Precision calculation of fine structure in helium and Li^+*

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(Received 24 April 2014; revised manuscript received 23 June 2014; published online 30 January 2015)

The fine structure constant α can be extracted from high-precision spectroscopy of the 2^3P_J fine structure splittings in helium and light helium-like ions. In this work, the 2^3P_J fine structure splittings of helium and Li^+ ion are calculated, including relativistic and QED corrections of order $m\alpha^4$, $m\alpha^4(m/M)$, $m\alpha^5$, $m\alpha^5(m/M)$, and Douglas–Kroll operators of $m\alpha^6$ and $m\alpha^6(m/M)$, which provide an independent verification for the previous calculations performed by Drake [*Can. J. Phys.* **80** 1195 (2002)] and by Pachucki and Yerokhin [*Phys. Rev. A* **79** 062516 (2009); *Phys. Rev. Lett.* **104** 070403 (2010); *Can. J. Phys.* **89** 1139 (2011)]. The results of the three groups agree with each other.

Keywords: fine structure, helium, Li^+ ion, QED theory

PACS: 31.15.ac, 37.10.De, 31.15.ap, 31.15.bw **DOI:** 10.1088/1674-1056/24/3/033101

1. Introduction

The fine structure of the 2^3P_J states of helium and light helium-like ions has attracted theoretical and experimental interest for several decades. Due to the fact that the fine structure splitting in a light atomic system is an intrinsically relativistic effect and is proportional to α^2 in the lowest order, study on the fine structure holds a potential for testing bound-state QED and for an accurate determination of the fine structure constant α. Many theoretical studies have concentrated on the fine structure of helium and helium-like ions since the work of Schwartz.[1] Early studies aiming at order $m\alpha^6$ (or α^4 Ry) corrections can be found in Refs. [2]–[5], which corresponds to the determination of α at a level of a few parts per million (ppm). Subsequently, Yan and Drake improved the calculations on the fine structure splittings of helium and helium-like ions ($Z \leq 10$) by including all terms up to $m\alpha^6$, at the level of 3 parts per billion (ppb).[6–8]

The calculations of higher-order corrections met serious difficulties. For the first time, Zhang *et al.*[9–12] derived the order $m\alpha^7$ relativistic Bethe logarithm correction. Although the computational uncertainty was much less than 1 kHz, there was an unexplained discrepancy between theoretical[13,14] and experimental values.[15–18] Pachucki and Serpirstein[19,20] pointed out several computational mistakes and inconsistencies in Zhang's calculation. In 2006, the entire $m\alpha^7$ order corrections were derived by Pachucki.[21] Nonetheless, the theoretical calculations turned out to be not only in disagreement with each other but also in disagreement with experiments.[22,23] Pachucki and Yerokhin[24] eliminated this disagreement by reevaluating the relativistic Bethe logarithm term. As a result, they determined the value of α with an accuracy of 31 ppb, in which the theoretical and experimental uncertainties were respectively 39 ppb and 16 ppb.[15–18,22,23,25] Later, the experimental uncertainty was reduced to 5 ppb by Smiciklas and Shiner,[26] where the uncalculated higher-order terms of order $m\alpha^8$ hindered α from a further improvement in precision.

Besides the helium atom, the fine structure of the Li^+ ion can be used for the α determination as well, in which the theoretical uncertainty is about 3×10^{-7}.[24] The experimental measurements of Li^+ have a precision of 4×10^{-6}.[27–30]

There are some other theoretical studies for energy levels of helium and helium-like ions based on different approaches. Qing *et al.* calculated the fine structure of helium and helium-like ions with the multi-configuration Dirac–Fock method, including the Breit interaction and QED corrections. Their results agree with experiments within about 1%.[31] Duan *et al.* calculated the nonrelativistic ground-state energy of helium using Hylleraas coordinates, as well as the relativistic and radiative corrections.[32]

In this paper, we intend to calculate relativistic corrections of order $m\alpha^4$, $m\alpha^4(m/M)$, $m\alpha^5$, $m\alpha^5(m/M)$, and Douglas–Kroll operators of $m\alpha^6$ and $m\alpha^6(m/M)$ corrections for the fine structure splittings of helium and Li^+, with a purpose of providing a third-party independent verification of previous theoretical work, and further improving computational accuracy for these operators, which is necessary for studying $m\alpha^8$ corrections.

*Project supported by the National Basic Research Program of China (Grant No. 2010CB832803).

