the electron excitation process. It should be mentioned that for electron excitation the cross section would be a sum of several terms of the form (29), one from each total angular momentum state. The present result then, namely Eq. (29), would predict an infinite number of small oscillations about a constant value for such inelastic cross sections at threshold.

Fine Structure of the 2³P and 3³P States of Helium

B. Schiff, C. L. Pekeris, and H. Lifson

Department of Applied Mathematics, The Weizmann Institute of Science, Rehovoth, Israel

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Nonrelativistic eigenvalues accurate to one part in 10^9 to 10^{10} have been obtained for the 2³P and 3³P states of helium by improving the method previously developed for calculating two-electron atom P-state wave functions, and by including up to 560 terms in the expansion. The corresponding values for the fine-structure splitting of the two levels are accurate to between 10^{-5} and 10^{-6} cm⁻¹, and the small discrepancy with experiment is presumed to be due to the neglect of quantum-electrodynamic correction terms of relative order α^2 in the calculation. The results for the 2³P state are in good agreement with those obtained recently by C. Schwartz.

INTRODUCTION

THE steadily increasing accuracy of recent measurements[1-6] of the fine structure of a two-electron atom ³P level has in its turn given rise to a number of theoretical determinations of the fine-structure splittings.[7-10] The ultimate object of these calculations is to verify the quantum electrodynamic contributions to the interaction between two electrons, and also to determine a more accurate value for the fine structure constant α.

In our preliminary calculations, published previously,[9] the fine-structure splittings of the 2³P and 3³P levels of helium were computed to an accuracy of one part in 10^3 to 10^4. The agreement with experiment was sufficiently close to verify the contribution of the $\alpha/2\pi$ anomalous magnetic moment of the electron to the fine-structure splitting.

In the present work, by improving the method used for calculating the wave function, and by including a larger number of terms in the expansion, we have been able to determine the fine-structure splittings to an

accuracy of one part in 10^5 to 10^6. Similar work has recently been done for the 2³P state by C. Schwartz,[10] whose results are in agreement with ours.

THE NONRELATIVISTIC EIGENVALUE

In our earlier calculation[9] we had extended the method previously developed for computing two-electron S-state wave functions[11] to the case of a P state. The wave function ψ was assumed to be of the form

$$\psi = F(r_1, r_2, r_3) \cos\theta_1 \pm F(r_2, r_1, r_3) \cos\theta_2 \qquad (1)$$

given by Breit,[12] with

$$F = r_1 e^{-\xi r_1 - \eta r_2} L(r_1, r_2, r_3), \qquad (2)$$

where r_1, r_2, and r_3 are the distances of the two electrons from the nucleus and the interelectron distance, respectively, and θ_1 and θ_2 are the polar angles of the lines joining the nucleus to the two electrons. As in the case of an S state,[11] $L(r_1, r_2, r_3)$ was developed into a power series of *perimetric* coordinates u, v, and w which are linear combinations of r_1, r_2, and r_3 so chosen as to each have the limits 0 to ∞ and to satisfy the condition

$$\xi r_1 + \eta r_2 = \tfrac{1}{2}(u+v+w). \qquad (3)$$

The coefficients in the expansion of L were obtained by substitution in the wave equation. The calculations were carried out for polynomials L of order n containing all terms such that the sum of the exponents of r_1, r_2,

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[9] C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. **126**, 1057 (1962).

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[11] C. L. Pekeris, Phys. Rev. **127**, 509 (1962).

