Ionization potential for excited S-states of the lithium atom

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Abstract

Nonrelativistic, relativistic, QED, and finite nuclear mass corrections to the energy levels are obtained for $nS_{1/2}, n = 3 \ldots 9$ states of the lithium atom. Computational approach is based on the explicitly correlated Hylleraas functions with the analytic integration and recursion relations. Theoretical predictions for the ionization potential of $nS_{1/2}$ states and transition energies $nS_{1/2} \to 2S_{1/2}$ are compared to known experimental values for ^{6,7}Li isotopes.

PACS numbers: 31.15.ac, 31.30.J-

I. INTRODUCTION

The high accuracy for transition frequencies in light few-electron atoms is the long standing goal of theoretical methods for evaluation of energy levels. Matching the experimental accuracy requires precise treatment of the electron correlations, relativistic and quantum electrodynamic (QED) effects. The only approach which consistently accounts for all corrections beyond the nonrelativistic approximation is the one based on the expansion of the energy in the fine structure constant α. Each expansion coefficient can be expressed in terms of the expectation value with the nonrelativistic wave function of some effective Hamiltonian [1] derived in the framework of the nonrelativistic QED (NRQED). This method has been advanced significantly in the last years by the calculation of $m\,\alpha^6$ corrections to helium energy levels [2, 3], $m\,\alpha^7$ to helium fine structure [4, 5], and leading relativistic and QED corrections in three- and four-electron systems [6–8].

We have recently performed accurate Hylleraas-type calculations for the ionization potential (IP) of the ground state $2^2S_{1/2}$ and the transition frequency $3S \rightarrow 2S$ [9]. These results are in good agreement with the other Hylleraas-type calculations by Yan and Drake [10] and in the approximate agreement with calculations using fully-correlated Gaussian functions by Stanke *et al.* [11]. Our theoretical predictions are consistent with measurements of the transition energy $3S \rightarrow 2S$ for ^{6,7}Li by Radziemski *et al.* [12], Bushaw *et al.*[13], Reinhardt *et al.* [14], but are anyway much less accurate than the most recent one by Sanchez *et al.* [15]

In this work, we present comprehensive high-precision calculations of energy levels of low-lying excited nS states with $n = 3\ldots9$ of lithium, leading to ionization potential (IP) and transition frequencies $nS \rightarrow 2S$, (the result for $3S \rightarrow 2S$ was previously obtained in [9]). The calculation including complete relativistic $m\,\alpha^4$ and QED $m\,\alpha^5$, estimate of $m\,\alpha^{6,7}$ QED terms and dominating recoil effects are performed for states the with principal number $n \leq 9$. This work is motivated by existing and planned precise measurements. Lorenzen and Niemax [32], Radziemski *et al.* [12] and recently DeGraffenreid and Sansonetti have measured the two-photon transition $4S \rightarrow 2S$ in ^{6}Li and ^{7}Li, providing precise benchmark data. Radziemski *et al.* in [12] performed measurements for transition frequencies including $n = 5, 6$, but no precise theoretical predictions with relativistic and QED effects have been published so far for these states.

The ground of accurate calculations of (light) atomic energy levels in the NRQED approach is the precise representation of the nonrelativistic wave function. The frequently used explicitly correlated Gaussian (ECG) functions give accurate nonrelativistic energies, but obtained wave function does not have the proper asymptotic at short (the cusp condition), and long distances. It limits this representation only to the calculation of leading relativistic and QED corrections. The important advantage of this basis are applications to the multielectron systems, what is very difficult to achieve with the other explicitly correlated methods.

The most accurate wave function in three-electron atoms are obtained in the Hylleraas basis set [17–19]. The calculations of matrix elements of nonrelativistic Hamiltonian, as well as relativistic and QED operators involve a combination Hylleraas integrals, which are obtained analytically using recursion relations [19, 20]. We have recently obtained high-precision results for the ground state of lithium using another type of exponentially correlated basis functions [21], which have good analytical properties. Although precision of the energies is not comparable with Hylleraas results, this basis is particularly convenient for evaluation of expectation values of the operators at higher orders of NRQED. [22].

Using variational method for the nonrelativistic energies for excited S-states, the results obtained here are the most precise have been ever published. They improve precision of the former variational Hylleraas results by Luchow and Kleindiens, [23] King [24] and Hylleraas-configuration-interaction method by Sims and Hagstrom [25] by several orders of magnitude.