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2. Methodology and energies

2.1. Variational wavefunction

After removing the center of mass motion, the three-body Hamiltonian can be expressed as (in atomic units of $\hbar = e = m = 1$)

$$H_0\Psi = E_0\Psi, \tag{1}$$

$$H_0 = -\frac{1}{2}\left(\frac{1}{M}+1\right)\nabla_{r_1}^2 - \frac{1}{2}\left(\frac{1}{M}+1\right)\nabla_{r_2}^2 - \frac{1}{M}\nabla_{r_1}\cdot\nabla_{r_2} + V, \tag{2}$$

where M is the nuclear mass, $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ represent the position vectors of the two electrons respectively, relative to the nucleus situated at the origin, $V = -Z/r_1 - Z/r_2 + 1/r_{12}$ is the Coulomb interaction, and $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$. The eigenvalue problems for helium and Li^+ are solved variationally by using the following generalized Hylleraas basis set:

$$\phi_{ijk}(\boldsymbol{r}_1,\boldsymbol{r}_2) = r_1^i r_2^j r_{12}^k \mathrm{e}^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \mathscr{Y}_{l_1 l_2}^{LM}(\boldsymbol{r}_1,\boldsymbol{r}_2). \tag{3}$$

In the above, $\mathscr{Y}_{l_1 l_2}^{LM}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the vector coupled product of spherical harmonics for the two electrons to form a common eigenvector of $\boldsymbol{L}^2$, L_z, and Π with the corresponding eigenvalues of $L(L+1)$, M, and $(-1)^{l_1+l_2}$, respectively. Here L is the total orbital angular momentum quantum number with its z-component being M, and l_1 and l_2 are orbital angular momentum quantum numbers for electrons 1 and 2 respectively.

Instead of generating nonlinear parameters in a quasirandom manner used by Korobov[33] and Pachucki,[24] we optimized the nonlinear parameters (α,β,γ) using Newton's method. For the case of infinite nuclear mass, our results for the nonrelativistic energies of $2\,^3\mathrm{P}$ states of helium and Li^+ ion are respectively

$$E_{\mathrm{He}}^{\infty} = -2.133164190779283205147, \tag{4}$$

$$E_{\mathrm{Li}^+}^{\infty} = -5.027715681397367762224, \tag{5}$$

which are accurate enough for our calculations of relativistic and radiative corrections.

2.2. Contributions to the fine structure splittings

According to bound-state quantum electrodynamic (QED) theory, atomic energy levels can be expressed in powers of the fine structure constant α,

$$E_{\mathrm{fs}} = E_{\mathrm{fs}}^4 + E_{\mathrm{fs}}^5 + E_{\mathrm{fs}}^6 + E_{\mathrm{fs}}^7 + O(\alpha^8). \tag{6}$$

The term E_{fs}^n is of the order $m\alpha^n\varepsilon_n$, where m is the electron mass and ε_n is an expectation value of a collection of operators or an effective Hamiltonian of this order that needs to be evaluated in theory. The leading contribution to fine structure splittings is the relativistic corrections E_{fs}^4 of order $m\alpha^4$, with the corresponding operators being called Breit (or Breit–Pauli) operators.[34] Since the spin-independent part contributes equally to all fine structure levels, only the spin-dependent part is needed for calculating the fine structure splittings

$$H^{(4)} = H_{\mathrm{Zso}} + H_{\mathrm{eso}} + H_{\mathrm{ess}}, \tag{7}$$

$$H_{\mathrm{Zso}} = \frac{1}{4}Z\alpha^2\left(\boldsymbol{\sigma}_1\cdot\left(\frac{\boldsymbol{r}_1}{r_1^3}\times\boldsymbol{p}_1\right) + \boldsymbol{\sigma}_2\cdot\left(\frac{\boldsymbol{r}_2}{r_2^3}\times\boldsymbol{p}_2\right)\right), \tag{8}$$

$$H_{\mathrm{eso}} = \frac{\alpha^2}{4r^3}(\boldsymbol{r}_{12}\times\boldsymbol{p}_2\cdot(\boldsymbol{\sigma}_2+2\boldsymbol{\sigma}_1) - \boldsymbol{r}_{12}\times\boldsymbol{p}_1\cdot(\boldsymbol{\sigma}_1+2\boldsymbol{\sigma}_2)), \tag{9}$$

$$H_{\mathrm{ess}} = \frac{1}{4}\alpha^2\left(\frac{\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2}{r_{12}^3} - \frac{3}{r_{12}^5}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{\sigma}_2\cdot\boldsymbol{r}_{12})\right), \tag{10}$$

where H_{Zso} is the spin–orbit interaction with the nucleus, H_{eso} is the spin–orbit interaction between two electrons, and H_{ess} is the spin–spin interaction between two electrons. In addition, there are anomalous magnetic moment corrections to Breit operators, which is $H^{(5)}$ of $m\alpha^5$ order correction

$$H^{(5)} = \frac{\alpha}{\pi}\left(H_{\mathrm{Zso}} + \frac{2}{3}\delta_{SS'}H_{\mathrm{eso}} + H_{\mathrm{ess}}\right). \tag{11}$$

The factor $\delta_{SS'}$ means that H_{eso} does not contribute to singlet-triplet mixing terms.

