Fine Structure of the $2\,^3P$ and $3\,^3P$ States of Helium*

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Using an extension of the method of Pekeris for S states, eigenvalues and eigenfunctions have been obtained for the $2\,^1P$, $2\,^3P$, $3\,^1P$, and $3\,^3P$ states of helium. The fine-structure splittings of the $2\,^3P$ and $3\,^3P$ states have been computed, including the α^3 quantum electrodynamic correction and the singlet-triplet correction. Determinants up to order $n=220$ were solved, and when the results were extrapolated to $n\to\infty$ good agreement was obtained with recent accurate measurements of the fine-structure splittings, substantiating the correctness of the α^3 terms.

RECENT improvements in the experimental techniques of fine-structure measurements[1–4] call for theoretical work aiming to (a) verify the $\alpha/2\pi$ Schwinger correction to the electron spin moment, and (b) determine a more accurate value of the fine-structure constant α.

We present here results of calculations of the fine-structure of the P states of helium which, when extrapolated and compared with available experimental data, substantiate the Schwinger correction for two-electron interaction. For an improvement in the value of α, further theoretical work and refinement of the experimental techniques is required.

The method described previously[5,6] for solving the Schrödinger wave equation for two-electron atoms has been extended to P states. The wave function ψ was assumed to be of the form

$$\psi=F(r_1,r_2,r_{12})\cos\theta_1\pm F(r_2,r_1,r_{12})\cos\theta_2, \tag{1}$$

given by Breit,[7] with

$$F=r_1e^{-\alpha r_1-\beta r_2}K(r_1,r_2,r_{12}). \tag{2}$$

As in the case of the S states,[5,6] K was developed into a power series of *perimetric* coordinates u, v, and w, which are linear combinations of r_1, r_2 and r_{12} so chosen as to have each the limits 0 to ∞ and to satisfy the condition

$$\alpha r_1+\beta r_2=\tfrac{1}{2}(u+v+w). \tag{3}$$

The coefficients in the expansion of K were determined by substitution in the wave equation as derived by Breit.[7] The calculations were carried out for polynomials K of the order n, containing all terms such that the sum of the exponents of r_1, r_2, and r_{12} is less than or equal to ω:

$$n=\tfrac{1}{6}(\omega+1)(\omega+2)(\omega+3),\quad \omega=6,\,7,\,8,\,9. \tag{4}$$

No attempt was made in this work to attain the highest eigenvalues for a given order n by varying α and β, as was done by Traub and Foley.[8] We assumed $\beta=Z$ and

$$\alpha^2=-2E-Z^2, \tag{5}$$

E denoting the energy eigenvalue. Condition (5) is biased to satisfy the asymptotic behavior at $r_1\to\infty$.

The quality of the wave functions used in the fine-structure calculations can be judged by comparing the theoretical nonrelativistic ionization energy

$$J=-2R_{\mathrm{He}^4}(2E+Z^2),\quad R_{\mathrm{He}^4}=109722.267\ \mathrm{cm}^{-1}, \tag{6}$$

given in Table I for the order $n=220$, with the extrapolated values. The extrapolation was made on the basis of the near constancy of the ratio of the differences in the eigenvalues computed for the four values of ω.[5] The difference between the extrapolated and experimental values could well be accounted for by relativistic, radiative, and mass-polarization corrections.

TABLE I. Values of the nonrelativistic ionization energy J in cm^{-1}.

No. of terms in expansion n	$2\,^1P$	$2\,^3P$	$3\,^1P$	$3\,^3P$
84	27 173.19	29 219.02	12 091.47	12 731.80
120	27 175.09	29 220.94	12 095.74	12 738.18
165	27 175.94	29 221.68	12 098.21	12 741.62
220	27 176.32	29 221.96	12 099.62	12 743.47
Extrapolated	27 176.64	29 222.14	12 101.50	12 745.61
Experiment	27 175.81[a]	29 223.86[a]	12 101.33[a]	12 746.13[b]

[a] G. Herzberg, Proc. Roy.. Soc. (London) **A248**, 309 (1958).
[b] W. C. Martin, J. Research Natl. Bur. Standards **A64**, 19 (1960).

With these wave functions we have determined the expectation values of the fine-structure operators H_3 and H_5.[9] As was shown by Breit[10] and Inglis,[11] the splitting $\Delta\nu_{01}$, $\Delta\nu_{12}$, and $\Delta\nu_{02}$ between the levels $J=0$, $J=1$ and $J=2$ can be expressed as linear combinations of two integrals C and D representing the contributions of the spin-orbit and spin-spin interactions, respectively.

