Bethe Logarithm and QED Shift for Lithium

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A novel finite basis set method is used to calculate the Bethe logarithm for the ground $2\,^2S_{1/2}$ and excited $3\,^2S_{1/2}$ states of lithium. The basis sets are constructed to span a huge range of distance scales within a single calculation, leading to well-converged values for the Bethe logarithm. The results are used to calculate an accurate value for the complete quantum electrodynamic energy shift up to order α^3 Ry. The calculated $3\,^2S_{1/2}$–$2\,^2S_{1/2}$ transition frequency for ^{7}Li is 27 206.092 6(9) cm^{-1}, and the ionization potential for the $2\,^2S_{1/2}$ state is 43 487.158 3(6) cm^{-1}. The ^{7}Li–^{6}Li isotope shift is also considered, and all the results compared with experiment.

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The exquisite accuracy of modern atomic transition frequency measurements has the potential to create new measurement tools for other purposes, such as measurement of the nuclear charge radius, or determination of the fundamental constants, provided that the underlying atomic theory is sufficiently well understood. For simple atoms such as helium and lithium, the nonrelativistic energies and lowest-order relativistic corrections can be calculated to spectroscopic accuracy [1–3], but the quantum electrodynamic (QED) corrections still represent a major obstacle to further progress. The principal difficulty is the calculation of the so-called Bethe logarithm, which determines the dominant part of the electron self-energy. This long-standing problem in atomic physics has been solved for hydrogen [4], and recently also for helium [5], but no results of useful accuracy have been obtained for any of the heavier atoms. The calculation is exceptionally difficult because the dominant contribution comes from a sum over inner shell excitations to intermediate states lying high in the photoionization continuum. In addition, high accuracy is required since the first few significant figures in the Bethe logarithm are state independent, and so cancel from the physically relevant transition frequencies.

The purpose of this Letter is to report the first complete account of the QED shift up to terms of order α^3 Ry for lithium, and to compare the results with recent high precision measurements. The mass-dependent part of the QED shift plays a key role in several recent proposals to use the isotope shift in lithium to measure the nuclear charge radius for exotic nuclei such as ^{11}Li.

For low-Z atoms and ions (where Ze is the nuclear charge), it is useful to expand the total energy of an atomic state in the form

$$E = E_{\rm NR} + E_{\rm rel} + E_{\rm QED}, \tag{1}$$

where $E_{\rm NR}$ is the nonrelativistic energy from the Schrödinger equation, $E_{\rm rel}$ is the lowest-order α^2 Ry relativistic correction from the Breit-Pauli interaction, and $E_{\rm QED}$ is the QED shift of order α^3 Ry (including $\ln\alpha$ terms) and higher. In addition to the expansion in powers of α, each of the terms in Eq. (1) has an expansion in powers of μ/M of the form

$$T = T^{(0)} + (\mu/M)T^{(1)} + \cdots, \tag{2}$$

where $\mu/M = m_{\rm e}/(m_{\rm e} + M)$ is the ratio of the electron reduced mass to the nuclear mass. Since $E_{\rm NR}$ and $E_{\rm rel}$ are known to sufficient accuracy from previous work, we will focus our attention on $E_{\rm QED}$, given by

$$E_{\rm QED} = E_{L,1} + E_{L,2} + E_{\rm HO}, \tag{3}$$

where $E_{L,1}$ and $E_{L,2}$ represent the lowest-order α^3 Ry electron-nucleus and electron-electron terms, respectively, and $E_{\rm HO}$ represents higher-order terms of $O(\alpha^4)$ Ry and higher. $E_{L,1}$ is given by the Kabir-Salpeter formula [6]

$$E_{L,1} = \frac{4}{3}\alpha^3 Z \sum_i \langle\delta(\mathbf{r}_i)\rangle\left[\ln(\alpha)^{-2} - \beta(nLS) + \frac{19}{30}\right], \tag{4}$$

where $\beta(nLS) \equiv \ln k_0(nLS)$ is the Bethe logarithm for a state with principal, angular momentum, and spin quantum numbers n, L, and S, respectively, and $E_{L,2}$ accounts for the Araki-Sucher terms [7]

$$E_{L,2}(nLS) = \left(\frac{14}{3}\ln\alpha + \frac{164}{15}\right)\sum_{i>j}\langle\delta(\mathbf{r}_{ij})\rangle - \frac{14}{3}Q, \tag{5}$$

where

$$Q = \frac{1}{4\pi}\sum_{i>j}\lim_{a\to 0}\langle r_{ij}^{-3}(a) + 4\pi(\gamma + \ln a)\delta(\mathbf{r}_{ij})\rangle, \tag{6}$$

γ is Euler's constant, and $r_{ij}^{-3}(a) = 0$ for $r_{ij} < a$. The leading higher-order terms in a hydrogenic approximation are

$$E_{\mathrm{HO}} = \tfrac{4}{3}\alpha^3 Z \sum_i \langle \delta(\mathbf{r}_i)\rangle [(3\pi\alpha Z)0.765\,406 + 0.404\,17\alpha/\pi + \cdots]. \quad (7)$$