The order $m\alpha^6$ corrections to the fine structure splittings contain two parts. The first part is the second-order perturbation corrections deduced by the Breit–Pauli operators,[34] denoted as $m\alpha_{\mathrm{B}}^6$ corrections. The validity of this second-order perturbation approach was justified by Douglas and Kroll.[2] The second part is the 15 spin-dependent operators H_{DK}, denoted as $m\alpha_{\mathrm{DK}}^6$ corrections. The Douglas–Kroll operators were first derived by Douglas and Kroll in the frame of the Bethe–Salpeter equation;[2] then these operators were rederived by Pachucki using an effective field method.[35] The Douglas–Kroll operators arise from the Feynman diagrams involving the exchange of one, two, and three photons, as well as radiative corrections to the electron magnetic moment. The matrix elements were first calculated by Daley and coworkers.[36] Then higher precision values for these operators were obtained by Yan and Drake[7] and by Pachucki.[19] Thus, the total expression for the $m\alpha^6$ order corrections is

$$H^{(6)} = \langle H^{(4)}(E^0 - H^0)^{-1}H^{(4)}\rangle + \langle H_{\mathrm{DK}}\rangle_{15}, \tag{12}$$

where $H^{(4)}$ contains both the spin-dependent and spin-independent parts of Breit–Pauli operators. The expressions of the Douglas–Kroll operators can be written as follows:

$$H_{\mathrm{DK}}^1 = \frac{3}{8}\alpha^3(Z\alpha)\nabla_1^2\frac{1}{r_1^3}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_1\times\boldsymbol{p}_1), \tag{13}$$

$$H_{\mathrm{DK}}^2 = -\alpha^3\frac{(Z\alpha)}{r_{12}^3 r_1^3}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_1\times\boldsymbol{r}_{12})(\boldsymbol{r}_{12}\cdot\boldsymbol{p}_2), \tag{14}$$

$$H_{\mathrm{DK}}^3 = \frac{1}{2}\alpha^3(Z\alpha)\frac{1}{r_{12}^3 r_1^3}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{\sigma}_2\cdot\boldsymbol{r}_1), \tag{15}$$

$$H_{\mathrm{DK}}^4 = \frac{1}{2}\alpha^4\frac{1}{r_{12}^4}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_{12}\times\boldsymbol{p}_2), \tag{16}$$

$$H^5_{\rm DK} = -\frac{1}{2}\alpha^4\frac{1}{r_{12}^6}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{\sigma}_2\cdot\boldsymbol{r}_{12}), \quad (17)$$

$$H^6_{\rm DK} = {\rm i}\frac{1}{4}\alpha^4\nabla_1^2\frac{1}{r_{12}}\boldsymbol{\sigma}_1\cdot(\boldsymbol{p}_1\times\boldsymbol{p}_2), \quad (18)$$

$$H^7_{\rm DK} = {\rm i}\frac{3}{4}\alpha^4\nabla_1^2\frac{1}{r_{12}^3}(\boldsymbol{r}_{12}\cdot\boldsymbol{p}_2)\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_{12}\times\boldsymbol{p}_1), \quad (19)$$

$$H^8_{\rm DK} = -\frac{5}{8}\alpha^4\nabla_1^2\frac{1}{r_{12}^3}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_{12}\times\boldsymbol{p}_1), \quad (20)$$

$$H^9_{\rm DK} = \frac{3}{4}\alpha^4\nabla_1^2\frac{1}{r_{12}^3}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_{12}\times\boldsymbol{p}_2), \quad (21)$$

$$H^{10}_{\rm DK} = {\rm i}\frac{3}{8}\alpha^4\frac{1}{r_{12}^5}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_{12}\times(\boldsymbol{r}_{12}\cdot\boldsymbol{p}_2)\boldsymbol{p}_1), \quad (22)$$

$$H^{11}_{\rm DK} = -\frac{3}{2}\alpha^4\nabla_1^2\frac{1}{r_{12}^5}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{\sigma}_2\cdot\boldsymbol{r}_{12}), \quad (23)$$

$$H^{12}_{\rm DK} = {\rm i}\frac{1}{4}\alpha^4\nabla_1^2\frac{1}{r_{12}^3}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{\sigma}_2\cdot\boldsymbol{p}_1), \quad (24)$$

$$H^{13}_{\rm DK} = -\frac{\rm i}{8}\alpha^4\nabla_1^2\frac{1}{r_{12}^3}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{\sigma}_2\cdot\boldsymbol{p}_2)), \quad (25)$$

$$H^{14}_{\rm DK} = -\frac{1}{16}\alpha^4\frac{1}{r_{12}^3}(\boldsymbol{\sigma}_1\cdot\boldsymbol{p}_2)(\boldsymbol{\sigma}_2\cdot\boldsymbol{p}_1), \quad (26)$$

$$H^{15}_{\rm DK} = -\frac{3}{16}\alpha^4\frac{1}{r_{12}^5}\boldsymbol{\sigma}_2\cdot(\boldsymbol{r}_{12}\times(\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_{12}\times\boldsymbol{p}_1))\boldsymbol{p}_2). \quad (27)$$

For the sake of convenience, we first consider the case of infinite nuclear mass. We then consider finite nuclear mass corrections. The finite nuclear mass corrections of each order can be divided according to the effects of mass polarization and nuclear recoil. The mass polarization effect can be accounted for to all orders by reevaluating the expectation values of all operators using a wavefunction with the mass polarization term $\boldsymbol{\nabla}_{\boldsymbol{r}_1}\cdot\boldsymbol{\nabla}_{\boldsymbol{r}_2}/M$ included explicitly in the Hamiltonian and taking difference with the infinite nuclear mass results. The terms $\nu^{\rm r}_{01}$ and $\nu^{\rm r}_{12}$ in Tables 1 and 2 represent the mass polarization effects to the Douglas–Kroll operators for helium and Li^+, respectively. It is convenient to denote those terms as $m\alpha^6_{\rm DK}(m/M)$. On the other hand, the mass polarization effects to the second-order perturbation terms are labeled as $m\alpha^6_{\rm B}(m/M)$.

