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$1\,^1S$ and $2\,^3S$ States of Helium

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The method described previously for the solution of the wave equation of two-electron atoms has been applied to the $1\,^1S$ and $2\,^3S$ states of helium, with the purpose of attaining an accuracy of 0.001 cm^{-1} in the nonrelativistic energy values. For the $1\,^1S$ state we have extended our previous calculations by solving determinants of orders 252, 444, 715, and 1078, the last yielding an energy value of -2.903724375 atomic units, with an estimated error of the order of 1 in the last figure. Applying the mass-polarization and relativistic corrections derived from the new wave functions, we obtain a value for the ionization energy of 198 312.0258 cm^{-1}, as against the value of 198 312.011 cm^{-1} derived previously from the solution of a determinant of order 210. With a Lamb shift correction of -1.339, due to Kabir, Salpeter, and Sucher, this leads to a theoretical value for the ionization energy of 198 310.687 cm^{-1}, compared with Herzberg's experimental value of $198\,310.8_2 \pm 0.15$ cm^{-1}.

For the $2\,^3S$ state we have solved determinants of orders 125, 252, 444, and 715, the last giving an energy value of -2.17522937822 a.u., with an estimated error of the order of 1 in the last figure. This corresponds to a nonrelativistic ionization energy of 38 453.1292 cm^{-1}. The mass-polarization and relativistic corrections bring it up to 38 454.8273 cm^{-1}. Using the value of 74.9 ry obtained by Dalgarno and Kingston for the Lamb-shift excitation energy K_0, we get a Lamb-shift correction to the ionization energy of the $2\,^3S$ state of -0.16 cm^{-1}. The resulting theoretical value of 38 454.66 cm^{-1} for the ionization potential is to be compared with the experimental value, which Herzberg estimates to be $38\,454.73 \pm 0.05$ cm^{-1}. The electron density at the nucleus $D(0)$ comes out 33.18416, as against a value of 33.18388 ± 0.00023 which Novick and Commins deduced from the hyperfine splitting. We have also determined expectation values of several positive and negative powers of the three mutual distances, which enter in the expressions for the polarizability and for various sum rules.

1. INTRODUCTION

THE recent renewed interest in accurate solutions of the wave equation for two-electron atoms has come from the experimental side, when Herzberg[1] initiated his program of a precise spectroscopic measurement of the ionization potential of He, in order to determine the Lamb shift in the ground state. The parallel theoretical investigation of Chandrasekhar and Herzberg[1] first brought to light a gross discrepancy of 21.5 cm^{-1} between theory and experiment, where none had been suspected. This gap was soon reduced by these authors[2] to 2, and subsequently by Hart and Herzberg[3] to 1, while simultaneously, on the experimental side, Herzberg and Zbinden[2] succeeded in reducing an initial uncertainty[4] of 15 cm^{-1} to 1 cm^{-1}. Some reported reversals from this trend[5] were promptly dispelled. At this stage the Lamb shift just began to emerge above the noise level, since Kabir and Salpeter[6] and Sucher[7] showed that its magnitude is only -1.339 cm^{-1}. When Herzberg[8] completed his spectroscopic determination of the ionization energy, achieving an accuracy of ± 0.15 cm^{-1}, the best theoretical value available was that of Kinoshita[9] obtained variationally[10] from a 39-term solution, for which the uncertainty was estimated to be ± 0.5 cm^{-1}.

In the solution given by the author,[11] an accuracy of 0.01 cm^{-1} for the nonrelativistic energy value was aimed at. This precision could also be ascribed to the value obtained for the ionization potential if the Lamb-shift correction were known to the same degree of accuracy. At present, the Lamb-shift correction is subject to an uncertainty of an order of magnitude higher,[6] principally because it depends on a knowledge of the oscillator strengths f_{0n} for transitions from the ground state to the excited states; and while the ground-state wave function is known with considerable accuracy, no comparable accuracy has as yet been attained for the wave functions of the excited states. In this investigation we aimed at achieving an accuracy of 0.001 cm^{-1} in the nonrelativistic energy values of the $1\,^1S$ and $2\,^3S$ states. In the case of the ground state it was necessary to go to a determinant of order 1078, while in the case of the $2\,^3S$ state, the convergence was more rapid and a determinant of order 715 sufficed. One may reasonably expect that within a year or so, accurate wave functions for the excited states will be forthcoming, and that the Lamb-shift correction will then be delineated within correspondingly narrow limits. The problem of firmly establishing the magnitude of the Lamb shift in two-electron atoms is thus thrown back to the experimentalists. What is needed is a reduction, for the second time, of the experimental uncertainty in the ionization potential of He by a factor of 100 to ± 0.0015 cm^{-1}.

