

Excited S States of Helium†

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As part of a program aiming to determine *all the observed* term-values of two-electron atoms on the basis of the Schrödinger wave equation, we have evaluated the $1s\ ns$ levels of helium up to $n=9$, in both the singlet and the triplet states. Our previous method, using *perimetric* coordinates, was extended to allow for the asymmetry between the $1s$ and the excited electrons. The mass polarization and relativistic corrections were also determined. The difference between the ionization energies $J(220)$, obtained by solving a determinant of order 220, and the experimental values, ranges from 3.6 cm^{-1} for $3\ ^1S$ to 5.8 cm^{-1} for $9\ ^1S$, and from 0.5 cm^{-1} for $3\ ^3S$ to 5.7 cm^{-1} for $9\ ^3S$. The extrapolated values indicate that with a faster computer than WEIZAC it should be feasible to determine all of the 31 observed $1s\ ns$ levels ($n \leq 17$) of helium to within the experimental accuracy.

1. INTRODUCTION

THE purpose of this investigation is to do spectroscopy from scratch by solving the Schrödinger wave equation for two-electron atoms to an accuracy comparable with the experimental accuracy of the term values. This goal has already been achieved¹⁻³ in the case of the $1\ ^1S$, $2\ ^1S$, and $2\ ^3S$ states of He, and the $1\ ^1S$ and $2\ ^3S$ states⁴ of Li^+ , while in the case of the $2\ ^1S$ state of Li^+ the large discrepancy found⁴ between the theoretical and experimental term values showed that the 8517.4 \AA line on which the latter was based had been incorrectly identified as the $2\ ^1S-2\ ^1P$ transition. In this paper we extend the analysis to the $1s\ ns$ states of He, going up to the $9\ ^1S$ and $9\ ^3S$ levels. The results are shown in Table I for the singlet states and in Table II for the triplet states. While the precision obtained by solving a determinant of maximum order 220 falls short of the experimental accuracy of about 0.05 cm^{-1} , especially at the highly excited levels, the results do indicate that with a faster computer than WEIZAC it should be feasible to establish theoretically

with sufficient accuracy all the 31 experimental term values in the S states of He.

One can appreciate the magnitude of the task, even for the S states, by noting that if we attempted to solve variationally the hydrogenic radial wave equation we would need at least $n+1$ constants to describe the state of quantum number n , having n nodes. In the case of the S states of two-electron atoms, the wave function ψ depends on the sides r_1, r_2, r_3 of the triangle, so that the $1s\ ns$ state could require n^3 constants for its representation. Indeed, in our scheme of using as a base for ψ polynomials which include all terms $r_1^a r_2^b r_3^c$ such that the sum of the exponents ($a+b+c$) is less than or equal to ω , we see from Tables I and II that the first time the root of the $1s\ ns$ state appears is at $\omega_{\min}=n-1$ for the singlet states, and at $\omega_{\min}=n-2$ for the triplet states. Since the number of terms⁵ k in the polynomials for a given ω is

$$k = (1/6)(\omega+1)(\omega+2)(\omega+3), \quad (1)$$

it follows that the minimum order of the determinant k

TABLE I. The excited singlet S states of helium. Values of the nonrelativistic ionization energy ν , the mass-polarization correction $-\epsilon_M$, and the relativistic correction E_j , in units of cm^{-1} . $J = (\nu - \epsilon_M + E_j)$. $\nu = R_{\text{He}}^4(2e^2 - 4)$. $R_{\text{He}}^4 = 109722.267\text{ cm}^{-1}$. k denotes the order of the determinant. $-e^2$ is the nonrelativistic energy eigenvalue.