The other part of the finite nuclear mass corrections are recoil terms which disappear in the case of infinite nuclear mass. The $m\alpha^4(m/M)$ and $m\alpha^5(m/M)$ order recoil corrections are

$$H_{m4} = \frac{m}{M}(H_{\rm rec}+2H_{\rm Zso}), \quad (28)$$

$$H_{m5} = \frac{\alpha}{2\pi}\frac{m}{M}(H_{\rm rec}+2H_{\rm Zso}), \quad (29)$$

$$H_{\rm rec} = \frac{Z\alpha^2}{2}\left(\frac{1}{r_1^3}\boldsymbol{\sigma}_1\cdot(\boldsymbol{r}_1\times\boldsymbol{p}_2)+\frac{1}{r_2^3}\boldsymbol{\sigma}_2\cdot(\boldsymbol{r}_2\times\boldsymbol{p}_1)\right). \quad (30)$$

Table 1. Contributions of the Douglas–Kroll operators to the fine structure intervals in the $2^3{\rm P}_J$ state of helium (in units of $10^{-6}R_\infty c\alpha^4 = 9.329027$ MHz).

Terms	ν^∞_{01}	ν^∞_{12}	$\nu^{\rm r}_{01}$	$\nu^{\rm r}_{12}$	Ref.
$H^1_{\rm DK}$	0.224210	0.448420	0.000081	0.000162	[19]
	0.224210174(5)	0.448420348(2)	0.000080677(4)	0.000161355(7)	
$H^2_{\rm DK}$	0.016418	0.032836	−0.000013	−0.000026	[19]
	0.01641779936(2)	0.03283559872(4)	−0.000012813(1)	−0.000025626(2)	
$H^3_{\rm DK}$	0.010 203	−0.004081	−0.000045	0.000018	[19]
	0.010 20318863(2)	−0.00408127545(4)	−0.000044842(1)	0.000017936(1)	
$H^4_{\rm DK}$	0.034557	0.069115	−0.000002	−0.000003	[19]
	0.0345573889(1)	0.0691147778(2)	−0.000001542(1)	−0.000003084(1)	
$H^5_{\rm DK}$	0.081157	−0.032463	−0.000009	0.000003	[19]
	0.0811568994(2)	−0.0324627597(1)	−0.000008726(1)	0.000003490(3)	
$H^6_{\rm DK}$	0.000221	0.000442	0.000007	0.000015	[19]
	0.0002208628(2)	0.0004417256(4)	0.000007413(2)	0.000014836(4)	
$H^7_{\rm DK}$	0.006456	0.012912	−0.000022	−0.000044	[19]
	0.006455970(2)	0.012911941(3)	−0.000022142(4)	−0.000044283(6)	
$H^8_{\rm DK}$	−0.093084	−0.186167	−0.000009	−0.000018	[19]
	−0.093083603(1)	−0.186167207(3)	−0.000008782(3)	−0.000017564(5)	
$H^9_{\rm DK}$	−0.171228	−0.342456	0.000054	0.000108	[19]
	−0.1712277769(1)	−0.342455538(2)	0.000053829(2)	0.000107659(4)	
$H^{10}_{\rm DK}$	−0.008671	−0.017343	0.000001	0.000002	[19]
	−0.008671408(8)	−0.01734281(2)	0.000001093(4)	0.0000021(7)	
$H^{11}_{\rm DK}$	−0.786253	0.314501	0.000235	−0.000094	[19]
	−0.78625269(3)	0.314501078(4)	0.000235154(5)	−0.000094061(7)	
$H^{12}_{\rm DK}$	0.135711	−0.054284	−0.000032	0.000013	[19]
	0.13571106(3)	−0.05428442(1)	−0.00003198(4)	0.00001279(3)	
$H^{13}_{\rm DK}$	0.213103	−0.085241	−0.000061	0.000024	[19]
	0.21310315(3)	−0.08524126(1)	−0.00006083(4)	0.00002433(3)	
$H^{14}_{\rm DK}$	−0.010325	0.004130	0.000000	0.000000	[19]
	−0.0103254461(3)	0.004130184(2)	0.000000016(2)	0.000000006(1)	
$H^{15}_{\rm DK}$	−0.004457	0.001783	0.000004	−0.000001	[19]
	−0.00445711(3)	0.001782846(4)	0.000003637(4)	−0.000001455(2)	
Total	−0.351982	0.162103	0.000190	0.000158	[19]
	−0.35198156(5)	0.16210322(3)	0.00019016(6)	0.00015840(5)	

Table 2. Contributions of the Douglas–Kroll operators to the fine structure intervals in the $2\,^3\mathrm{P}_J$ state of Li^+ ion (in units of $10^{-6}R_\infty c\alpha^4 = 9.329027$ MHz).