Another result obtained from the solution of the wave function for the $2\,^3S$ state is an accurate value of the

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[10] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[11] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958). This paper will be referred to as I.

TABLE I. Values for the $1\,^1S$ state of the nonrelativistic energy $-\epsilon^2$, the mass polarization correction $-\epsilon_M$, and the relativistic correction to the ionization potential E_j. J denotes the theoretical value of the ionization potential, excluding the Lamb-shift correction. $R_{\mathrm{He}^4}=109722.267$ cm^{-1}; $\alpha^2=5.32504\times10^{-5}$.

n	252	444	715	1078	Extrapolated	Units
ω	12	15	18	21		
ϵ	1.704031775	1.704031794	1.704031799	1.704031800	1.704031800	a.u.
ϵ^2	2.903724290	2.903724356	2.903724370	2.903724375	2.903724376	a.u.
$2\epsilon^2-4$	1.807448581	1.807448712	1.807448741	1.807448750	1.807448754	ry
$\epsilon^2(A/N)^{\mathrm{a}}$	0.15906968	0.15906953	0.15906950	0.15906948		a.u.
$\langle p_1{}^4\rangle$	54.08851	54.08832	54.08822	54.08815	54.08802	a.u.
$\langle\delta(\mathbf{r}_2)\rangle$	1.810337	1.810389	1.810410	1.810419	1.810427	a.u.
$\langle\delta(\mathbf{r}_{12})\rangle$	0.106413	0.106377	0.106362	0.106355	0.106345	a.u.
$-(2/\alpha^2)E_2$	0.278224	0.278202	0.278195	0.278192	0.278189	α^2 ry
$(2\epsilon^2-4)R_{\mathrm{He}^4}$	198317.3558	198317.3702	198317.3734	198317.3743	198317.3747	cm^{-1}
$-\epsilon_M{}^{\mathrm{a}}$	-4.785432	-4.785427	-4.7854263	-4.7854256	-4.7854	cm^{-1}
E_j	-0.5580	-0.5612	-0.5625	-0.5631	-0.5636	cm^{-1}
J	198312.0124	198312.0236	198312.0254	198312.0258	198312.0259	cm^{-1}

[a] The quantities tabulated in I (Table IV) are $\epsilon^2(A/N)$ and $-\epsilon_M$, not $-\epsilon^2(A/N)$ and ϵ_M.

electron density $D(0)$ at the nucleus. In connection with the recent precision measurement of the hyperfine splitting,[12,13] in He^3 this quantity, which depends significantly on the spatial distribution of nuclear currents and magnetic moments,[14] provides a restrictive criterion on the choice of nuclear models.

2. THE $1\,^1S$ STATE OF HELIUM

The method developed by the author for the solution of the Schrödinger wave equation for two-electron atoms[11] is based on the use of perimetric coordinates u, v, and w, which are defined by

$$u=\epsilon(r_2+r_{12}-r_1), \tag{1}$$

$$v=\epsilon(r_1+r_{12}-r_2), \tag{2}$$

$$w=2\epsilon(r_1+r_2-r_{12}), \tag{3}$$

where r_1 and r_2 denote the distances of the electrons from the nucleus, r_{12} their mutual distance, E the energy, and $\epsilon=\sqrt{-E}$. The wave function ψ, which in S-states is a function of the distances r_1, r_2, and r_{12} only, is expanded in the form