k	ω	$2\ ^1S$	$3\ ^1S$	$4\ ^1S$	$5\ ^1S$	$6\ ^1S$	$7\ ^1S$	$8\ ^1S$	$9\ ^1S$
56	5	32012.197	13415.423	7341.838	4621.576	3169.568			
84	6	32023.437	13428.486	7351.986	4630.060	3179.707	2314.486		
120	7	32028.436	13435.782	7358.447	4635.347	3184.672	2320.893	1764.057	
165	8	32030.769	13439.895	7362.574	4638.895	3187.789	2324.065	1768.355	1389.007
220	9	32031.909	13442.253	7365.221	4641.324	3189.932	2326.066	1770.509	1392.025
Extrapolated		32033.042	13445.483	7369.979	4646.787	3195.487	2330.889		
$-\epsilon_M(220)$		-0.287	-0.082	-0.037	-0.021	-0.013	-0.009		
$E_j(220)$		0.401	0.141	0.064	0.034	0.021			
$J(220)$		32032.023	13442.311	7365.248	4641.338	3189.940			
$J(\text{extrapolated})$		32033.16	13445.54	7370.01	4646.80	3195.50			
Experimental ^a		32033.26	13445.87	7370.48	4647.18	3195.81	2331.77	1775.93	1397.83

^a See reference 6.

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¹ C. L. Pekeris, Phys. Rev. **112**, 1649 (1958). This paper will be referred to in the sequel as I.

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

³ C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).

⁴ C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

⁵ Because n is used in this paper to designate the quantum number, we let k denote the order of the determinant.

TABLE II. The excited triplet S states of helium. Values of the nonrelativistic ionization energy ν , the mass-polarization correction $-\epsilon_M$, and the relativistic correction E_j , in units of cm^{-1} . $J = (\nu - \epsilon_M + E_j)$. $\nu = R_{\text{He}}(2e^2 - 4)$. $R_{\text{He}} = 109722.267 \text{ cm}^{-1}$. k denotes the order of the determinant. $-\epsilon^2$ is the nonrelativistic energy eigenvalue.

k	ω	2^3S	3^3S	4^3S	5^3S	6^3S	7^3S	8^3S	9^3S
56	5	38453.029	15073.235	8009.672	4952.480	3343.081	1435.423		
84	6	38453.081	15073.385	8011.779	4960.341	3365.011	2419.207	1078.755	
120	7	38453.107	15073.401	8012.249	4962.605	3371.186	2434.452	1831.702	...
165	8	38453.119	15073.410	8012.345	4963.294	3373.282	2439.259	1842.651	...
220	9	38453.125	15073.420	8012.361	4963.503	3374.047	2441.087	1846.410	1443.110
Extrapolated		38453.129		8012.364	4963.593	3374.507	2442.344		
$-\epsilon_M$ (220)		-0.224	-0.057	-0.022	-0.011	-0.006	-0.003	-0.002	
E_j (220)		1.922	0.527	0.214	0.107	0.061	0.037	0.023	
J (220)		38454.823	15073.890	8012.552	4963.599	3374.103	2441.121	1846.431	
J (extrapolated)		38454.827		8012.556	4963.689	3374.562	2442.378		
Experimental ^a		38454.74	15073.92	8012.60	4963.72	3374.58	2442.46	1849.39	1448.77

^a See reference 6.

needed to represent the $1s ns$ state grows like n^3 . For the highest observed level⁶ of 17^3S , $\omega_{\min} = 15$, $k_{\min} = 816$. This is not prohibitively large, especially since at high n the first root in the singlet states ($\omega = n - 1$) gives a term value which is correct to within about 0.5%, while the second root in the triplet states ($\omega = n - 1$) is also good to better than 1%.