[12] G. Breit, Phys. Rev. **35**, 569 (1930).

and r_3 is less than, or equal to, ω:

$$n = \tfrac{1}{6}(\omega+1)(\omega+2)(\omega+3),\tag{4}$$

and eigenvalues were computed for the low-lying P states of helium for $\omega = 3,4,\cdots 9$, the last-mentioned value of ω corresponding to $n=220$. The parameters ξ and η were given the values $\eta = Z$, $\xi = (-2E-Z^2)^{1/2}$, where E is the energy eigenvalue and Z the atomic number, in order that the wave function should have the correct asymptotic behavior as one or other of the electrons tends to infinity. We shall refer to this scheme of computation as "method C" because of its analogy with a similar method used for obtaining S-state wave functions.[11] The results obtained have been published previously,[9] together with the corresponding values obtained for the fine-structure splitting. The $n=220$ eigenvalues for the $2\,^1P$ and $2\,^3P$ states were estimated to be accurate to within about one part in 10^6, and the fine structure splittings of the latter state to within one part in 10^3 to 10^4. This degree of accuracy is, however, considerably below that of some recent experimental determinations of the ionization energies[13] and of the

TABLE I. Nonrelativistic ionization energy J of the $2\,^3P$ state in cm^{-1}. Comparison of results from C and D schemes.

n	ω	C scheme	D scheme
20	3	29166.766	29210.757
35	4	29200.862	29221.312
56	5	29213.953	29221.792
84	6	29219.015	29222.096
120	7	29220.944	29222.133
165	8	29221.676	29222.148
220	9	29221.958	29222.152

fine structure.[2-6] We therefore decided, following Traub and Foley,[8] to improve the results by relaxing the conditions on the asymptotic behavior of the wave function, i.e., by allowing the parameters ξ and η to vary. Using a given number of terms n in the expansion of the wave function, the eigenvalue was optimized with respect to the values of ξ and η as well as with respect to the expansion coefficients. The results obtained for the $2\,^3P$ state of helium using this scheme, to which we shall refer as "method D," are given together with the corresponding results obtained by method C in Table I, in order to illustrate the relative rates of convergence obtained using the two schemes. The nonrelativistic ionization energy J has been tabulated in cm^{-1}, where

$$J = -2R_{\mathrm{He^4}}(2E+Z^2), \quad R_{\mathrm{He^4}} = 109722.267 \text{ cm}^{-1}.\tag{5}$$

It will be seen that the use of the D scheme leads to a more rapid convergence; for example, the D eigenvalue for $n=84$ is already better than the C eigenvalue for order 220. In view of this improvement, the computations were carried out using the D scheme up to

[13] G. Herzberg, Proc. Roy. Soc. (London) A248, 309 (1958).

TABLE II. Nonrelativistic eigenvalues for the $2\,^3P$ state in atomic units.

n	ω	$-E$	n	ω	$-E$
20	3	2.133112254831	35	4	2.133160354235
56	5	2.133162543742	84	6	2.133163928235
120	7	2.133164094685	165	8	2.133164164111
220	9	2.133164180840	286	10	2.133164187632
364	11	2.133164189423	455	12	2.133164190275
560	13	2.133164190534			
Extrapolated value (odd ω)			Extrapolated value (even ω)		
		2.133164190699			2.133164190610

order $n=560$ for the low-lying P states of helium. The optimization was carried out up to order $n=120$ or 165, the values of ξ and η used for higher orders being estimated by extrapolation. The optimum values of η were found to be very close to $\eta=Z$, and we therefore took $\eta=Z$ and optimized with respect to the value of ξ only in the case of all but the $2\,^3P$ state. Full mathematical details of both methods C and D will be published in a forthcoming paper which will also deal with the calculation of the relativistic corrections for a two-electron P state.

The nonrelativistic eigenvaules for the $2\,^3P$ and $3\,^3P$ states of helium are tabulated in atomic units of energy in Tables II and III. It was found that the differences both of the optimum value of ξ and of the eigenvalue behaved unsmoothly as one went up from order to order. However, they did exhibit a smooth behavior if one considered the results for odd values of ω alone or for even values of ω alone. We have therefore tabulated the results for odd and even values of ω separately. Using the last three values obtained (the values for orders 220, 364, and 560 in the case of odd ω, and 165, 286, and 455 for even ω), and assuming a constant ratio of differences, extrapolations were made to estimate the eigenvalue which would be obtained by including an infinite number of terms in the expansion. The results of the extrapolations have been included in the tables. They can, however, only be considered as a rough guide to the type of results which would be obtained if the