$$\psi=e^{-\frac{1}{2}(u+v+w)}\sum_{l,m,n=0}^{\infty}A(l,m,n)L_l(u)L_m(v)L_n(w), \tag{4}$$

and the coefficients $A(l,m,n)$ are determined from the *wave equation*. They are connected by the recursion relation I(22) containing 33 terms, and the vanishing of the determinant of these coefficients provides the condition for the energy eigenvalues ϵ. In I (Table III) are given eigenvalues obtained from the solution of determinants of orders $n=95$, 125, 161, and 203, these corresponding to wave functions represented by complete polynomials of orders $\omega=8$, 9, 10, and 11, respectively, in the variables u, v, and w, where

$$\omega=l+m+n. \tag{5}$$

It was found that the ratios of the differences of the ϵ-values were nearly constant, and this was made the basis for extrapolation to $n=\infty$ in order to obtain some notion as to the degree of convergence of the results. Let ϵ_1, ϵ_2, ϵ_3, ϵ_4 denote eigenvalues obtained for four equally spaced values of ω. Then to the extent that the successive ratios,

$$x_1=(\epsilon_3-\epsilon_2)/(\epsilon_2-\epsilon_1),\quad x_2=(\epsilon_4-\epsilon_3)/(\epsilon_3-\epsilon_2), \tag{6}$$

are nearly equal, the extrapolation is made by the formula

$$\epsilon_\infty=\epsilon_1+(\epsilon_2-\epsilon_1)/(1-x)^a, \tag{7}$$

where the constants x and a are determined from

$$ax=x_1,\quad (a+1)x/2=x_2. \tag{8}$$

Here x may be negative in the case of oscillating differences.

The value for ϵ obtained in I from the solution of the determinant of order 203 was 1.704031757, and the extrapolated value was 1.704031794. A determinant of order 210, in which were included the large coefficients $A(l,m,n)$ selected from among the first 438, yielded a value of 1.704031781 for ϵ. Table I gives the results of the solution of determinants of orders $n=252$, 444, 715, and 1078. These are spaced at intervals of 3 in ω. The chief result is the solution for $n=1078$, where also the vector was refined to high accuracy, while the lower orders were done mainly for the purpose of exhibiting the rate of convergence of the results, and providing a basis for extrapolation. The nonrelativistic ionization energy is given in Rydbergs in the line marked $(2\epsilon^2-4)$, and in units of cm^{-1} in the line $(2\epsilon^2-4)R_{\mathrm{He}^4}$. ϵ_M denotes the shift in the energy level due to the mass-polarization, and is given by

$$\epsilon_M=2\epsilon^2(m/M)(A/N)R_{\mathrm{He}^4}\ \mathrm{cm}^{-1}, \tag{9}$$

where m denotes the mass of the electron, M that of the nucleus, and N is a normalization constant defined

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

Table II. Expectation values of various functions for the $1\,{}^1S$ state.

$$V=(-1/r_1-1/r_2+1/2r_{12}).\quad S(k)=\sum_n f_{0n}(E_0-E_n)^k,\quad f_{0n}=\tfrac{1}{3}(E_0-E_n)\,|\psi_0(\mathbf{r}_1+\mathbf{r}_2)\psi_n|^2.$$

E_0 and E_n denote the energies of the ground state and of the nth excited state, respectively, measured in Rydbergs, lengths being measured in units of a_0.