2. METHOD C

In order to solve the wave equation

$$H\psi - E\psi = 0, \quad (2)$$

or its equivalent variational form

$$I = (\psi, H\psi) - E(\psi, \psi) = \text{minimum}, \quad (3)$$

we put

$$\psi = \sum_{n=0}^k A_n f_n, \quad (4)$$

where the base functions f_n need not be orthogonal. Substitution in (3) yields the variational equation

$$\sum_{n=0}^k A_n [(f_n, Hf_m) - E(f_n, f_m)] = 0, \quad m = 0, 1, \dots, k. \quad (5)$$

Equation (5) shows that the quantity R defined by

$$R = \mathcal{p}(H\psi - E\psi) = \sum_n A_n \mathcal{p}(Hf_n - Ef_n), \quad \mathcal{p} = r_1 r_2 r_3, \quad (6)$$

has to be orthogonal to every base function f_m which is included in (4). The factor \mathcal{p} comes from the expression for the volume element

$$dx_1^3 dx_2^3 = 8\pi^2 r_1 r_2 r_3 dr_1 dr_2 dr_3. \quad (7)$$

In the methods A and B used¹⁻³ for the ground state and the $n=2$ state, the variables r_1 , r_2 , and r_3 were replaced by the *perimetric* coordinates u , v , w defined by

$$u = \epsilon x, \quad v = \epsilon y, \quad w = 2\epsilon z, \quad \epsilon^2 = -E, \quad (8)$$

$$x = r_2 + r_3 - r_1, \quad y = r_1 + r_3 - r_2, \quad z = r_1 + r_2 - r_3, \quad (9)$$

⁶ W. C. Martin, J. Research Natl. Bur. Standards A64, 19 (1959).

and ψ was assumed to have the form

$$\psi = e^{-\frac{1}{2}(u+v+w)} F(u, v, w) = e^{-\epsilon(r_1+r_2)} F(u, v, w). \quad (10)$$

For the expansion of F in (4), we used as f_n the orthonormal Laguerre functions $e^{-\frac{1}{2}u} L_l(u)$

$$F = \sum_{l, m, n=0}^{\omega} A(l, m, n) L_l(u) L_m(v) L_n(w), \quad (11)$$

and on the basis of their properties determined the $R(l, m, n)$ in the representation

$$R = \mathcal{p}H\psi - E\mathcal{p}\psi = \sum R(l, m, n) L_l(u) L_m(v) L_n(w). \quad (12)$$

The condition of the orthogonality of the f_n to R yields

$$R(l, m, n) = 0, \quad (13)$$

which is Eq. (I 22) giving the recursion relation between the $A(l, m, n)$, and the secular determinant for ϵ that follows from it. Equation (13) can be obtained directly by substituting (11) in the original wave equation (2) multiplied by \mathcal{p} , without reference to the variational form (3). This was the procedure followed in I.

By the use of method B for the 2^1S state,³ we obtained an accuracy in ϵ^2 of three parts in 10^9 at a determinant of order $k=615$, although for this state the level became bound ($\epsilon^2 > 2$) only for $k > 9$. However, for the higher excited states the convergence of method B became increasingly poorer, because the symmetrical form of the exponent in (10) does not reflect the actual asymmetry that exists between the $1s$ electron and the excited one. Thus, the 3^1S state became bound only at $k > 50$, and at $k=615$, $\epsilon_B^2(615) = 2.060999777$ a.u., a value which is exceeded in method C, to be described presently, already at $k=35$, where $\epsilon_C^2(35) = 2.061027832$ a.u. The 4^1S state becomes bound only at $k=444$, for which order the state 5^1S is still unbound.

It is clear that method B is not suitable for the treatment of the excited states, and that modifications have to be introduced to allow explicitly for the asymmetry between the two electrons. We have to

seek solutions of the form

$$\psi = [e^{-\beta r_1 - \alpha r_2} G(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \pm e^{-\beta r_2 - \alpha r_1} G(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3)], \quad (14)$$

where β is of the order Z for the $1s$ electron, and α^2 is of the order of the ionization energy of the ns electron. In the present exploratory investigation we have used two sets of *perimetric* coordinates

$$u = \alpha x, \quad v = \beta y, \quad w = \gamma z, \quad (15)$$

and

$$u' = \alpha y, \quad v' = \beta x, \quad w' = \gamma z, \quad \gamma = \alpha + \beta, \quad (16)$$