II. ENERGY LEVELS IN THE NRQED APPROACH

In this section we summarize contributions to the energy levels in the NRQED expansion as a power series in fine structure constant α and reduced electron mass to nuclear mass ratio $\eta = -\mu/m_N = -m/(m+m_N)$

$$\begin{aligned} E \;=\; & m\,\alpha^2 \left[\mathcal{E}^{(2,0)} + \eta\,\mathcal{E}^{(2,1)} + \eta^2\,\mathcal{E}^{(2,2)}\right] \\ & + m\,\alpha^4 \left[\mathcal{E}^{(4,0)} + \eta\,\mathcal{E}^{(4,1)}\right] + m\,\alpha^5 \left[\mathcal{E}^{(5,0)} + \eta\,\mathcal{E}^{(5,1)}\right] \\ & + m\,\alpha^6\,\mathcal{E}^{(6,0)} + m\,\alpha^7\,\mathcal{E}^{(7,0)}, \end{aligned} \tag{1}$$

and each dimensionless coefficient $\mathcal{E}^{(m,n)}$ is calculated separately as an expectation value of the corresponding operator. The leading contribution $\mathcal{E}^{(2,0)} \equiv \mathcal{E}_0$ is an eigenvalue of the nonrelativistic Hamiltonian for three-electron atom with infinitely heavy nucleus

$$\mathcal{H}_0 = \sum_a \frac{p_a^2}{2} - \sum_a \frac{Z}{r_a} + \sum_{a>b} \frac{1}{r_{ab}}. \tag{2}$$

The first and second order finite mass nonrelativistic corrections are given by

$$\mathcal{E}^{(2,1)} = \mathcal{E}^{(2,0)} - \sum_{a<b} \langle \vec{p}_a \cdot \vec{p}_b \rangle, \tag{3}$$

$$\mathcal{E}^{(2,2)} = -\sum_{a<b} \langle \vec{p}_a \cdot \vec{p}_b \rangle + \frac{1}{2} \sum_{a<b} \langle \vec{p}_a \cdot \vec{p}_b \rangle_{\rm mp}, \tag{4}$$

where

$$\langle \ldots \rangle_{\rm mp} = 2 \left\langle \ldots \frac{1}{(\mathcal{E}_0 - \mathcal{H}_0)'} \, \vec{p}_a \cdot \vec{p}_b \right\rangle \tag{5}$$

is the mass polarization second order term.

In order to calculate leading relativistic corrections $\mathcal{E}^{(4,0)} = \langle \mathcal{H}^{(4,0)} \rangle$ we consider the Breit-Pauli Hamiltonian [26], which for states with vanishing angular momentum and spin the expectation value can be simplified to the form

$$\begin{aligned} \mathcal{H}^{(4,0)} &= \sum_a \left[-\frac{\vec{p}_a^{\,4}}{8} + \frac{\pi\, Z\, \alpha}{2}\, \delta^3(r_a) \right] \\ &\quad + \sum_{a>b} \left[\pi\, \delta^3(r_{ab}) - \frac{1}{2}\, p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3} \right) p_b^j \right]. \end{aligned} \tag{6}$$

The finite nuclear mass correction $\mathcal{E}^{(4,1)}$ to the leading relativistic contribution has the parts resulting from Eq. (6) due to mass scaling $\mathcal{E}_{\rm ms}^{(4,1)}$ and mass polarization perturbation $\langle \mathcal{H}^{(4,0)} \rangle_{\rm mp}$ and additional recoil term $\mathcal{E}_{\rm r}^{(4,1)}$

$$\mathcal{E}^{(4,1)} = \mathcal{E}_{\rm ms}^{(4,1)} + \langle \mathcal{H}^{(4,0)} \rangle_{\rm mp} + \mathcal{E}_{\rm r}^{(4,1)}, \tag{7}$$

$$\begin{aligned} \mathcal{E}_{\rm ms}^{(4,1)} &= -\frac{4}{8} \sum_a \langle \vec{p}_a^{\,4} \rangle + 3 \left\{ \frac{\pi\, Z\, \alpha}{2} \sum_a \langle \delta^3(r_a) \rangle \right. \\ &\quad \left. + \pi \sum_{a>b} \langle \delta^3(r_{ab}) \rangle - \frac{1}{2} \sum_{a>b} \left\langle p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\, r_{ab}^j}{r_{ab}^3} \right) p_b^j \right\rangle \right\}, \end{aligned} \tag{8}$$

$$\mathcal{E}_{\rm r}^{(4,1)} = -\frac{Z}{2} \sum_{a,b} \left\langle p_a^i \left(\frac{\delta^{ij}}{r_a} + \frac{r_a^i\, r_a^j}{r_a^3} \right) p_b^j \right\rangle. \tag{9}$$

There is also a correction of the order $m\,\alpha^4$, which is due to the finite nuclear size

$$\mathcal{E}_{\rm nuc}^{(4,0)} = \frac{2\pi\, Z}{3} \frac{r_c^2}{\lambda\!\!\!^{-2}} \sum_a \langle \delta^3(r_a) \rangle, \tag{10}$$

where $r_{\rm c}^2$ is the averaged square of the charge radius and $\lambda\!\!\!^{-}$ is the electron Compton wavelength divided by $2\,\pi$.