n	252	444	715	1078	Extrapolated
$\langle r_1^2\rangle$	1.19348333	1.19348309	1.19348303	1.19348301	1.19348299
$\langle r_1\rangle$	0.929472381	0.929472316	0.929472302	0.929472297	0.929472293
$\langle 1/r_1\rangle$	1.688316596	1.688316754	1.688316789	1.688316796	1.688316798
$\langle 1/r_1^2\rangle$	6.0173826	6.0173997	6.0174053	6.0174071	6.0174080
$\langle r_{12}^2\rangle$	2.51644015	2.51643954	2.51643939	2.51643934	2.51643932
$\langle r_{12}\rangle$	1.42207040	1.42207029	1.42207027	1.42207026	1.42207025
$\langle 1/r_{12}\rangle$	0.945818478	0.945818459	0.945818455	0.945818451	
$\langle 1/r_{12}^2\rangle$	1.464798	1.464781	1.464776	1.464773	1.464770
$\langle 1/r_1r_2\rangle$	2.708656	2.708656	2.708656	2.708656	2.708656
$\langle 1/r_1r_{12}\rangle$	1.920947	1.920945	1.920945	1.920944	
$\langle \mathbf{r}_1\cdot\mathbf{r}_2\rangle$	−0.064736742	−0.064736684	−0.064736669	−0.064736665	−0.064736664
$\langle V\rangle$	−2.903723953	−2.903724279	−2.903724351	−2.903724367	−2.903724372
$\langle V^2\rangle$	13.976384	13.976417	13.976427	13.976430	13.976432
$S(-1)$	0.752497727	0.752497601	0.752497571	0.752497561	0.752497553
$S(0)$	2	2	2	2	
$S(1)$	8.16745059	8.16745036	8.16745034	8.16745028	
$S(2)$	121.3300	121.3334	121.3348	121.3354	121.3360
U	1.97279	1.97818	1.98257	1.98444	
T	0.45640	0.46440	0.46941	0.47391	

in I(39). E_j is the relativistic correction to the ionization potential:

$$E_j=\alpha^2[-\tfrac{1}{4}Z^4+\tfrac{1}{2}\langle p_1^4\rangle-2\pi Z\langle\delta(\mathbf{r}_2)\rangle-2\pi\langle\delta(\mathbf{r}_{12})\rangle]-2E_2,\tag{10}$$

in Rydbergs. The theoretical value of the ionization potential J given in the last line is the sum of the quantities in the preceding three lines. The extrapolated value[15] of J differs by 2 units of 10^{-4} cm^{-1} from the sum of the three terms above it, and by only one unit from the value obtained for $n=1078$. The uncertainty in the latter, based on the correction terms included in (9) and (10), is thus of the order of magnitude of 10^{-4} cm^{-1}. In support of this optimistic estimate we may cite the fact that the difference between the J-values of $n=203$ and the extrapolated value in I was 0.022 cm^{-1}, which is close to the figure of 0.025 cm^{-1} by which the 203-value falls short of our new value. It is unlikely that a value for J of 198312.026 cm^{-1} would be off by much more than the margin of 0.001 cm^{-1} aimed at in this investigation. If we add to the above the Lamb-shift correction of -1.339 cm^{-1} due to Kabir and Salpeter[6] and Sucher,[7] we get a theoretical value for the ionization potential of 198 310.687 cm^{-1}, as compared with Herzberg's[8] experimental value of $198\,310.8_2$ ± 0.15 cm^{-1}.

The Lamb-shift correction is at present subject to an uncertainty of 0.2 cm^{-1}. The leading terms in the Lamb shift[6] of the ionization potential ΔE_j are represented by

$$\Delta E_j=E_{L,1}-E_{L,2}-E_{L,2'}.\tag{11}$$

Here $E_{L,1}$ denotes the Lamb shift of the one-electron ion, and has the value of 3.534 cm^{-1} for helium. The last term is given by

$$E_{L,2'}=-\frac{28}{3}\alpha^3\langle\delta(\mathbf{r}_{12})\rangle\ln\left(\frac{1}{\alpha}\right)\text{ ry},\tag{12}$$

and is equal to -0.2082 cm^{-1} for the $1\,{}^1S$ state. The uncertainty in the Lamb-shift correction stems primarily from the parameter K_0 in the expression

$$E_{L,2}=\frac{16}{3}\alpha^3Z\langle\delta(\mathbf{r}_2)\rangle\left[2\ln\frac{1}{\alpha}-\ln\frac{K_0}{\text{ry}}+\frac{19}{30}\right],\tag{13}$$

which represents the average excitation energy of the $1\,{}^1S$ state. K_0 is defined by

$$\ln K_0=\frac{\sum_n f_{0n}(E_0-E_n)^2\ln(E_0-E_n)}{\sum_n f_{0n}(E_0-E_n)^2},\tag{14}$$

where

$$f_{0n}=\tfrac{1}{3}(E_0-E_n)\,|\psi_0(\mathbf{r}_1+\mathbf{r}_2)\psi_n|^2.\tag{15}$$

