad (\text{B1})$$

and the factor b in the relativistic correction E_j ,

$$E_j = b \left[-\frac{1}{4} Z^4 + \frac{1}{2} \langle p_1^4 \rangle - 2\pi Z \langle \delta(\mathbf{r}_2) \rangle - 2\pi \langle \delta(\mathbf{r}_{12}) \rangle \right. \\ \left. - (2/\alpha^2) E_2 \right] \text{ cm}^{-1}, \quad (\text{B2})$$

$$a = 2(m/M)R, \quad b = \alpha^2 R. \quad (\text{B3})$$

We have used R_M for R in a and b .

The values of R_M , a , and b used are listed below in

Element	R_M	a	b
H^1	109677.577	119.4634	5.840375
He^4	109722.267	30.08387	5.842755
Li^7	109728.727	17.163109	5.843099

units of cm^{-1} . With these, one can recover from our tables the original values in atomic units, which have been determined to a higher precision than that to which the constants are known. The accuracy of the latter is less than is given in the table; they were used merely to exhibit in units of cm^{-1} the rate of convergence of ϵ_M and E_j which in any case are less than 20 cm^{-1} even for Li .