Leading QED corrections of order $m\,\alpha^5$ is given by [27]

$$\begin{aligned}
\mathcal{E}^{(5,0)} &= \frac{4\,Z}{3}\left[\frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0\right] \sum_a \langle\delta^3(r_a)\rangle \\
&\quad + \left[\frac{164}{15} + \frac{14}{3}\,\ln\alpha\right] \sum_{a<b} \langle\delta^3(r_{ab})\rangle \\
&\quad - \frac{7}{6\,\pi} \sum_{a<b} \left\langle P\left(\frac{1}{r_{ab}^3}\right)\right\rangle,
\end{aligned} \tag{11}$$

where the Bethe logarithm $\ln k_0$ has the form

$$\ln k_0 \equiv \frac{\left\langle \sum_a \vec{p}_a\,(H_0 - E_0)\,\ln\big[2\,(H_0 - E_0)\big]\,\sum_b \vec{p}_b \right\rangle}{2\,\pi\,Z\,\sum_c \langle\delta^3(r_c)\rangle} \tag{12}$$

and

$$\begin{aligned}
\langle\phi|P\left(\frac{1}{r^3}\right)|\psi\rangle &= \lim_{a\to 0} \int \mathrm{d}^3r\,\phi^*(\vec{r})\Big[\\
&\quad \frac{1}{r^3}\,\Theta(r-a) + 4\,\pi\,\delta^3(r)\,(\gamma + \ln a)\Big]\,\psi(\vec{r}).
\end{aligned} \tag{13}$$

The finite nucleus mass correction to the leading QED contribution [28]

$$\mathcal{E}^{(5,1)} = \mathcal{E}^{(5,1)}_{\mathrm{ms}} + \mathcal{E}^{(5,1)}_{\mathrm{mp}} + \mathcal{E}^{(5,1)}_{\mathrm{r}}, \tag{14}$$

consists of the mass scaling part

$$\mathcal{E}^{(5,1)}_{\mathrm{ms}} = 3\,\mathcal{E}^{(5,0)} - \frac{4\,Z}{3} \sum_a \langle\delta^3(r_a)\rangle + \frac{14}{3} \sum_{a<b} \langle\delta^3(r_{ab})\rangle\,, \tag{15}$$

and additional recoil terms from Salpeter correction at order $O(\mu/M)$.

$$\begin{aligned}
\mathcal{E}^{(5,1)}_{\mathrm{r}} &= -Z^2\left[\frac{2}{3}\ln(\alpha^{-1}) + \frac{62}{9} - \frac{8}{3}\,\ln k_0\right] \sum_a \langle\delta^3(r_a)\rangle \\
&\quad + \frac{7}{6\,\pi} \sum_a \left\langle P\left(\frac{1}{r_a^3}\right)\right\rangle,
\end{aligned} \tag{16}$$

and $\mathcal{E}^{(5,1)}_{\mathrm{mp}}$ due to mass polarization perturbation of $\mathcal{E}^{(5,0)}$. The mass scaling contribution apart from scaling with factor 3 for all operators in Eq. (11) has two additional terms coming from scaling of the Bethe logarithm and $P(1/r^3)$ operator.

Considering $m\,\alpha^6$ corrections, they are well known for the hydrogen atom [29]. Corresponding calculations in multielectron systems have been performed only for low-lying states of the helium atom [2] and helium-like ions [3]. For three-electron atom we use an approximate formula on the basis of hydrogenic values

$$E^{(6)} \;=\; Z^2 \left[\frac{427}{96} - 2\ln(2)\right] \sum_a \langle \delta^3(r_a)\rangle, \tag{17}$$

since complete calculations are too difficult to perform presently. This approximation includes dominating electron-nucleus one-loop radiative correction [29]. We neglect two-loop radiative, electron-electron radiative and the purely relativistic corrections. We expect them to be relatively small compared to the dominating term being about 10% or less.

Due to the numerical significance, one includes approximately $m\,\alpha^7$ contribution which is known exactly only for hydrogenic systems [29].

$$\begin{aligned} E^{(7)}_{\rm H}(n) \;=\; & m\,\frac{\alpha}{\pi}\,\frac{(Z\,\alpha)^6}{n^3}\,\big[A_{60}(n) + \ln(Z\,\alpha)^{-2}\,A_{61}(n) \\ & + \ln^2(Z\,\alpha)^{-2}\,A_{62}\big] + m\left(\frac{\alpha}{\pi}\right)^2 \frac{(Z\,\alpha)^5}{n^3}\,B_{50} \\ & + m\left(\frac{\alpha}{\pi}\right)^3 \frac{(Z\,\alpha)^4}{n^3}\,C_{40}. \end{aligned} \tag{18}$$