TABLE III. Nonrelativistic eigenvalues for the $3\,^3P$ state in atomic units.

n	ω	$-E$	n	ω	$-E$
20	3	2.057935485531	35	4	2.058002349387
56	5	2.058068531414	84	6	2.058074510758
120	7	2.058080140100	165	8	2.058080589072
220	9	2.058080990936	286	10	2.058081035396
364	11	2.058081070314	455	12	2.058081076879
560	13	2.058081081650			
Extrapolated value (odd ω)			Extrapolated value (even ω)		
		2.058081083539			2.058081081129

TABLE IV. Values of fine structure integrals C and D for the $2\,^3P$ state (in units of $\frac{1}{2}\alpha^2$Ry).

n	ω	C_Z	C_e	C	D
20	3	0.136006630	0.136191777	−0.068281466	−0.054066497
56	5	0.138426711	0.137170045	−0.067325438	−0.054161181
120	7	0.138627888	0.137260501	−0.067259688	−0.054171300
220	9	0.138635535	0.137272016	−0.067269322	−0.054173418
364	11	0.138635968	0.137274098	−0.067272016	−0.054173801
560	13	0.138636449	0.137274640	−0.067272348	−0.054173900
Extrapolated				−0.067272394	−0.054173934
35	4	0.138438939	0.137372116	−0.067616757	−0.054227138
84	6	0.138654233	0.137281821	−0.067265310	−0.054178943
165	8	0.138645392	0.137274352	−0.067262951	−0.054174283
286	10	0.138638281	0.137274454	−0.067270231	−0.054173958
455	12	0.138636994	0.137274715	−0.067271915	−0.054173938
Extrapolated				−0.067272421	−0.054173937

computations were to be carried out to a much higher order.

DETERMINATION OF THE FINE STRUCTURE

As Breit[14] and Inglis[15] have shown, the fine-structure splittings $\Delta\nu_{01}$, $\Delta\nu_{12}$, and $\Delta\nu_{02}$ between the $J=0$, $J=1$, and $J=2$ levels may be expressed as linear combinations of two integrals C and D representing the contributions of the spin-orbit and spin-spin interactions, respectively. The integral C may be written in the form

$$C = ZC_Z - 3C_e, \tag{6}$$

where C_Z and C_e arise from the coupling of the spin with the orbital angular momentum of the electrons relative to the nucleus and to each other, respectively. Both C and D are of order of magnitude α^2 compared to the value of the nonrelativistic eigenvalue E. The only corrections of order α^3 are those arising from the anomalous magnetic moment of the electron. Adding these corrections, we get[7]

$$C = Z[1 + (\alpha/\pi)]C_Z - [3 + (2\alpha/\pi)]C_e, \tag{7}$$

while the integral D is multiplied by the factor

TABLE V. Values of fine structure integrals C and D for the $3\,^3P$ state (in units of $\frac{1}{2}\alpha^2$Ry).

n	ω	C_Z	C_e	C	D
20	3	0.03723374	0.03871872	−0.02084779	−0.01489151
56	5	0.03964354	0.03916374	−0.01910095	−0.01485215
120	7	0.04012142	0.03919107	−0.01866303	−0.01481964
220	9	0.04019922	0.03919126	−0.01858534	−0.01481310
364	11	0.04021130	0.03919288	−0.01857566	−0.01481237
560	13	0.04021090	0.03919325	−0.01857661	−0.01481227
35	4	0.03759291	0.03814664	−0.01962835	−0.01465293
84	6	0.03972583	0.03902243	−0.01880618	−0.01479360
165	8	0.04013370	0.03916436	−0.01861059	−0.01480879
286	10	0.04020001	0.03918727	−0.01857854	−0.01481133
455	12	0.04020899	0.03919180	−0.01857634	−0.01481198

[14] G. Breit, Phys. Rev. **36**, 383 (1930).
[15] D. R. Inglis, Phys. Rev. **61**, 297 (1942).