E_0 and E_n denote the energies of the initial state and of the nth excited state, respectively, and ψ_0 and ψ_n are the corresponding wave functions. In the absence of accurate wave functions for the excited states, the oscillator strengths f_{0n} are known only approximately[6,16,17] at present. Kabir and Salpeter arrive at a

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[15] The J-values in Table I are given to at least one figure more than is warranted by the known precision of Rydberg's constant. However, when expressed in Rydberg units, the ten significant figures are justified, and these can later be converted to cm^{-1} when a more accurate value of the Rydberg constant becomes available.

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[17] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **247**, 245 (1958).

value of 4.39 for $\ln K_0$, with an estimated uncertainty of the order of ± 0.2.

TABLE III. Ordering of the indices l, m, n in the antisymmetrical case.

l	m	n	ω	p	l	m	n	ω	p
0	1	0	1	1	0	4	0	4	11
0	1	1	2	2	1	2	1	4	12
0	2	0	2	3	1	3	0	4	13.
0	1	2	3	4	0	1	4	5	14
0	2	1	3	5	0	2	3	5	15
0	3	0	3	6	0	3	2	5	16
1	2	0	3	7	0	4	1	5	17
0	1	3	4	8	0	5	0	5	18
0	2	2	4	9	1	2	2	5	19
0	3	1	4	10	1	3	1	5	20

In view of the enormous amount of computations required to get a sufficiently accurate value for $\ln K_0$ directly from (14), especially for the excited states, the following method of inferring a rough value may be of interest.

Let $S(k)$ and $P(k)$ be defined by

$$S(k)=\sum_n f_{0n}(E_0-E_n)^k, \tag{16}$$

$$P(k)=(d/dk)\ln S(k). \tag{17}$$

Then $\ln K_0$ is equal to $P(2)$. Now the $S(k)$ are known from the sum rules[16]

$$S(-2)=\tfrac{1}{4}\alpha, \tag{18}$$

$$S(-1)=\tfrac{1}{3}\langle(\mathbf{r}_1+\mathbf{r}_2)^2\rangle, \tag{19}$$

$$S(0)=Z, \tag{20}$$

$$S(1)=(8/3)[\epsilon^2+\epsilon^2(A/N)], \tag{21}$$

$$S(2)=(64\pi/3)\langle\delta(\mathbf{r}_2)\rangle. \tag{22}$$

Here α denotes the polarizability, for which Dalgarno and Kingston[16] get a value of $1.39a_0{}^3$, and the other S-values are given in Table II. Another datum can be inferred from Kabir and Salpeter's asymptotic expression[6] for f_{0n}, namely, that $S(2.5)=\infty$. In the vicinity of $k=2$ we may therefore attempt a representation

$$S(k)=B/(2.5-k)^a, \tag{23}$$

and determine the constants B and a by fitting the values of $S(1)$ and $S(2)$. The result is

$$a=\log_3[S(2)/S(1)]=2.456,\quad B=22.11, \tag{24}$$

$$\ln K_0=2a=4.91. \tag{25}$$

$S(0)$ comes out 2.33, as against the correct value of 2. Fitting a polynomial for $1/S(k)$ at the points $k=-1$, 0, 1, 2, 2.5, and evaluating the derivative of the polynomial at $k=2$, leads to a value of 4.50 for $\ln K_0$.

Table II also gives expectation values of various powers of the three triangular distances for the $1\,^1S$ state. The deviation at $n=1078$ of the expectation value of 2.903724367 for the potential energy $\langle -V\rangle$ from the value of 2.903724375 obtained for ϵ^2 is partly due to insufficient iteration of the eigenvector. The expectation values of $\langle V^2\rangle$ will be useful for the eventual determination of $\langle H^2\rangle$, where it enters as a component term.