It involves one-, two-, and three-loop corrections, and values of A, B, and C coefficients may be found in [29]. Following Ref. [37] these hydrogenic values of order $m\,\alpha^7$ are extrapolated to lithium, according to

$$\begin{aligned} \mathcal{E}^{(7)}(Z) \;=\; & \big[2\,\mathcal{E}^{(7)}(1S,Z) + \mathcal{E}^{(7)}(nX, Z-2)\big] \\ & \times \frac{\langle \delta^3(r_1) + \delta^3(r_2) + \delta^3(r_3)\rangle_{\rm Li}}{2\,\langle\delta^3(r)\rangle_{1S,Z} + \langle\delta^3(r)\rangle_{nX,Z-2}}, \end{aligned} \tag{19}$$

for $X = S$, and for states with higher angular momenta $\mathcal{E}^{(7)}(nX, Z)$ is neglected. We expect this approximate formula to be accurate to 25%. This completes QED corrections to transition frequencies and the ionization energy in lithium atom at the present level of accuracy.

III. THE WAVE FUNCTION AND MATRIX ELEMENTS

Here we present short summary of the construction of the wave function. It is based on the work of Yan and Drake [18] and was used in our former papers [9, 19]. The wave function for

S-state is expressed as a linear combination of terms ψ, the antisymmetrized product $\mathcal{A}$ of the spatial function ϕ and the spin singlet function χ,

$$\psi = \mathcal{A}[\phi(\vec{r}_1, \vec{r}_2, \vec{r}_3)\,\chi]\,, \tag{20}$$

$$\phi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = e^{-w_1\,r_1 - w_2\,r_2 - w_3\,r_3}\, r_{23}^{n_1}\, r_{31}^{n_2}\, r_{12}^{n_3}\, r_1^{n_4}\, r_2^{n_5}\, r_3^{n_6}\,, \tag{21}$$

$$\chi = \alpha(1)\,\beta(2)\,\alpha(3) - \beta(1)\,\alpha(2)\,\alpha(3)\,, \tag{22}$$

with n_i being non-negative integers, $w_i \in R_+$. The matrix element of the nonrelativistic Hamiltonian H_0 in Eq. (2) or any spin independent operator can be expressed after spin variables reduction as

$$\begin{aligned} \langle\psi|H_0|\psi'\rangle = {} & \langle 2\,\phi(r_1, r_2, r_3) + 2\,\phi(r_2, r_1, r_3) - \phi(r_3, r_1, r_2) \\ & -\phi(r_2, r_3, r_1) - \phi(r_1, r_3, r_2) - \phi(r_3, r_2, r_1)| \\ & H_0\,|\phi'(r_1, r_2, r_3)\rangle\,. \end{aligned} \tag{23}$$

All these spatial matrix elements can be evaluated as a linear combination of Hylleraas integrals of the form

$$\begin{aligned} f(n_1, n_2, n_3, n_4, n_5, n_6) = {} & \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi} \int \frac{d^3 r_3}{4\,\pi} \\ & \times e^{-w_1\,r_1 - w_2\,r_2 - w_3\,r_3} \\ & \times r_{23}^{n_1-1}\, r_{31}^{n_2-1}\, r_{12}^{n_3-1}\, r_1^{n_4-1}\, r_2^{n_5-1}\, r_3^{n_6-1}\,, \end{aligned} \tag{24}$$

with non-negative integers n_i. The recurrence relation method for evaluation of integrals with nonnegative n_i was derived in [20].

The total wave function is combined from ϕ terms with n_i satisfying

$$\sum_{i=1}^{6} n_i \leq \Omega\,, \tag{25}$$

for Ω up to 13. For each Ω we minimize energy with respect to the free parameters w_i, and divide the whole basis set into five sectors, each one with its own set of w_i's [18, 19]. To avoid numerical instabilities, within each sector we drop the terms with $n_4 > n_5$ (or $n_4 < n_5$) and for $n_4 = n_5$ drop terms with $n_1 > n_2$ (or $n_1 < n_2$). For further improvement, the basis with $\Omega = 13$ was extended by completing each sectors using functions with $\Omega = 6$. Such basis is denoted by $\Omega = 13.6$. And finally, for ground state, the largest basis with $\Omega = 13.10$ has been used.