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[5] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958)
[6] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
[7] G. Breit, Phys. Rev. **35**, 569 (1930).
[8] J. Traub and H. M. Foley, Phys. Rev. **116**, 914 (1959).
[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of Two Electron Atoms* (Academic Press Inc., New York, 1957), p. 181.
[10] G. Breit, Phys. Rev. **36**, 383 (1930).
[11] D. R. Inglis, Phys. Rev. **61**, 297 (1942).

TABLE II. Fine-structure splitting of the $2\,^3P$ state in cm^{-1}

No. of terms in expansion	ω	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
84	6	0.988845	0.080342	1.069188
120	7	0.988504	0.078479	1.066983
165	8	0.988255	0.077450	1.065705
220	9	0.988103	0.076897	1.065000
Extrapolated		0.987905	0.076271	1.064175

C can be written in the form

$$C=ZC_z-3C_e, \tag{7}$$

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. Applying the correction[12] of order α^3 ry, we get

$$C=Z[1+(\alpha/\pi)]C_z-[3+(2\alpha/\pi)]C_e, \tag{8}$$

while D is multiplied by the factor $[1+(\alpha/\pi)]$. A correction has also to be added to $\Delta\nu_{01}$, and subtracted from $\Delta\nu_{12}$, arising from the depression of the $^3P_1$ level by the close-lying $^1P_1$ state.[12] This singlet-triplet correction amounts to 0.000158 cm^{-1} for $2\,^3P$, and 0.000042 cm^{-1} for $3\,^3P$ for an order $n=220$, and an extrapolation to $n\rightarrow\infty$ yields the same results. The resulting fine-structure splitting of the $2\,^3P$ and $3\,^3P$ states of helium, including both of the above corrections are shown in Tables II and III. The extrapolation is based on extrapolated values of C_z, C_e, and D. The theoretical results are compared with experimental values in Tables IV and V.

TABLE III. Fine-structure splitting of the $3\,^3P$ state in cm^{-1}.

No. of terms in expansion	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
84	0.270611	0.028700	0.299311
120	0.271025	0.026678	0.297702
165	0.271109	0.025212	0.296321
220	0.271067	0.024181	0.295248
Extrapolated	0.270565	0.021861	0.292425

[12] G. Araki, M. Ohta, and K. Mano, Phys. Rev. **116**, 651 (1959).

TABLE IV. Comparison between theoretical and observed fine-structure splitting of the $2\,^3P$ state.

	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
Araki *et al.*[a]	0.9975	0.0760	1.0734
Traub and Foley[b]	0.9852	0.0834	1.0686
Authors: Order 220	0.988103	0.076897	1.065000
Extrapolated	0.987905	0.076271	1.064175
Experiment	0.987985[c] ±0.000063	0.076438[d] ±0.000003	1.064423[c, d] ±0.000066

[a] See reference 12.
[b] See reference 8.
[c] See reference 4.
[d] See reference 3.

Because of the near equality of C_z and C_e, the α terms in Eq. (8) nearly cancel out, so that C is unaffected by the correction of order α^3 ry, while D is multiplied by the factor $[1+(\alpha/\pi)]$. This correction will therefore have the largest effect on the interval $\Delta\nu_{01}=-C-5D$. In Table VI we have tabulated our extrapolated values of $\Delta\nu_{01}$ both without and with this correction, together with the experimental values. The results support the α^3 ry correction.

TABLE V. Comparison between theoretical and observed fine-structure splitting of the $3\,^3P$ state.

	$\Delta\nu_{01}$	$\Delta\nu_{12}$	$\Delta\nu_{02}$
Araki[a]	0.218	0.0176	0.235
Authors: Order 220	0.271067	0.024181	0.295248
Extrapolated	0.270565	0.021861	0.292425
Experiment[b]	0.270646 ±0.000007	0.021967 ±0.000005	0.292613 ±0.000012

[a] G. Araki, Proc. Phys.-Math. Soc. Japan **19**, 128 (1937).
[b] See reference 2.

TABLE VI. Effect of correction of order α^3 ry.

	$2\,^3P$	$3\,^3P$
$\Delta\nu_{01}$ (extrapolated) without correction	0.986081	0.270070
$\Delta\nu_{01}$ (extrapolated) with correction	0.987905	0.270565
$\Delta\nu_{01}$ experiment	0.987985[a] ±0.000063	0.270646[b] ±0.000007

[a] See reference 4.
[b] Reference 2.