Terms	ν_{01}^{∞}	ν_{12}^{∞}	ν_{01}^{r}	ν_{12}^{r}
H_{DK}^1	6.46373552(3)	12.92747105(7)	0.0006922(4)	0.0013844(4)
H_{DK}^2	0.13262262697(3)	0.26524525394(5)	−0.000077262(3)	−0.000155524(5)
H_{DK}^3	−0.27423683179(3)	0.109694732 71(1)	−0.000293408(2)	0.000117363(1)
H_{DK}^4	0.42376839085(5)	0.847536781 7(1)	−0.000019 992(1)	−0.000039983(1)
H_{DK}^5	0.96024258006(2)	−0.38409703202(2)	−0.000072558(3)	0.000029023(2)
H_{DK}^6	0.052219382(2)	0.104438765(4)	0.000054018(4)	0.000108035(5)
H_{DK}^7	−0.131183672(2)	−0.262367344(4)	−0.000159844(4)	−0.000319689(5)
H_{DK}^8	−1.94546744(3)	−3.89093488(5)	0.00002961(3)	0.00005922(5)
H_{DK}^9	−2.90113853(3)	−5.80227707(6)	0.00050753(2)	0.001015005(2)
H_{DK}^{10}	−0.190166682(1)	−0.380333364(2)	0.000017630(1)	0.000035260(2)
H_{DK}^{11}	−13.51613716(2)	5.40645486(6)	0.00230011(5)	−0.00092005(2)
H_{DK}^{12}	2.64156635(5)	−1.05662654(2)	−0.00037156(4)	0.00014863(2)
H_{DK}^{13}	3.6506565(5)	−1.4602626(3)	−0.0006017(3)	0.0002407(4)
H_{DK}^{14}	−0.241562055(4)	0.096624822(1)	0.000013353(6)	−0.000005341(4)
H_{DK}^{15}	−0.0341450529(3)	0.0136580211(2)	0.000031806(2)	−0.000012722(1)
Total	−4.9092260(4)	6.5342263(3)	0.0020499(5)	0.0016843(6)

Since the H_{Zso} appears in the $m\alpha^4$ order relativistic corrections, H_{rec} is the only term needed to be considered in this part. The $m\alpha^6$ order recoil corrections, labeled as $m\alpha^6_{\mathrm{recoil}}(m/M)$, are much more complicated. It was first discussed by Zhang[11] using Bethe–Salpeter formalism, followed by a reconsideration by Pachucki and Sapirstein[20] using effective Hamiltonian approach that yields a sign difference in ν_6 (see Eq. (36)). Eventually the results of $m\alpha^6_{\mathrm{recoil}}(m/M)$ turned out to be consistent after Drake revised the sign.[14] The $m\alpha^6_{\mathrm{recoil}}(m/M)$ order recoil corrections are listed below.

$$\nu_1 = \frac{\mathrm{i}Z}{4}\frac{m}{M}\alpha^4 p_1^2 \frac{1}{r_1}\boldsymbol{\sigma}_1\cdot(\boldsymbol{p}_1\times\boldsymbol{p}_2), \tag{31}$$

$$\nu_2 = -\frac{\mathrm{i}Z}{4}\frac{m}{M}\alpha^4 p_1^2 \frac{\boldsymbol{r}_1}{r_1^3}(\boldsymbol{\sigma}_1\cdot\boldsymbol{r}_1\times\boldsymbol{p}_1)\cdot(\boldsymbol{p}_1+\boldsymbol{p}_2), \tag{32}$$

$$\nu_3 = -\frac{3Z}{4}\frac{m}{M}\alpha^4 p_1^2 \boldsymbol{\sigma}_1\cdot\frac{\boldsymbol{r}_1}{r_1^3}\times(\boldsymbol{p}_1+\boldsymbol{p}_2), \tag{33}$$

$$\nu_4 = Z\frac{m}{M}\alpha^4 \boldsymbol{\sigma}_1\cdot\frac{\boldsymbol{r}_{12}}{r_1 r_{12}^3}\times(\boldsymbol{p}_1+\boldsymbol{p}_2), \tag{34}$$

$$\nu_5 = Z\frac{m}{M}\alpha^4 \boldsymbol{\sigma}_1\cdot\frac{\boldsymbol{r}_{12}}{r_{12}^3}\times\frac{\boldsymbol{r}_1}{r_1^3}(\boldsymbol{r}_1\cdot(\boldsymbol{p}_1+\boldsymbol{p}_2)), \tag{35}$$

$$\nu_6 = Z^2\frac{m}{M}\alpha^4 \boldsymbol{\sigma}_1\cdot\frac{\boldsymbol{r}_1}{r_1^3}\times\frac{\boldsymbol{r}_2}{r_2^3}(\boldsymbol{r}_1\cdot\boldsymbol{p}_1), \tag{36}$$

$$\nu_7 = -\frac{Z^2}{2}\frac{m}{M}\alpha^4 \boldsymbol{\sigma}_1\cdot\frac{\boldsymbol{r}_1}{r_1^4}\times(\boldsymbol{p}_1+\boldsymbol{p}_2), \tag{37}$$

$$\nu_8 = -\frac{Z^2}{4}\frac{m}{M}\alpha^4 \sigma_1\cdot\frac{\boldsymbol{r}_2}{r_2^3}\sigma_2\cdot\frac{\boldsymbol{r}_1}{r_1^3}. \tag{38}$$

Finally, the corrections of orders $m\alpha^6_{\mathrm{B}}$, $m\alpha^6_{\mathrm{B}}(m/M)$, and $m\alpha^7$ are not considered in this work.