IV. NUMERICAL RESULTS

Numerical results for nonrelativistic energies of the ground state and excited states nS, $n = 3\ldots9$ with different size N of basis sets are presented in Table I. Extrapolated values $\Omega = \infty$ are obtained by fitting the function $X(\Omega) = X_0 + X_1/\Omega^n$ with some integer n. All numerical values are the most accurate among known in the literature. We improve the accuracy of the excited $n = 4\ldots7$ states approximately by 3 orders compared to the recent results by Sims *et al.* [25] with Hylleraas-CI method and King's with Hylleraas functions [24]. The quality of the wave function is getting worse for higher n and the energy for the $9S$ is about 3 orders less accurate compared to the one of the ground state. It means, that this sector division is getting non-optimal for highly excited states. This is a reason why we used $\Omega = 13.10$ only in the case of the ground state. For excited states the better progress could be achieved by finding better sector division rather than increasing the basis size.

The benchmark results for different methods are those for the ground state. Hylleraas functions seem to be the most optimal ones due to good analytical properties. Relatively small number of variational parameters (i.e. 15) allows one an efficient optimization of the wave function even with very big set of trial functions ($\geq$ 10000). The problem is the slowness of the sextuple precision arithmetics, which has to be used in optimization based on the analytical gradient. Gaussian functions do not require such a high precision arithmetics [11], but improper analytical properties limit their high-precision applications to leading relativistic and QED effects. The right analytic properties are critical for the evaluation of higher order QED effects. Anyway, Gauss correlated functions can be easly extended to few-electron atomic and molecular systems. This extension is not possible up to now with Hylleraas due to very complicated integrals in matrix elements calculations. The problem is even more severe for exponentially correlated functions. Inspite of it, we have recently been able to obtain accurate matrix elements with this basis [21], which is promising at high order QED calculations as a complementary tool for the Hylleraas method [22].

In the next step of this work, we calculate various matrix elements to obtain corrections to the energy levels of the lithium states. The exception is the Bethe logarithm and its recoil correction for nS state of lithium with $n = 2, 3$. We use values calculated by Yan and Drake and collected in the paper [10]. For lithium states with $n = 4\ldots9$ we assume interpolated values using the formula $\ln k_0(n^2S_{1/2}) = \ln k_0(1^1S_0)_{\mathrm{Li}^+} + a/n^3$, where the constant a reproduces numerical value

TABLE I: Nonrelativistic energy $\mathcal{E}_0$ of the ground state and excited singlet S-states $n = 3...9$ for lithium atom.

Ω	N	$2S$	$3S$	$4S$	$5^1S_{1/2}$
10	4 172	-7.478 060 323 864 52	-7.354 098 421 319 29	-7.318 530 845 758 2	-7.303 551 578 678 0
11	6 412	-7.478 060 323 902 25	-7.354 098 421 422 84	-7.318 530 845 945 4	-7.303 551 579 120 3
12	9 576	-7.478 060 323 908 48	-7.354 098 421 439 14	-7.318 530 845 967 3	-7.303 551 579 195 5
13	13 944	-7.478 060 323 909 68	-7.354 098 421 441 50	-7.318 530 845 985 3	-7.303 551 579 213 7
13.6	15 952	-7.478 060 323 910 02	-7.354 098 421 442 66	-7.318 530 845 990 3	-7.303 551 579 219 0
13.10	30 632	-7.478 060 323 910 097			
∞		-7.478 060 323 910 2(2)	-7.354 098 421 443 2(4)	-7.318 530 845 994(2)	-7.303 551 579 222(3)
King [24]			-7.354 098 355	-7.318 530 816	-7.303 551 551
PP [22]		-7.478 060 323 448			
Sims, Hangstrom [25]		-7.478 060 323 452	-7.354 098 420 933	-7.318 530 845 331	-7.303 551 578 291
Stanke *et al.*[11]		-7.478 060 323 81	-7.354 098 421 113		
Yan *et al.* [10]		-7.478 060 323 892 4			
		$6S$	$7S$	$8S$	$9S$
10	4 172	-7.295 859 508 912 2	-7.291 392 268 995	-7.288 569 820 050	-7.286 673 539 36
11	6 412	-7.295 859 510 430 7	-7.291 392 273 172	-7.288 569 830 260	-7.286 673 578 96
12	9 576	-7.295 859 510 704 4	-7.291 392 273 915	-7.288 569 832 052	-7.286 673 584 90
13	13 944	-7.295 859 510 787 2	-7.291 392 274 112	-7.288 569 832 732	-7.286 673 586 35
13.6	15 952	-7.295 859 510 808 3	-7.291 392 274 160	-7.288 569 832 747	-7.286 673 586 71
∞		-7.295 859 510 815(6)	-7.291 392 274 22(5)	-7.288 569 832 76(9)	-7.286 673 587 1(3)
King [24]		-7.295 859 384			
Sims, Hangstrom [25]		-7.295 859 509 943	-7.291 392 273 116		

for $\ln k_0(3^2S_{1/2}) = 2.982\,36(6) + 2\ln(Z)$ with $\ln k_0(1^1S_0)_{\mathrm{Li}^+} = 2.982\,624\,6 + 2\ln(Z)$. The error bar of the interpolated value can be assumed conservatively for $4S$ as 150 % of the one for $3S$ state. For higher n uncertainties can be reduced significantly since the Bethe logarithm value is approaching fast to the asymptotic result. The similar analysis and resulting approach can be applied for recoil corrections to the Bethe logarithm. Other numerical mean values for Li^+ are taken from the recent work by Yerokhin and Pachucki [3]. These results for two-electron ions are obtained with much higher precision and their uncertainties can be neglected in the further analysis.

