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Triplet Intervals of Helium

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The triplet intervals of the deepest P-state of helium are calculated by making use of the wave function recently determined by the present authors. The polarization of the s-orbital, the admixture of the singlet, and the quantum-electrodynamic fourth-order correction are all taken into account. The theoretical values of the intervals are ${}^3P_0-{}^3P_1=997.457\,11\times10^{-3}$ cm^{-1} and ${}^3P_1-{}^3P_2=75.974\,45\times10^{-3}$ cm^{-1}.

1. INTRODUCTION

THE quantitative study of the helium triplet is very important in order to examine whether the quantum mechanics of the many-electron system provides us with accurate conclusions not only in its nonrelativistic form but also in its semirelativistic part. The triplet intervals were theoretically calculated by several authors,[1] but their results were not satisfactory for this purpose. Recently the wave function was improved for the deepest P-state of helium by the present authors.[2] The purpose of the present paper is to examine to what extent the new function improves the theoretical values of the triplet intervals. The polarization of the s-orbital, the admixture of the singlet state, and the quantum-electrodynamic fourth-order correction are all taken into account. The result is greatly improved as compared with the calculation by Araki,[3,4] although there is yet some discrepancy between theory and experiment.

2. DIAGONAL ELEMENTS OF SPIN-DEPENDENT HAMILTONIAN

We shall first consider the general structure of the interval formula in a simple way in order to see the origin of each term. The spin-dependent part of the Hamiltonian of a He-like atom consists of the spin-orbit coupling, the spin-spin coupling, and the quantum-electrodynamic fourth-order correction to them if we take into account terms up to the order of c^{-3}. We denote them by H_{so}, H_{ss}, δH_{so}, and δH_{ss}, respectively. The spin-orbit coupling can be divided into the self and mutual parts which are denoted by $H_{\mathrm{so}}{}^s$ and $H_{\mathrm{so}}{}^m$, respectively. If we make use of the conventional notation the explicit expression of these couplings and corrections are given by[1,4–6]

$$H_{\mathrm{so}}{}^s=2\mu^2Z(r_1{}^{-3}\mathbf{S}_1\cdot\mathbf{L}_1+r_2{}^{-3}\mathbf{S}_2\cdot\mathbf{L}_2)-2\mu^2r_{12}{}^{-3}(\mathbf{S}_1\cdot\mathbf{L}_{12}+\mathbf{S}_2\cdot\mathbf{L}_{21}),\qquad(2.1)$$

$$H_{\mathrm{so}}{}^m=-4\mu^2r_{12}{}^{-3}(\mathbf{S}_1\cdot\mathbf{L}_{21}+\mathbf{S}_2\cdot\mathbf{L}_{12}),\qquad(2.2)$$

$$H_{\mathrm{ss}}=4\mu^2r_{12}{}^{-3}[\mathbf{S}_1\cdot\mathbf{S}_2-3r_{12}{}^{-3}(\mathbf{x}_{12}\cdot\mathbf{S}_1)(\mathbf{x}_{12}\cdot\mathbf{S}_2)],\qquad(2.3)$$

$$H_{\mathrm{so}}=H_{\mathrm{so}}{}^s+H_{\mathrm{so}}{}^m,\qquad(2.4)$$

$$\delta H_{\mathrm{so}}=\alpha\pi^{-1}(H_{\mathrm{so}}{}^s+\tfrac{1}{2}H_{\mathrm{so}}{}^m),\qquad(2.5)$$

$$\delta H_{\mathrm{ss}}=\alpha\pi^{-1}H_{\mathrm{ss}}.\qquad(2.6)$$

The spin-spin coupling and its correction both include another term, the contact interaction. They are entirely omitted here because they have no influence on the triplet intervals.