3. Calculation and numerical results

The fine structure splittings ν_{01} and ν_{12} are defined by

$$\nu_{01} = \frac{1}{\hbar}[E(2\,^3P_0) - E(2\,^3P_1)], \tag{39}$$

$$\nu_{12} = \frac{1}{\hbar}[E(2\,^3P_1) - E(2\,^3P_2)]. \tag{40}$$

Convergence studies for the operators H_{Zso}, H_{eso}, H_{ess}, and H_{rec} are presented in Tables 3 and 4 for the $2\,^3\mathrm{P}_J$ states of helium and Li^+, respectively. One can see that numerical accuracy of these operators can reach a precision of 12–14 significant digits. A comparison of our results with previous work by Yan[8] shows some discrepancies. Yan used about 800 terms of the basis set, while we used more than 4000, which may explain the discrepancies.

Numerical results of the Douglas–Kroll operators of $m\alpha^6$ order corrections are listed in Tables 1 and 2 for the fine structure intervals of $2\,^3\mathrm{P}_J$ of helium and Li^+, respectively. A term-by-term comparison with previous work by Pachuchi[19] is presented as well. The total uncertainties of the Douglas–Kroll operators to the fine structure intervals are reduced to a level of Hz or even sub-Hz, which is beyond the need for the fine structure constant determination. We do not calculate the second-order perturbation corrections of Breit–Pauli operators; instead, we used Pachucki's and Drake's results that are in good accordance. The numerical results of the finite mass recoil operators, of $m\alpha^6_{\mathrm{DK}}(m/M)$ order, are presented in Tables 5 and 6 for the fine structure intervals of helium and Li^+, respectively.

The numerical results of contributions of all corrections to the fine structure intervals are listed in Tables 7, 8, and 9 for the $2\,^3\mathrm{P}_J$ states of helium and Li^+, respectively. A detailed term-by-term comparison with previous work is presented as well. Our values of $m\alpha^4$, $m\alpha^4(m/M)$, $m\alpha^5$, and $m\alpha^5(m/M)$ order corrections agree with previous calculations[14,24,38] perfectly due to the high-precision values for H_{Zso}, H_{eso}, H_{ess}, and H_{rec} in Tables 3 and 4. The uncertainties of these orders are entirely due to the fundamental physical constants. For the $m\alpha^6$ order and $m\alpha^6(m/M)$ order corrections, we calculate the Douglas–Kroll operators (see Tables 1, 2, 5, and 6). The uncertainties of $m\alpha^6_{\mathrm{DK}}$ and $m\alpha^6_{\mathrm{DK}}(m/M)$ order contributions have

Table 3. Convergence study of the reduced matrix elements of the spin-dependent Breit operators for the helium 2^3P_J state (in 10^{-2} Hartree energy).

N	$H_{\rm Zso}$	$H_{\rm eso}$	$H_{\rm ess}$	$H_{\rm rec}$
330	8.4897378850499	−12.6095056373538	3.02139811093456	−24.3857864184
572	8.4897373469196	−12.6095020929114	3.02139735464371	−24.3857722648
910	8.4897373175681	−12.6095018217647	3.02139730622268	−24.3857725138
1360	8.4897373092048	−12.6095018189000	3.02139730484638	−24.3857725695
1938	8.4897373075347	−12.6095018145917	3.02139730411845	−24.3857725814
2660	8.4897373073108	−12.6095018142919	3.02139730404594	−24.3857725810
3542	8.4897373072539	−12.6095018141765	3.02139730402795	−24.3857725814
4600	8.4897373072423	−12.6095018141887	3.02139730402862	−24.3857725818
Extrap.	8.489737307240(2)	−12.609501814187(1)	3.021397304028 60(2)	−24.3857725820(2)
Yan[8]	8.48973728	−12.60950184	3.021397308	−24.3857712

Table 4. Convergence study of the reduced matrix elements of the spin-dependent Breit operators for the Li^+ ion 2^3P_J state (in 10^{-2} Hartree energy).