In Tables II and III we present numerical coefficients of the expansion for ionization potential and transition energies. For the states A and B we use

$$\nu_{A,B}^{(m,n)} = \mathcal{E}_A^{(m,n)} - \mathcal{E}_B^{(m,n)} \,. \tag{26}$$

TABLE II: Coefficients of expansion of ionization potential in powers of α and η in Li.

energy	$2S$	$3S$	$4S$	$5S$
$\nu^{(2,0)}$	$0.198\,146\,911\,241\,4(6)$	$0.074\,185\,008\,774\,5(11)$	$0.038\,617\,433\,335(12)$	$0.023\,638\,166\,56(3)$
$\nu^{(2,1)}$	$0.211\,013\,905\,524(3)$	$0.077\,249\,063\,623(3)$	$0.039\,780\,535\,98(3)$	$0.024\,197\,632\,87(5)$
$\nu^{(2,2)}$	$0.235\,286\,452\,52(3)$	$0.111\,626\,634\,4(4)$	$0.063\,438\,041(3)$	$0.040\,673\,914(5)$
$\nu^{(4,0)}$	$0.240\,534\,3(4)$	$0.061\,784\,2(18)$	$0.024\,249(2)$	$0.011\,831(3)$
$\nu^{(4,0)}_{\mathrm{fs}}$	$-0.870\,799\langle r^2_{\mathrm{ch}}\rangle$	$-0.204\,103\langle r^2_{\mathrm{ch}}\rangle$	$-0.077\,195\langle r^2_{\mathrm{ch}}\rangle$	$-0.037\,082\langle r^2_{\mathrm{ch}}\rangle$
$\nu^{(4,1)}$	$0.013\,50(3)$	$0.009\,749(3)$	$0.00463(1)$	$0.0026(2)$
$\nu^{(5,0)}$	$-2.858\,8(6)$	$-0.666(3)$	$-0.252(3)$	$-0.121(2)$
$\nu^{(5,1)}$	$-1.889(3)$	$-0.437(18)$	$-0.15(2)$	$-0.076(12)$
$\nu^{(6,0)}$	$-12.0(1.2)$	$-2.8(7)$	$-1.06(10)$	$-0.51(5)$
$\nu^{(7,0)}$	$147.(37)$	$32.(8)$	$12.(3)$	$5.4(14)$

energy	$6S$	$7S$	$8S$	$9S$
$\nu^{(2,0)}$	$0.015\,946\,098\,17(4)$	$0.011\,478\,861\,62(11)$	$0.008\,656\,420\,4(3)$	$0.006\,760\,174\,9(8)$
$\nu^{(2,1)}$	$0.016\,256\,776\,7(2)$	$0.011\,668\,857\,5(2)$	$0.008\,780\,947\,5(8)$	$0.006\,846\,157\,944$
$\nu^{(2,2)}$	$0.028\,239\,866(4)$	$0.020\,732\,792(12)$	$0.015\,861\,5(3)$	$0.012\,523\,281\,5$
$\nu^{(4,0)}$	$0.006\,71(2)$	$0.004\,25(3)$	$0.003\,25(7)$	$0.002\,6(3)$
$\nu^{(4,0)}_{\mathrm{fs}}$	$-0.020\,577\langle r^2_{\mathrm{ch}}\rangle$	$-0.012\,579\langle r^2_{\mathrm{ch}}\rangle$	$-0.008\,238\langle r^2_{\mathrm{ch}}\rangle$	$-0.005\,681\langle r^2_{\mathrm{ch}}\rangle$
$\nu^{(4,1)}$	$0.001\,8(2)$	$0.011(3)$	$0.008(3)$	$0.005(3)$
$\nu^{(5,0)}$	$-0.067(2)$	$-0.042\,0(11)$	$-0.027\,9(11)$	$-0.018\,9(11)$
$\nu^{(5,1)}$	$-0.042(12)$	$-0.027(10)$	$-0.018(6)$	$-0.013(4)$
$\nu^{(6,0)}$	$-0.28(3)$	$-0.17(2)$	$-0.114(11)$	$-0.078(8)$
$\nu^{(7,0)}$	$2.9(3)$	$1.8(5)$	$1.1(3)$	$0.8(2)$