The J-dependence of the diagonal elements of these operators was discussed by Araki.[7] It was shown that the diagonal elements of the spin-orbit and spin-spin couplings in the $LSJM$ scheme are proportional to K and $3K(K+1)-4L(L+1)S(S+1)$, respectively, where K is given by

$$K=J(J+1)-L(L+1)-S(S+1).\qquad(2.7)$$

Therefore the element vanishes for $S=0$. The proportion factor is independent of J and M and we can calculate it in the most convenient case, namely in the case of $J=M=L+1$ and $S=1$. Thus we have

$$(LSJM|H_{\mathrm{so}}|LSJM)=K\zeta,\qquad(2.8)$$

$$(LSJM|H_{\mathrm{ss}}|LSJM)=\{3K(K+1)-4L(L+1)S(S+1)\}\eta,\qquad(2.9)$$

$$\zeta=(2L)^{-1}\int\int\psi_{LL}{}^*(A_{12z}+A_{21z})\psi_{LL}dv_1dv_2,\qquad(2.10)$$

$$\eta=\frac{\mu^2}{2L(2L-1)}\int\int|\psi_{LL}|^2\frac{\partial^2}{\partial z_1\partial z_2}\frac{1}{r_{12}}dv_1dv_2,\qquad(2.11)$$

where ψ_{Lm} denotes the triplet orbital for $M_L=m$, and $\mathbf{A}_{12}$ and $\mathbf{A}_{21}$ are defined by

$$H_{\mathrm{so}}=2\mathbf{S}_1\cdot\mathbf{A}_{12}+2\mathbf{S}_2\cdot\mathbf{A}_{21}.\qquad(2.12)$$

The parameter ζ is divided into the nuclear and electronic parts as follows [see (2.1), (2.2), (2.4), (2.10), and (2.12)]:

$$\zeta=\tfrac{1}{2}(Z\zeta^N-3\zeta^e),\qquad(2.13)$$

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[1] H. A. Bethe and E. E. Salpeter, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, p. 269.

[2] Araki, Mano, and Ohta, Progr. Theoret. Phys. (Kyoto) **22**, 469 (1959).

[3] G. Araki, Proc. Phys. Math. Soc. Japan **19**, 128 (1937).

[4] G. Araki, Phys. Rev. **101**, 1410 (1956); **103**, 1906(E) (1956).

[5] H. Araki, Progr. Theoret. Phys. (Kyoto) **17**, 619 (1957).

[6] G. Araki and S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **6**, 673 (1951).

[7] G. Araki, Progr. Theoret. Phys. (Kyoto) **3**, 154 (1948).

$$\zeta^N=\mu^2L^{-1}\int\int\psi_{LL}^*(r_1^{-3}L_{1z}+r_2^{-3}L_{2z})\psi_{LL}dv_1dv_2, \qquad (2.14)$$

$$\zeta^e=\mu^2L^{-1}\int\int\psi_{LL}^*r_{12}^{-3}(L_{12z}+L_{21z})\psi_{LL}dv_1dv_2. \qquad (2.15)$$

The same method can be applied to δH_{so} and δH_{ss}. Their diagonal elements are given by (2.8) and (2.9), respectively, if we replace ζ and η with $\delta\zeta$ and $\delta\eta$, respectively, where the last two parameters are given by

$$\delta\zeta=(\alpha/\pi)\{\tfrac{1}{2}Z\zeta^N-\zeta^e\}, \qquad (2.16)$$

$$\delta\eta=(\alpha/\pi)\eta. \qquad (2.17)$$

If we neglect the admixture of the singlet, the triplet intervals are given by

$$\begin{aligned}E(^3L_{L+1})-E(^3L_L)&\\ =2(L+1)\{(\zeta+\delta\zeta)+3(2L-1)(\eta+\delta\eta)\},&\qquad (2.18)\end{aligned}$$

$$\begin{aligned}E(^3L_L)-E(^3L_{L-1})&\\ =2L\{(\zeta+\delta\zeta)-3(2L+3)(\eta+\delta\eta)\},&\qquad (2.19)\end{aligned}$$

$$\begin{aligned}E(^3L_{L+1})-E(^3L_{L-1})&\\ =2(2L+1)\{(\zeta+\delta\zeta)-3(\eta+\delta\eta)\}.&\qquad (2.20)\end{aligned}$$