N	$H_{\rm Zso}$	$H_{\rm eso}$	$H_{\rm ess}$	$H_{\rm rec}$
440	88.128069059002	−88.11386341683	19.83021792691	−253.91341723771
572	88.128068250305	−88.11386156081	19.83021758889	−253.91340135310
728	88.128068190137	−88.11386116658	19.83021752015	−253.91339987777
910	88.128068222769	−88.11386081786	19.83021744769	−253.91339683841
1120	88.128068220457	−88.11386079110	19.83021744246	−253.91339643861
1360	88.128068227693	−88.11386075113	19.83021743548	−253.91339622344
1632	88.128068224205	−88.11386074800	19.83021743498	−253.91339618291
1938	88.128068225407	−88.11386074491	19.83021743423	−253.91339615780
2280	88.128068224298	−88.11386074230	19.83021743366	−253.91339610976
2660	88.128068224315	−88.11386074201	19.83021743362	−253.91339611116
3080	88.128068224273	−88.11386074183	19.83021743361	−253.91339611050
3542	88.128068224225	−88.11386074180	19.83021743360	−253.91339611060
4048	88.128068224254	−88.11386074182	19.83021743359	−253.91339611056
Extrap.	88.1280682242 48(3)	−88.11386074186(2)	19.830217433 59(1)	−253.9133961105(1)
Yan[8]	88.12806823035	−88.11386078985	19.830217422 24	−253.913373

Table 5. Contributions of finite nuclear mass recoil operators for the $m\alpha^6_{\rm recoil}(m/M)$ order corrections to the fine structure intervals in the 2^3P_J state of helium atom (in kHz).

	ν_{01}		ν_{12}	
Terms	Pachucki [20]	This work	Pachucki [20]	This work
ν_1	0.480	0.4796188(2)	0.959	0.9592376(4)
ν_2	0.165	0.16517387(6)	0.330	0.3303478(1)
ν_3	−1.103	−1.103133 4(4)	−2.206	−2.2062669(8)
ν_4	0.129	0.12893636(7)	0.258	0.2578727(1)
ν_5	0.042	0.04226475395(5)	0.085	0.0845295079(1)
ν_6	−0.236	−0.2361892078(3)	−0.472	−0.4723784156(6)
ν_7	−0.471	−0.4706405451(7)	−0.941	−0.941281090(1)
ν_8	−0.354	−0.3546377702(5)	0.141	0.1414551081(2)
Total	−1.348	−1.3486071(5)	−1.847	−1.8464837(9)

been reduced by two orders of magnitude, as shown in Table 7.

We also provide a comparison of the total intervals with other theories and experiments. In Tables 8 and 9, we take values of uncalculated terms from other theories in order to sum up all contributions. For the helium atom, one can see that our total intervals agree with the values from Ref. [38], but differ from Drake's calculation.[14] This is due to the mistakes of the derivations and calculations of $m\alpha^7$ order corrections in Refs. [9]– [12]. It should be pointed out that the total intervals have slight discrepancies between our values and the values of Pachucki and Yerokin.[38] This is due to the shift of about 0.5 kHz for the $m\alpha^6_{\rm B}(m/M)$ order corrections in both ν_{01} and ν_{12} (see Table 7). For the Li^+ ion, we reproduce the results of Pachucki and Yerokhin.[24] The total uncertainties of the intervals come from other higher-order corrections not calculated in this work. The largest uncertainty in the total intervals for both helium and Li^+ is due entirely to the unknown $m\alpha^8$ order corrections.

Table 6. Contributions of finite nuclear mass recoil operators for the $m\alpha^6_{\rm recoil}(m/M)$ order corrections to the fine structure intervals in the $2\,^3{\rm P}_J$ state of Li^+ ion (in kHz).

Terms	ν_{01}	ν_{12}
ν_1	6.501479(5)	13.002959(9)
ν_2	1.9708751(9)	3.941750(2)
ν_3	−13.330096 9(9)	−26.660194(2)
ν_4	0.948101065(2)	1.896202129(3)
ν_5	0.2906374565(5)	0.581274913(1)
ν_6	−3.574080709(6)	−7.14816142(1)
ν_7	−5.8846802(3)	−11.7693603(5)
ν_8	−5.335104284(7)	2.134041714(3)
Total	−18.412869(5)	−24.02149(1)

Table 7. Comparison of the contributions to the fine structure intervals of helium in $2\,^3{\rm P}_J$ (in MHz).

Contributions	ν_{01}	ν_{12}	Ref.
$m\alpha^4$	29564.59537	2317.23186	[14]
	29564.59588(2)	2317.23189(3)	
$m\alpha^4(m/M)$	−0.83097	3.00964	[14]
	−0.83016(3)	3.00955(4)	
$m\alpha^5$	54.70786	−22.54822	[14]
	54.70785688(5)	−22.54821252(6)	
$m\alpha^5(m/M)$	−0.00382	0.00321	[14]
	−0.00381687(7)	0.00321358(8)	
$m\alpha^6_{\rm DK}$	−3.33519(3)	1.53393(5)	[14]
	−3.3351993(1)	1.53390160(2)	
$m\alpha^6_B$	1.72758(4)	−8.04038(5)	[14]
	1.72768(2)	−8.04032(10)	[37]
$m\alpha^6_{\rm DK}(m/M)$	0.00179	0.00146	[14]
	0.00177371(5)	0.00147874(5)	
$m\alpha^6_{recoil}(m/M)$	−0.00135	−0.00185	[14]
	−0.0013486071(5)	−0.0018464837(9)	
$m\alpha^6_B(m/M)$	−0.01081(5)	0.01019(11)	[14]
	−0.01039	0.00951	[37]

Table 8. The final results of the fine structure intervals for helium in $2\,^3{\rm P}_J$ (in MHz).