All nonrelativistic and leading relativistic contributions are extrapolated results and their uncertainties are purely numerical. Coefficients $\nu^{(4,1)}$ are difficult to calculate precisely because of significant cancellation among involved states. Additionally, numerical instabilities become observable for states with higher n. Thus, in Tables II and III we have applied for $n \geq 7$ the interpolation rule analogous to the one for Bethe logarithm with $1/n^3$ dependence and asymptotics corresponding to $\mathrm{Li}^+(1\,^1S_0)$. Resulting predictions for leading QED effects are limited by numerical uncertainties of the Bethe logarithm and its recoil correction. Recoil corrections give very small contributions to the final results of the ionization potential and transition frequencies. They should be considered at the level of the systematic uncertainties. The most significant uncertainties originate from estimations of higher order QED corrections of 10% for $\nu^{(6,0)}$ and 25 % for $\nu^{(7,0)}$ and are presented in Tables II and III.

We are now at position to present theoretical predictions of ionization potentials and transi-

TABLE III: Coefficients of expansion of transition energy in powers of α and η in Li. Units are cm^{-1}.

energy	$3S-2S$	$4S-2S$	$5S-2S$	$6S-2S$
$\nu^{(2,0)}$	$0.123\,961\,902\,467(2)$	$0.159\,529\,477\,90(2)$	$0.174\,508\,744\,66(4)$	$0.182\,200\,813\,03(5)$
$\nu^{(2,1)}$	$0.133\,764\,841\,901(4)$	$0.171\,233\,369\,56(3)$	$0.186\,816\,272\,64(6)$	$0.194\,757\,128\,90(8)$
$\nu^{(2,2)}$	$0.123\,659\,818\,1(4)$	$0.171\,848\,410(3)$	$0.194\,612\,536(8)$	$0.207\,046\,585(4)$
$\nu^{(4,0)}$	$0.178\,751(2)$	$0.216\,286(3)$	$0.228\,704(3)$	$0.233\,815(3)$
$\nu^{(4,0)}_{\rm fs}$	$-0.666\,696\,\langle r^2_{\rm ch}\rangle$	$-0.793\,605\,\langle r^2_{\rm ch}\rangle$	$-0.833\,717\,\langle r^2_{\rm ch}\rangle$	$-0.850\,221(1)\,\langle r^2_{\rm ch}\rangle$
$\nu^{(4,1)}$	$0.003\,782(10)$	$0.008\,88(3)$	$0.010\,9(2)$	$0.012\,0(4)$
$\nu^{(5,0)}$	$-2.193(3)$	$-2.607(3)$	$-2.738(3)$	$-2.792(2)$
$\nu^{(5,1)}$	$-1.46(2)$	$-1.74(2)$	$-1.82(2)$	$-1.85(2)$
$\nu^{(6,0)}$	$-9.2(9)$	$-10.9(11)$	$-11.5(12)$	$-11.7(12)$
$\nu^{(7,0)}$	$115.(29)$	$135.(34)$	$141.(35)$	$144.(36)$

energy	$7S-2S$	$8S-2S$	$9S-2S$
$\nu^{(2,0)}$	$0.186\,668\,049\,5(2)$	$0.189\,490\,490\,6(4)$	$0.191\,386\,735\,9(9)$
$\nu^{(2,1)}$	$0.199\,345\,047\,9(3)$	$0.202\,232\,958\,0(6)$	$0.204\,167\,747\,6(12)$
$\nu^{(2,2)}$	$0.214\,553\,658(9)$	$0.219\,425\,02(8)$	$0.222\,762\,9(2))$
$\nu^{(4,0)}$	$0.236\,279(4)$	$0.237\,285(8)$	$0.236\,62(9)$
$\nu^{(4,0)}_{\rm fs}$	$-0.858\,220(2)\,\langle r^2_{\rm ch}\rangle$	$-0.862\,560(4)\,\langle r^2_{\rm ch}\rangle$	$-0.865\,118(8)\,\langle r^2_{\rm ch}\rangle$
$\nu^{(4,1)}$	$0.012\,6(3)$	$0.012\,9(3)$	$0.013\,1(2)$
$\nu^{(5,0)}$	$-2.818(2)$	$-2.831(1)$	$-2.840(1)$
$\nu^{(5,1)}$	$-1.87(1)$	$-1.87(1)$	$-1.87(1)$
$\nu^{(6,0)}$	$-11.8(12)$	$-11.9(12)$	$-11.9(12)$
$\nu^{(7,0)}$	$145.(36)$	$146.(37)$	$146.(37)$

tion frequencies for different isotopes of lithium. We consider the stable ^{6}Li and ^{7}Li with masses in atomic units $6.015122794(16)$ [33], $7.0160034256(45)$ [34] and nuclear charge radii in fermii $2.540(28)$ [35], $2.390(30)$ [36] respectively. Final results are presented in Table IV. The uncertainties of the ionization potentials for the states with low n are coming from estimations of higher QED effects and numerical uncertainty of leading QED from the Bethe logarithm. For higher n, only the second uncertainty is important. It is different for transition frequencies, where the unknown higher QED corrections are dominating, nevertheless the Bethe logarithm uncertainty is at the moment the bottleneck of theoretical predictions.