In the preceding discussion we have dealt with the energy eigenvalue and with expectation values of operators, which depend on the over-all behavior of the wave function in the whole of space, rather than on its properties at a particular point. We shall now study one such local property, namely the extent to which our solutions derived by solving determinants of increasing order, reproduce the known linear terms[18,19] in the expansion of the wave function at the origin:

$$\psi=1-Z(r_1+r_2)+\tfrac{1}{2}r_{12}+\cdots. \tag{26}$$

Representing the expansion of our solution in the form

$$\psi=1-U(r_1+r_2)+Tr_{12}+\cdots, \tag{27}$$

we give in Table II the values of U and T, which at $n=\infty$ should approach the exact values of 2 and $\frac{1}{2}$, respectively. We see that though the energy parameter ϵ is determined at $n=1078$ to an estimated accuracy of one part in 10^{10}, the value of the coefficient T still shows a gross deviation of 5% from its true value.

3. THE $2\,^3S$ STATE OF HELIUM

The $2\,^3S$ state can be dealt with by our method in a manner similar to the ground state, the only change required being that in the expansion (4) we have to put

$$A(l,m,n)=-A(m,l,n), \tag{28}$$

in order that the wave function be antisymmetrical in the two electrons. The coefficients $A(l,m,n)$ are again

TABLE IV. The determinant of order 7 for the antisymmetrical case.

B_1	B_2	B_3	B_4	B_5	B_6	B_7
$-48Z+9+64\epsilon$						
$8Z-6-8\epsilon$	$-64Z+23+160\epsilon$					
$44Z-6-52\epsilon$	$-4Z+2-16\epsilon$	$-112Z+17+160\epsilon$				
1	$16Z-16-32\epsilon$	4ϵ	$-80Z+43+288\epsilon$			
$-4Z+2+4\epsilon$	$52Z-10-108\epsilon$	$12Z-8-8\epsilon$	$-8Z+4-36\epsilon$	$-136Z+35+360\epsilon$		
$-12Z+12\epsilon$	12ϵ	$90Z-9-114\epsilon$		$-6Z+3-36\epsilon$	$-196Z+23+292\epsilon$	
$-4Z+4+4\epsilon$	-4ϵ	$30Z-11-66\epsilon$		$-2Z+1$	$-12Z+6+24\epsilon$	$-164Z+31+396\epsilon$

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TABLE V. Values for the $2\,^3S$ state of the nonrelativistic energy $-\epsilon^2$, the mass polarization correction $-\epsilon_M$, and the relativistic correction to the ionization potential E_j. J denotes the theoretical value of the ionization potential, excluding the Lamb-shift correction. $R_{\mathrm{He}^4}=109722.267$ cm^{-1}; $\alpha^2=5.32504\times10^{-5}$.

n	125	252	444	715	Extrapolated	Units
ω	10	13	16	19		
ϵ.	1.47486303758	1.47486584437	1.47486588434	1.47486588483	1.47486588483	a.u.
ϵ^2	2.17522097961	2.17522925888	2.17522937680	2.17522937822	2.17522937824	a.u.
$(2\epsilon^2-4)$	0.35044195923	0.35045851777	0.35045875360	0.35045875644	0.35045875647	ry
$\epsilon^2(A/N)$	0.00745487852	0.00744233891	0.00744213349	0.00744213074	0.00744213071	a.u.
$\langle p_1{}^4\rangle$	41.830336	41.835955	41.835507	41.835544	41.835541	a.u.
$\langle\delta(\mathbf{r}_2)\rangle$	1.3196009	1.3204316	1.3203474	1.3203558	1.3203550	a.u.
$-(2/\alpha^2)E_2$	0.003259516	0.003256937	0.003256860	0.003256860	0.003256860	α^2 ry
$(2\epsilon^2-4)R_{\mathrm{He}^4}$	38451.286218	38453.103059	38453.128935	38453.129247	38453.129250	cm^{-1}
$-\epsilon_M$	-0.22427162	-0.22389436	-0.22388818	-0.22388810	-0.22388810	cm^{-1}
E_j	1.96220	1.91760	1.92248	1.92196	1.92201	cm^{-1}
J	38453.02415	38454.79677	38454.82753	38454.82732	38454.82737	cm^{-1}

determined from the recursion relation I(22). We have arranged them into a one-dimensional array by the following procedure. Let

$$A(l,m,n)=B_p,\quad p=1,2,3\cdots \tag{29}$$

$$p(l,m,n)=(1/24)\omega(\omega+2)(2\omega-1)-(1/16)[1-(-1)^\omega]+l(m+n)+m. \tag{30}$$