3. ADMIXTURE OF SINGLET

The state of definite L and M involves three kinds of states. Their J values are given by $J=L\pm1$ and $J=L$. The first two states belong to the pure triplet. The latter includes the triplet and the singlet. If we denote the wave function in the $LSJM$ scheme by Ψ_{LSJM}, we have

$$\Psi_{L1JM}=C_0\chi_0\psi_{LM}+C_1\chi_1\psi_{L\,M-1}+C_{-1}\chi_{-1}\psi_{L\,M+1}, \qquad (3.1)$$

$$\Psi_{L0JM}=\chi_s\psi_{LM}', \qquad (3.2)$$

for $J=L$ where χ_0, χ_1, χ_{-1} are the spin functions of the triplet corresponding to $M_s=0, 1, -1$, respectively, χ_s is the spin function of the singlet, ψ_{Lm} and ψ_{Lm}' are the orbitals of the triplet and singlet states, respectively, for $M_L=m$, and the coefficients are given by

$$C_0=-M\{L(L+1)\}^{-\frac{1}{2}}, \qquad (3.3)(a)$$

$$C_1=\{(L-M+1)(L+M)\}^{\frac{1}{2}}\{2L(L+1)\}^{-\frac{1}{2}}, \qquad (3.3)(b)$$

$$C_{-1}=-\{(L-M)(L+M+1)\}^{\frac{1}{2}}\{2L(L+1)\}^{-\frac{1}{2}}. \qquad (3.3)(c)$$

From (2.12), (3.1), and (3.2) we have

$$\begin{aligned}(\Psi_{L0JM},\ &H_{\mathrm{so}}\Psi_{L1JM})\\ &=C_0(\psi_{LM}'|A_{12z}-A_{21z}|\psi_{LM})\\ &\quad-2^{-\frac{1}{2}}C_1(\psi_{LM}'|A_{12}^+-A_{21}^+|\psi_{L\,M-1})\\ &\qquad+2^{-\frac{1}{2}}C_{-1}(\psi_{LM}'|A_{12}^--A_{21}^-|\psi_{L\,M+1}) \qquad (3.4)\end{aligned}$$

for $J=L$, where we use the following notation for any vector $\mathbf{A}$:

$$A^+=A_x+iA_y,\quad A^-=A_x-iA_y. \qquad (3.5)$$

The matrix elements of $A_{12z}-A_{21z}$, $A_{12}^+-A_{21}^+$, and $A_{12}^--A_{21}^-$ with respect to the orbital function are proportional to C_0, C_1, and C_{-1}, respectively.[8] The proportion factor is independent of M and we can calculate it for $M=L$. Thus we have

$$(\Psi_{L0JM},H_{\mathrm{so}}\Psi_{L1JM})=-2\{L(L+1)\}^{\frac{1}{2}}\zeta', \qquad (3.6)$$

$$\zeta'=\tfrac{1}{2}Z\zeta'^N+\tfrac{1}{2}\zeta'^e, \qquad (3.7)$$

$$\zeta'^N=\mu^2L^{-1}\int\int(\psi_{LL}')^*(r_1^{-3}L_{1z}-r_2^{-3}L_{2z})\psi_{LL}dv_1dv_2, \qquad (3.8)$$

$$\zeta'^e=\mu^2L^{-1}\int\int(\psi_{LL}')^*r_{12}^{-3}(L_{12z}-L_{21z})\psi_{LL}dv_1dv_2. \qquad (3.9)$$

These parameters are all real as is easily seen.

The nondiagonal matrix element of H_{ss} is represented by a similar expression to (3.4) in which $A_{12}^+-A_{21}^+$, etc., are replaced with $\mu^2(\nabla_1^+\nabla_{2z}-\nabla_{1z}\nabla_2^+)r_{12}^{-1}$, etc. This element vanishes because the equation $\nabla_1^+\nabla_{2z}r_{12}^{-1}=\nabla_{1z}\nabla_2^+r_{12}^{-1}$, etc., hold. Therefore we have the following secular equation for $J=L$:

$$\begin{vmatrix}E-E_t & 2\{L(L+1)\}^{\frac{1}{2}}\zeta'\\ 2\{L(L+1)\}^{\frac{1}{2}}\zeta' & E-E_s\end{vmatrix}=0, \qquad (3.10)$$

where E_t and E_s are the diagonal elements of the Hamiltonian in the triplet and singlet states, respectively. The two roots of the secular equation are written in the following form:

$$E^{(+)}=E_s+\delta E_{st}, \qquad (3.11)$$

$$E^{(-)}=E_t-\delta E_{st}, \qquad (3.12)$$

where

$$\begin{aligned}\delta E_{st}=\{(E_s-E_t)^2 2^{-2}+4L(L+1)(\zeta')^2\}^{\frac{1}{2}}&\\ -\tfrac{1}{2}(E_s-E_t).&\qquad (3.13)\end{aligned}$$

This quantity is positive and represents the displacement of the levels caused by mixing of the singlet and triplet. If $|\zeta'|$ is very small as compared with E_s-E_t, the displacement is approximately given by

$$\delta E_{st}=4L(L+1)(\zeta')^2/(E_s-E_t). \qquad (3{:}14)$$

In this case $E^{(+)}$ and $E^{(-)}$ represent the singlet and triplet levels, respectively.

4. ORBITALS

The orbital eigenfunctions of the deepest triplet and singlet P states of helium were determined variationally by the present authors.[2] They are given in the following form:

$$\psi=\sum_{k=0}^{3}a_k\psi_k, \qquad (4.1)$$

where all functions are normalized: $\|\psi\|=\|\psi_k\|=1$,

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[8] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1957), p. 61.

($k=0$, 1, 2, 3). The basic functions are given by

$$\psi_0=2^{-\frac{1}{2}}(1\mp P)F(\kappa,\mu;r_1,r_2)Z_{sp}(\omega_1,\omega_2), \qquad (4.2)$$

$$\psi_1=2^{-\frac{1}{2}}(1\mp P)G(\kappa,\mu_1;r_2,r_1)Z_{sp}(\omega_1,\omega_2), \qquad (4.3)$$

$$\psi_2=2^{-\frac{1}{2}}(1\mp P)F(\kappa,\mu_2;r_1,r_2)Z_{sp}(\omega_1,\omega_2), \qquad (4.4)$$

$$\psi_3=2^{-\frac{1}{2}}(1\mp P)G(\kappa,\mu_3;r_1,r_2)Z_{pd}(\omega_1,\omega_2), \qquad (4.5)$$

where P is the exchange operator, $1-P$ corresponds to the triplet and $1+P$ to the singlet. Z_{sp} and Z_{pd} are the normalized angular functions of the P state corresponding to the *sp* and *pd* configurations, respectively:

$$Z_{sp}(\omega_1,\omega_2)=Y_{00}(\omega_1)Y_{1m}(\omega_2), \qquad (4.6)$$

$$\begin{aligned}Z_{pd}(\omega_1,\omega_2)&\\ =(20)^{-\frac{1}{2}}&[\{2(2-m)(2+m)\}^{\frac{1}{2}}Y_{10}(\omega_1)Y_{2m}(\omega_2)\\ &-\{(2-m)(3-m)\}^{\frac{1}{2}}Y_{11}(\omega_1)Y_{2\ m-1}(\omega_2)\\ &-\{(2+m)(3+m)\}^{\frac{1}{2}}Y_{1-1}(\omega_1)Y_{2\ m+1}(\omega_2)], \qquad (4.7)\end{aligned}$$

where $Y_{lm}(\omega)$ is the normalized spherical surface harmonic corresponding to the azimuthal quantum number l and the orbital magnetic quantum number m, and ω stands for the spherical surface coordinates θ and φ. The normalized radial functions are defined by

$$F(\kappa,\mu;r_1,r_2)=N_F(\kappa,\mu)r_2e^{-(\kappa r_1+\mu r_2)}, \qquad (4.8)$$

$$G(\kappa,\mu;r_1,r_2)=N_G(\kappa,\mu)r_<r_2e^{-(\kappa r_1+\mu r_2)} \qquad (4.9)$$