In comparison to other theoretical values including relativistic and QED effects, especially with those by Yan *et al.* [10] obtained in Hylleraas basis set, we observe good agreement for IP($2S$) and $\nu(3S-2S)$. However. there are no published analogous results for the higher excited states. In comparison to recent experimental values we observe that theoretical predictions are about two orders of magnitude less accurate than measurements of IP($2S$) by Bushaw *et al.* [13], $\nu(3S-2S)$

by Sanchez *et al.* [15, 31] and $\nu(4S-2S)$ by DeGraffenreid and Sansonetti [16]. This indicates the necessity for further development in theoretical methods to improve the numerical accuracy of Bethe logarithms and to complete evaluation of QED effects at $m\,\alpha^6$ order. For higher excited states there are no as precise measurement as those mentioned above. For transition energies with $n=5,6$ we observe discrepancies of our theoretical predictions with experimental value by Radziemski *et al.* [12]. We guess that these experimental values are not so accurate as claimed. This situation is probably similar to that in the transition $\nu(4S-2S)$, where DeGraffenreid and Sansonetti [16] have already corrected the former experimental value in [12].

V. SUMMARY

We have performed precise calculation of the nonrelativistic, leading relativistic and QED contributions to ionization energies of low lying S-states in the Li atom. Higher order relativistic and QED corrections are calculated approximately using the known formulas for the hydrogen atom. Obtained results are much more accurate than any previously published calculations, and in generally are in good agreement with experimental values. The discrepancies with Radziemski *et al.* [12] for higher excited states of Li suggests the need of experimental verification.

Acknowledgments

Authors acknowledge support by NIST Precision Measurement Grant No. PMG 60NANB7D6153. D.K. acknowledges additional support from Nicolaus Copernicus University, grant No. 371-CH

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TABLE IV: The ionization and the transition energies for ^{6}Li and ^{7}Li in units cm^{-1}. The results for IP $(2S)$ and the transition frequency $\nu(3S-2S)$ for ^{7} Li were obtained previously in Ref. [9]. The second column refers to the type of the work, experimental versus theoretical.

n	e/t	$\nu(nS-2S)$	IP(nS)	$\nu(nS-2S)$	IP(nS)
		^{6} Li		^{7} Li	
2	t		43 486.556 4(8)		43 487.159 0(8)
Yan *et al.* [10]	t				43 487.158 3(10)
Bushaw *et al.*[30]	e				43 487.159 40(18)
3	t	27 205.711 7(7)	16 280.844 8(4)	27 206.093 7(7)	16 281.065 4(4)
Stanke *et al.*[11]	t	27 205.710 45		27 206.092 41	
Yan *et al.* [10]	t	27 205.711 5(10)		27 206.093 6(10)	
Radziemski *et al.* [12]	e	27 205.712 9(10)		27 206.095 2(10)	
Reinhardt *et al.* [14]	e	27 205.711 5(9)		27 206.094 04(9)	
Sanchez *et al.* [15]	e	27 205.712 014(8)		27 206.094 082(6)	
Sanchez *et al.* [31]	e	27 205.712 013(6)			
4	t	35 011.544 5(8)	8 475.011 9(4)	35 012.033 6(8)	8 475.125 5(4)
Lorenzen, Niemax [32]	e			35 012.033 7(7)	
Radziemski *et al.* [12]	e	35 011.543 2(10)		35 012.032 6(10)	
DeGraffenreid, Sansonetti [16]	e	35 011.544 497(30)		35 012.033 582(26)	
5	t	38 298.935 3(8)	5 187.621 2(4)	38 299.468 8(8)	5 187.690 0(4)
Radziemski *et al.* [12]	e	38 298.928 3(10)		38 299.462 7(10)	
6	t	39 987.045 2(8)	3 499.511 2(3)	39 987.601 5(8)	3 499.557 6(3)
Radziemski *et al.* [12]	e	39 987.027(4)		39 987.586(3)	
7	t	40 967.425 0(8)	2 519.131 2(2)	40 967.994 4(8)	2 519.164 7(2)
8	t	41 586.832 2(8)	1 899.724 4(2)	41 587.409 8(8)	1 899.749 5(2)
9	t	42 002.963 1(8)	1 483.593 3(1)	42 003.546 2(8)	1 483.612 7(1)

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