The scheme which we have adopted for ordering the (l,m,n) is illustrated in Table III. For each value of p the recursion relation I(22) takes on the form

$$\sum_k C_{pk}B_k=0, \tag{31}$$

$$C_{pk}=a_{pk}+\epsilon b_{pk}, \tag{32}$$

where the a_{pk} and b_{pk} are integers, and

$$C_{pk}=C_{kp}. \tag{33}$$

A sample of the determinant is shown in Table IV.

We have solved the determinant by the iteration method described in I, and the results for the orders $n=125$, 252, 444, and 715 are shown in Table V. The convergence of the values of the energy parameter ϵ with increasing order of the determinant n, is more rapid in the $2\,^3S$ than in the $1\,^1S$ state. The value of 1.47486588483 for ϵ_{715} is probably correct to within the order of a unit in the last figure, judging by its closeness to the extrapolated value, and similarly for the nonrelativistic energy value $-\epsilon_{715}{}^2=-2.17522937822$. The solution of the determinant of order 715 thus yields a nonrelativistic energy value which appears to be reliable to one part in 10^{12}—an accuracy which ought to suffice for any foreseeable application in the future. Equally, the theoretical value of the ionization potential J based on the correction terms included in (9) and (10), excluding the Lamb shift correction, probably does not deviate by more than one unit in the last figure from 38 454.8273 cm^{-1}. Traub and Foley,[20] using a 12-parameter variational wave function, get a value for J of 38 452.12 cm^{-1}.

The leading terms in the Lamb shift correction to the ionization potential are given by ΔE_j in (11), where the Lamb shift of the one-electron ion $E_{L,1}$ is 3.534 cm^{-1}, as for the $1\,^1S$ state, while the term $E_{L,2'}$ vanishes with $\langle\delta(\mathbf{r}_{12})\rangle$ because of the antisymmetry of the wave function. Taking Dalgarno and Kingston's[16] value of 74.9 ry for the average excitation energy K_0 of the $2\,^3S$ state, we get for the leading terms of the Lamb-shift correction

$$\Delta E_j=3.534-3.698=-0.164\text{ cm}^{-1}. \tag{34}$$

The accuracy of this figure is hard to assess, but improved values should be forthcoming soon. This leads to a theoretical value of the ionization potential of 38 454.663 cm^{-1}.

The experimental value of the ionization potential has been estimated by Herzberg[21] to be 38 454.73 cm^{-1}, with an uncertainty of less than ±0.05 cm^{-1}. This is based on his[8] term-value of 29 223.86 cm^{-1} for the $2\,^3P_1$ state and Meggers'[22] value of 9230.869 cm^{-1} for the transition $2\,^3S_1-2\,^3P_1$, but using Edlén's vacuum correction.

It would be of interest to attain higher precision in the experimental term-value of the $2\,^3S$ state. We may expect that an accurate theoretical value for the Lamb shift will be determined before long, though the problem is more complicated in the case of the $2\,^3S$ state. The reason for this is that in addition to transitions of the $2s$ electron one must also consider transitions of the $1s$ electron, and by far the greater contribution to both numerator and denominator in (14) comes from the latter, as was shown by Dalgarno and Kingston.[16] In view of this added complication, it is of interest to obtain a rough estimate of K_0 by the method described in Eqs. (16) to (25). Values of $S(k)$ are given in Table VI. We get

$$a=\log_3[S(2)/S(1)]=2.477,\quad B=15.8917, \tag{35}$$

$$\ln K_0=2a=4.95. \tag{36}$$

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[20] J. Traub and H. M. Foley, Phys. Rev. **111**, 1098 (1958).