where $r_<$ denotes the smaller one of r_1 and r_2, and $N_F(\kappa,\mu)$ and $N_G(\kappa,\mu)$ are the normalization constants. We can consider ψ_3 as representing the polarization of the s orbital instead of the configuration mixing.[9] The parameters are determined by the variation method[2,9] and their numerical values are shown in Table I. The expectation values of energy are compared with experiment in the same table, where E_∞ and E_{calc} denote the energy expectation value corresponding to the rest and moving nucleus, respectively.[2] The number of figures in agreement may give an indication of the accuracy of the wave functions although it may have no precise significance.

Table I. Numerical values of the parameters for the orbitals and of the energy, in atomic units.

	^3P	^1P
κ	1.991 185 792	2.003 024 271
μ	0.544 574 887 8	0.482 362 881 4
μ_1	1.335 750 000	0.807 500 000
μ_2	1.975 000 000	1.437 000 000
μ_3	0.921 250 000	1.119 000 000
a_0	0.990 273 307	1.000 566 493
a_1	0.023 487 573 6	−0.007 028 260 02
a_2	0.013 873 997 3	−0.000 406 779 024
a_3	−0.016 443 103 5	−0.018 107 143 9
E_∞	−2.132 897 96	−2.123 495 89
E_{calc}	−2.132 612 64	−2.123 198 66
E_{obs}	−2.132 968 6 (±7)[a]	−2.123 637 3 (±7)

[a] The error in the last figure.

Table II. Numerical values of the parameters for the triplet intervals, in mK.

ζ^N	204.819 461	ζ'^N	−143.70
ζ^e	202.528 576	ζ'^e	−105.14
ζ	−98.973 403	ζ'	−196.27
η	26.583 976 9		

Table III. Triplet intervals, in mK (^3P_J denotes the energy level). 1 mK$\equiv10^{-3}$ cm^{-1}.

	Theoretical value (including corrections)	Observed value Brochard *et al.*[a] Wieder and Lamb[b]	Moore[c]	Quantum-electrodynamic correction
$^3P_0-{}^3P_1$	997.457 11	988.0 ±0.4[a]	996	1.841 84
$^3P_1-{}^3P_2$	75.974 45	76.8 ±0.2[a] 76.449±0.012[b]	78	−0.762 28
$^3P_0-{}^3P_2$	1073.431 56	1064.8 ±0.4[a]	1074	1.079 56

[a] Brochard, Chabbal, Chantrel, and Jacquinot, J. Phys. radium **18**, 596 (1957).

[b] I. Wieder and W. E. Lamb, Phys. Rev. **107**, 125 (1957).

[c] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.

5. NUMERICAL VALUES OF TRIPLET INTERVALS

The parameters ζ, ζ', their nuclear and electronic parts, and η can be evaluated by the standard method.[3] Their numerical values in mK (10^{-3} cm^{-1}) are shown in Table II. In order to convert energy (in atomic units) into wave number we adopt $4\mu^2=11.687\,111\,2$ cm^{-1}. The theoretical values of the triplet intervals are compared with experiment in Table III. The contribution from δH_{so} and δH_{ss} (quantum-electrodynamic correction) is shown in the last column of the same table. The correction arising from the admixture of the singlet amounts to 0.149 16 mK. The intervals shown in Table III include all these corrections.

The theoretical values are certainly improved as compared with the result of the previous calculation,[3,4] but yet there remains a distinct discrepancy between theory and experiment. If we estimate the accuracy of the wave function from the energy eigenvalue, the theoretical values are correct within 1 mK. However, this estimation may have no reliable basis because the accuracy of the wave function may be different for different physical quantities. We see that there is a discrepancy between the experimental values measured by different authors. In order to clarify the reason for the discrepancy, it is necessary to perform both the calculation and the measurement with improved accuracy.

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[9] G. Araki, Kgl. Norske Videnskab. Selskabs, Forh. **30**, 158 (1957); Festskrift Til Egil Hylleraas På Sekstiårsdagen, May 15, 1958.