TABLE VI. Fine structure splitting of the $2\,^3P$ level in cm^{-1} (including single-triplet correction of magnitude 0.0001582 cm^{-1}).

n	ω	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
20	3	0.9893762	0.0828963	1.0722725
56	5	0.9879663	0.0767572	1.0647236
120	7	0.9879221	0.0763139	1.0642360
220	9	0.9879811	0.0763578	1.0643390
364	11	0.9879946	0.0763713	1.0643660
560	13	0.9879970	0.0763727	1.0643697
Extrapolated		0.9879977	0.0763728	1.0643704
35	4	0.9897808	0.0780739	1.0678548
84	6	0.9880501	0.0763021	1.0643522
165	8	0.9879752	0.0763156	1.0642907
286	10	0.9879917	0.0763600	1.0643517
455	12	0.9879963	0.0763700	1.0643663
Extrapolated		0.9879978	0.0763729	1.0643707
Experiment		0.987985[a] ±0.000063	0.076438[b] ±0.000003 0.076426[c] ±0.000002	1.064423[d] ±0.000066 1.064411[e] ±0.000065

[a] See Ref. 5.   [d] See Refs. 4, 5.
[b] See Ref. 4.   [e] See Refs. 6, 5.
[c] See Ref. 6.

$[1 + (\alpha/\pi)]$. The only term of order α^4 for which an explicit formula has been derived is the so-called singlet-triplet correction, which has to be added to $\Delta\nu_{01}$ and subtracted from $\Delta\nu_{12}$ to allow for the depression of the $^3P_1$ level due to the close-lying $^1P_1$ level.

Using the D-type wave functions, we have computed the values of the integrals C and D for the $2\,^3P$ and $3\,^3P$ states of helium up to order 560. The method used in the calculation was the same as that employed for computing the remainder of the relativistic corrections, and details will be given in a forthcoming paper on this subject. The results, including the corrections of order α^3, are given in Tables IV and V in units of $\frac{1}{2}\alpha^2$Ry. The corresponding values of the fine-structure splittings,

TABLE VII. Fine structure splitting of the $3\,^3P$ level in cm^{-1} (including singlet-triplet correction of magnitude 0.000042 cm^{-1}).

n	ω	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
20	3	0.278465	0.034759	0.313224
56	6	0.272787	0.024783	0.297569
120	7	0.271032	0.022414	0.293446
220	9	0.270710	0.021998	0.292708
364	11	0.270671	0.021946	0.292617
560	13	0.270672	0.021952	0.292624
35	4	0.271417	0.029028	0.300445
84	6	0.271070	0.023403	0.294473
165	8	0.270721	0.022171	0.292892
286	10	0.270664	0.021969	0.292633
455	12	0.270667	0.021952	0.292619
Experiment		0.270646[a] ±0.000007	0.021967[a] ±0.000005	0.292613[a] ±0.000012

[a] See Ref. 3.

TABLE VIII. Results obtained by C. Schwartz for the $2\,^3P$ state of helium.

n	ω	$-E$ (In atomic units)	C (In units of $\frac{1}{2}\alpha^2$Ry)	D (In units of $\frac{1}{2}\alpha^2$Ry)
39	3	2.133155369966	−0.066940618	−0.054113067
69	4	2.133162942721	−0.067053800	−0.054152301
111	5	2.133164012406	−0.067214490	−0.054167177
167	6	2.133164164417	−0.067256786	−0.054172026
239	7	2.133164186301	−0.067269638	−0.054173411
329	8	2.133164189955	−0.067271742	−0.054173791
439	9	2.133164190626	−0.067272065	−0.054173895
Extrapolated		2.13316419080		−0.054173934

TABLE IX. Comparison between theoretical and observed fine-structure splitting of the $2\,^3P$ state (including single-triplet correction of magnitude 0.0001582 cm^{-1}).