[21] G. Herzberg (private communication).

[22] W. F. Meggers, J. Research Natl. Bur. Standards **14**, 487 (1935).

TABLE VI. Expectation values of various functions for the $2\,^3S$ state.

$$V=(-1/r_1-1/r_2+1/2r_{12}),\quad S(k)=\sum_n f_{0n}(E_0-E_n)^k,\quad f_{0n}=\tfrac{1}{3}(E_0-E_n)|\psi_0(\mathbf{r}_1+\mathbf{r}_2)\psi_n|^2.$$

E_0 and E_n denote the energies of the $2\,^3S$ state and of the nth excited state, respectively, measured in Rydbergs, lengths being measured in units of a_0.

n	125	252	444	715	Extrapolated
$\langle r_1^2\rangle$	11.4373177	11.4635124	11.4643041	11.4643213	11.4643217
$\langle r_1\rangle$	2.54883477	2.55042160	2.55046191	2.55046267	2.55046268
$\langle 1/r_1\rangle$	1.154708349	1.154665077	1.154664166	1.154664153	1.154664153
$\langle 1/r_1^2\rangle$	4.1701299	4.1704717	4.1704434	4.1704457	4.1704456
$\langle r_{12}^2\rangle$	22.9923236	23.0445817	23.0461624	23.0461969	23.0461975
$\langle r_{12}\rangle$	4.44431371	4.44745376	4.44753369	4.44753519	4.44753522
$\langle 1/r_{12}\rangle$	0.2682804874	0.2681995391	0.2681978818	0.2681978557	0.2681978553
$\langle 1/r_{12}^2\rangle$	0.0889448013	0.0889067652	0.0889060161	0.0889060052	0.0889060050
$\langle 1/r_1r_2\rangle$	0.5609066279	0.5607332322	0.5607296916	0.5607296364	0.5607296356
$\langle 1/r_1r_{12}\rangle$	0.3228030465	0.3226983780	0.3226962551	0.3226962221	0.3226962216
$\langle \mathbf{r}_1\cdot\mathbf{r}_2\rangle$	−0.05884408	−0.05877845	−0.05877714	−0.05877712	−0.05877712
$\langle V\rangle$	−2.175276455	−2.175230385	−2.175229391	−2.175229378	−2.175229378
$\langle V^2\rangle$	8.8387052	8.8392397	8.8391803	8.8391848	8.8391845
$S(-1)$	7.5856491	7.6031560	7.6036846	7.6036961	7.6036964
$S(0)$	2	2	2	2	2
$S(1)$	5.82046895	5.82045759	5.82045736	5.82045736	
$S(2)$	88.44050	88.49618	88.49053	88.49110	88.49105
$D(0)$	33.16519	33.18607	33.18395	33.18416	33.18414

$S(0)$ comes out 1.64 compared to the exact value of 2. Fitting a polynomial for $1/S(k)$ and getting the derivative from it at $k=2$, gives a value of 2.65 for $\ln K_0$.

The electron charge density at the nucleus $D(0)$ is given by $8\pi\langle\delta(\mathbf{r}_1)\rangle$, and is tabulated in Table VI. The value of 33.18416 for $D(0)_{715}$, which is subject to an uncertainty of the order of a unit in the last figure, is to be compared with the value of 33.18388 ± 0.00023 which Novick and Commins deduced from the observed hyperfine splitting.[20]

4. CONCLUSIONS

In this investigation we have shown that the new method yields nonrelativistic energy values for the $1\,^1S$ and $2\,^3S$ states of helium which are accurate to 0.001 cm^{-1}, or better. With the program ready, the problem of achieving even higher accuracy is only a matter of availability of computing time. It would be of interest to bracket the energy also by a *lower* bound, as Kinoshita does.[9,23] However, since the establishment of a lower bound involves rather lengthy computations, it is a question of economy whether one could not just as well carry out instead a solution of a higher order determinant, and gain an improved wave function into the bargain.

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[23] T. Kinoshita, Phys. Rev. **115**, 366 (1959).