where x , y , and z are defined in (9). These give

$$\beta r_1 + \alpha r_2 = \frac{1}{2}(u + v + w), \quad \beta r_2 + \alpha r_1 = \frac{1}{2}(u' + v' + w'), \quad (17)$$

and the permutation of $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$ is accomplished by the interchange of $u \leftrightarrow u'$, etc. As a base for the expansion of ψ , we used the f_n defined by

$$f(l, m, n) = [e^{-\frac{1}{2}(u+v+w)} L_l(u) L_m(v) L_n(w) \pm e^{-\frac{1}{2}(u'+v'+w')} L_l(u') L_m(v') L_n(w')], \quad (18)$$

the plus sign applying to the para states and the negative sign to the ortho states.

Putting

$$\psi = \sum_{l, m, n=0}^{\omega} C(l, m, n) f(l, m, n), \quad (19)$$

we can make use of the properties of the Laguerre functions to express the coefficients $R(l, m, n)$ in terms of the $C(l, m, n)$ in the expansion

$$R = \mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3 (H\psi - E\psi) = \sum R(l, m, n) f(l, m, n). \quad (20)$$

The condition of the orthogonality of R to the base functions $f(l, m, n)$ leads to

$$\sum_{l, m, n} R(l, m, n) T \begin{pmatrix} l, m, n \\ l', m', n' \end{pmatrix} = S(l', m', n') = 0, \quad (21)$$

where

$$T \begin{pmatrix} l, m, n \\ l', m', n' \end{pmatrix} = \delta(n, n') \left\{ \delta(l, l') \delta(m, m') + \frac{(-)^{m+m'} 4k (k-1)^{l+l'+m+m'}}{(1+k)^2 (k+1)} \times g(l, m') g(l', m) \right\}, \quad (22)$$

$$g(l, m) = \sum_{r=0}^a \frac{(-x)^r (l+m-r)!}{r! (l-r)! (m-r)!}, \quad (23)$$

$$k = (\beta/\alpha), \quad x = [(k+1)/(k-1)]^2, \quad (24)$$

and a is the smaller of the integers l, m . The $S(l', m', n')$ are homogeneous linear equations in the $C(l, m, n)$, the vanishing of whose determinant yields the energy eigenvalues ϵ . We have assumed that

$$\beta = Z, \quad \alpha = (2\epsilon^2 - Z^2)^{\frac{1}{2}}, \quad (25)$$

thus biasing our wave functions to secure proper behavior at ∞ , and foregoing the advantage that could be gained from independent variations in β as well as in α , which could yield higher values of ϵ for a given order of the determinant.

3. DISCUSSION OF RESULTS

The theoretical ionization energies J given in Tables I and II include the mass-polarization correction $-\epsilon_M$, and the relativistic correction E_j , but not the Lamb shift correction. The latter amounts to -0.104 cm^{-1} in the 2^1S state and to -0.109 cm^{-1} in the 2^3S state,⁷ and is probably around 0.01 cm^{-1} or less in the higher excited states. We note that the first time the root for the 7^1S state appears is at $k=84$ ($n=\omega-1$), and for the 7^3S state at $k=56$ ($n=\omega-2$). In the case of the 9^3S state, we skipped the first two roots. As in the 2^3S state studied previously,¹⁻³ the excited triplet states show more rapid convergence than do the singlet states. The sum of the mass-polarization and relativistic corrections ($-\epsilon_M + E_j$) comes down to the order 0.01 cm^{-1} beyond $n=9$. In getting the extrapolated values of J , we added to the extrapolated values of ν the values $-\epsilon_M$ and E_j obtained at $k=220$.

The difference between the extrapolated and the experimental term-values is around 0.3 cm^{-1} for the singlet states and about 0.1 cm^{-1} for the triplet states. These are higher than the experimental uncertainty about 0.05 cm^{-1} , but the indications are that such precision could be achieved with a few additional steps in ω .

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⁷ K. S. Suh and M. H. Zaidi (private communication).