	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
C. Schwartz	0.987995	0.0763720	1.064367
Present work (odd ω)	0.987998	0.0763728	1.064370
Present work (even ω)	0.987998	0.0763729	1.064371
Experiment	0.987985[a] ±0.000063	0.076438[b] ±0.000003 0.076426[d] ±0.000002	1.064423[c] ±0.000066 1.064411[e] ±0.000065

[a] See Ref. 5.
[b] See Ref. 4.
[c] See Refs. 4, 5.
[d] See Ref. 6.
[e] See Refs. 5, 6.

together with the experimental results, are given in Tables VI and VII in units of cm^{-1}, the value $\frac{1}{2}\alpha^2 R_{\mathrm{He}^4}$ $= 2.921374$ having been used to convert the figures from atomic units. We used this value of α in order to permit direct comparison of our results with those of Schwartz.[10]

In the case of the $2\,^3P$ state, if the results for even and odd values of ω are considered separately, the value of the integral D is found to change monotonically on going from order to order. In fact, as the order n is increased, the absolute value of D is found to increase for odd values of ω, and to decrease for even ω, as can be seen clearly from Table IV. The extrapolations for even and odd ω, calculated in the same way as in the case of the nonrelativistic eigenvalues, agree very well. On the other hand, neither C_Z nor C_e behave monotonically. It is possible, however, to extrapolate the combined integral C, and the results are included in the tables. The extrapolated values of C and D have also been used to determine the extrapolated values for the fine-structure splittings included in Table VI. Despite the unsmooth behavior of C_Z and C_e, the extrapolations do indicate that our values for these splittings are accurate to within one or two times 10^{-6} cm^{-1} for the $2\,^3P$ state. In the case of the $3\,^3P$ state, the absolute value of C appears to pass through a minimum somewhere near order 364, and no extrapolation of this type is therefore possible. The trend of the values for high orders would seem to indicate, however, that we have achieved an accuracy of at least 10^{-5} cm^{-1} in our computations of the fine-structure splittings for this state.

In the case of both the $2\,^3P$ and $3\,^3P$ states, the discrepancy between theory and experiment is considerably larger than the estimated error of our computations, and is presumably due to the neglect of the other corrections of order α^4. This conclusion is borne out by a comparison of our results with those of a similar calculation for the $2\,^3P$ state published recently by C. Schwartz.[10] He was able to obtain somewhat improved results by including terms with a factor of $(r_1+r_2)^{1/2}$ in the expansion of the wave function. In his case, the order n is given by

$$n=\tfrac{1}{3}(\omega+1)(\omega+2)(\omega+3)-1, \qquad (8)$$

and his results for order 439 are a little better than those of our calculation for order 560, although he did not optimize with respect to the parameters ξ and η. Schwartz's results are summarized in Table VIII. For the purposes of comparison, we have included the corrections of order α^3 in the tabulated values of C and D, which are given in units of $\frac{1}{2}\alpha^2$Ry. Schwartz's extrapolated value for C, excluding the α^3 corrections, is -0.067275287, while our corresponding values are -0.067275585 and -0.067275558 for even and odd ω, respectively, so that the agreement between the results of the two calculations is of the order of four parts in 10^6. The extrapolated values of D agree to within better than one part in 10^6, as will be seen from Tables IV and VIII. Our extrapolated values for the fine-structure splittings are compared with those of Schwartz in Table IX. The largest proportional difference occurs in the value of the small interval $\Delta\nu_{12}=2D-2C$, and is still only of the order of two parts in 10^5, whereas the discrepancy between theory and experiment amounts to almost one part in 10^3 in this case. The omission of the singlet-triplet correction from the results would only have the effect of slightly enlarging the discrepancy.

The computations up to order 220 were carried out on our WEIZAC computer, and for orders 220 to 560 on our CDC 1604A computer. The total machine time required to determine an eigenvalue on the latter computer ranged from about 5 h for order 220 to about 50 h for order 560. The corresponding times for computing the fine-structure splittings were about 1 and 5 h, respectively. Double precision arithmetic, equivalent to about 20 and 24 decimal places on the WEIZAC and 1604A, respectively, was used throughout the computation.