Contributions	ν_{01}	ν_{12}
$m\alpha^4(+m/M)$	29563.76546(4)[a]	2320.24143(5)[a]
	29563.76523[b]	2320.24142[b]
	29563.76545[c]	2320.24143[c]
$m\alpha^5(+m/M)$	54.70404001(9)[a]	−22.5449989(1)[a]
	54.70404[b]	−22.54501[b]
	54.70404[c]	−22.54500[c]
$m\alpha^6$	−1.60761(4)[a]	−6.50647(5)[a]
$m\alpha^6(m/M)$	−0.01037[b]	0.00980[b]
$m\alpha^7$(log)	0.08144[d]	−0.00592[d]
$m\alpha^7$(nlog)	0.01888[d]	−0.0144[d]
$m\alpha^8$	±0.0017[c]	±0.0017[c]
Theories	29616.95185(170)[a]	2291.17951(170)[a]
	29616.95229(170)[c]	2291.17891(170)[c]
	29616.94642(18)[b]	2291.15462(31)[b]
Experiments	29616.9509(9)[e]	2291.1740(14)[e]
	29616.95166(70)[f]	2291.17559(51)[f]
		2291.17753(35)[g]

[a] This work, [b] Ref. [14], [c] Ref. [38], [d] Ref. [24], [e] Ref. [18], [f] Ref. [22], [g] Ref. [25].

Table 9. Comparison of the contributions to the fine structure intervals of Li^+ in $2\,^3{\rm P}_J$ (in MHz).

Term	ν_{01}	ν_{12}
$m\alpha^4$	155342.8814(2)[a]	−62185.9266(2)[a]
$m\alpha^4(m/M)$	−1.5692(2)[a]	16.8824(3)[a]
$m\alpha^4(+m/M)$	155341.3122(3)[a]	−62169.0441(4)[a]
	155341.31076[b]	−62169.04386[b]
$m\alpha^5$	263.2450013(3)[a]	−339.6236156(5)[a]
$m\alpha^5(m/M)$	−0.0128019(5)[a]	0.0209009(7)[a]
$m\alpha^5(+m/M)$	263.2321995(6)[a]	−339.6027145(9)[a]
	263.23218[b]	−339.60303[b]
$m\alpha^6_{\rm DK}$	−45.9904476(5)[a]	61.3924038(5)[a]
$m\alpha^6_{\rm DK}(m/M)$	0.0191243(1)[a]	0.0157231(2)[a]
$m\alpha^6_{\rm recoil}(m/M)$	−0.018412869(5)[a]	−0.02402149(1)[a]
$m\alpha^6(+m/M)$	99.4518[b]	−169.48845[b]
$m\alpha^7$(log)	−0.87156[b]	−0.9234[b]
$m\alpha^7$(nlog)	1.45881[b]	−0.25758[b]
Theories	155704.583(48)[a]	−62679.316(58)[a]
	155704.584(48)[b]	−62679.318(58)[b]
	155703.4(15)[c]	−62679.4(5)[c]
Experiments	155709.0(20)[d]	−62667.4(20)[d]
	155704.27(66)[e]	−62678.41(65)[e]
		−62679.46(98)[f]

[a] This work, [b] Ref. [24], [c] Ref. [12], [d] Ref. [27], [e] Ref. [28], [f] Ref. [29].

4. Conclusion

In conclusion, we have performed an independent calculation of the fine structure intervals for the $2\,^3{\rm P}_J$ states of helium and Li^+ including $m\alpha^4$, $m\alpha^4(m/M)$, $m\alpha^5$, $m\alpha^5(m/M)$, $m\alpha^6_{\rm DK}$, $m\alpha^6_{\rm DK}(m/M)$, and $m\alpha^6_{\rm recoil}(m/M)$ order corrections. Our results agree with previous calculations at a sub-kHz level for these corrections. The numerical uncertainties of our results are negligible compared to the present experimental uncertainty. The current values of the $m\alpha^6_{\rm B}(m/M)$ order corrections have a shift of about 0.5 kHz for both ν_{01} and ν_{12} (see Tables 7 and 9), which was analyzed by Pachucki.[37] He pointed out that this discrepancy exceeds the present experimental precision of Ref. [26] and should be checked theoretically. The uncertainties of $m\alpha^6_{\rm B}(m/M)$ order and $m\alpha^7_{\rm log}$ order corrections exceed the experimental uncertainty, and the nonlogarithmic parts of $m\alpha^7_{\rm nlog}$ are only calculated by Pachucki. As a result, further verification is also needed. The most accurate value for α^{-1} determined from the helium fine structure is 137.03599955(368),[39] in combination with the experimental results of Smiciklas and Shiner[26] and the theoretical result of Pachucki and Yerokhin,[24] where the uncertainty is mainly caused by uncalculated higher-order terms. The uncalculated contribution of order $m\alpha^8$ is estimated to be ±1.7 kHz, resulting in a relative uncertainty of 2.7×10^{-8} for α.[40] A complete calculation of order $m\alpha^8$ terms is still a challenging task.

Acknowledgment

Yan Z C is supported by the Natural Sciences and Engineering Research Council of Canada, the computing facilities

of ACEnet and SHARCnet, and by the CAS/SAFEA International Partnership Program for Creative Research Teams.

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