All of the above terms can be readily calculated if accurate wave functions are available, with the exception of the Bethe logarithm defined by

$$\beta(nLS) = \frac{\mathcal{N}}{\mathcal{D}} \equiv \frac{\sum_n |\langle 0|\mathbf{p}|n\rangle|^2 (E_n - E_0)\ln|E_n - E_0|}{\sum_n |\langle 0|\mathbf{p}|n\rangle|^2 (E_n - E_0)}, \quad (8)$$

where $\langle \mathbf{r}_1, \mathbf{r}_2|0\rangle \equiv \Psi_0(\mathbf{r}_1, \mathbf{r}_2)$ refers to the nonrelativistic wave function of the state in question, and the sum over n covers all virtual intermediate states connected to $|0\rangle$ by the dipole transition operator $\mathbf{p} = \sum_i \mathbf{p}_i$ expressed in the momentum gauge.

The Bethe logarithm is difficult to calculate because the energy difference inside the summation weights very highly excited states. In fact, as shown in Ref. [5] for H and He, the partial sums up to energy E increase almost linearly with $\ln E$ up to about 10^6 eV, and one must go to much higher energies still ($\sim 10^{20}$ eV) to get a value accurate to several significant figures. The partial sums for Li are nearly the same. In addition, the dominant hydrogenic part of the Bethe logarithm comes from excitations of the inner $1s$ electron, not the more obvious valence electron usually associated with optical excitations. Usual methods of calculation based on pseudostate representations for the intermediate states fail because the highest energy represented in the pseudostate representation is typically 1000 eV or less, which is far below the region of maximum contribution to the Bethe logarithm.

Because of this lack of sufficiently high energies in the pseudostate expansion, the only method of calculation available until recently was an integral transformation method suggested by Schwartz [8] and employed by Baker *et al.* [9], Korobov [10], and Pachucki and Sapirstein [11] for helium. However, it is computationally very slow and difficult to implement. To avoid this problem, we have recently introduced a modified version of the pseudostate expansion method in which multiple layers of basis functions are constructed to cover a huge range of distance scales, and, correspondingly, a huge range of energy scales up to 10^{20} eV or more. Despite this huge range, the total basis set still remains reasonably compact, thus providing a very efficient and computationally tractable method of completing the sum over intermediate states for the Bethe logarithm.

Consider the ground $1s^2 2s\,^2S_{1/2}$ state of Li as an example (we will use the abbreviated notation $2\,^2S_{1/2}$). It is connected by electric dipole transitions to a complete set of intermediate ^2P states, with excitations of the inner $1s$ electrons being particularly important. In the pseudostate method, the actual spectrum of intermediate states is replaced by a set of pseudostates corresponding to the complete set of eigenvectors of the generalized eigenvalue problem for the Hamiltonian matrix expressed in a nonorthogonal finite basis set of functions. In the present case, the basis functions of ^2P symmetry are constructed according to

$$r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} \exp(-\alpha_t r_1 - \beta_t r_2 - \gamma_t r_3) \mathcal{Y}^{LM}_{(l_1 l_2)l_{12}, l_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (9)$$

where t labels different sets of nonlinear parameters, and $\mathcal{Y}$ denotes a vector coupled product of spherical harmonics. As described by Yan and Drake [2], the ranges of possible values for j_{12}, j_{23}, and j_{31} are divided into five sectors with separately optimized nonlinear parameters in each sector. For each sector, the basis set is generated such that $j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \le \Omega_t$, , where Ω_t is an integer. For the first five sets,

$$(l_1, l_2, l_3) = (0, 0, 1), \quad (10)$$

$$(\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5) = (2, 2, 2, 2, 3), \quad (11)$$

which gives rise to a total of 19 terms (see Table I of Ref. [2]). The nonlinear parameters are exactly the same as those for the ground state [2]. This forms the ground layer of longest range basis functions. The next step is to augment the ground layer with successive layers of shorter range functions of the form

$$r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{[-Zr_1 - (Z-1)g^K r_2 - (Z-2)r_3/n]} \times \mathcal{Y}^{LM}_{(l_1 l_2)l_{12}, l_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3), \quad (12)$$

with $K = 0, \ldots, \Omega$ and Ω is a given integer. In the above, n is the principal quantum number of the outer electron in the state of interest, Z is the nuclear charge, $(l_1, l_2, l_3) = (0, 1, 0)$, and $g = 9$. Thus, the distance scale grows progressively shorter with increasing K for the p electron. The basis is generated such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \le \Omega - K + 2, \quad (13)$$

so that the numbers of terms progressively decrease with increasing K. The result is to build a pyramid of basis functions with each layer of the pyramid having fewer terms and a shorter distance scale in proportion to $1/g^K$ for the p electron. After diagonalization, the energy of the highest pseudostate is of the order of $g^{2\Omega}$ Ry. In order to assess the convergence, a series of calculations is done with Ω increasing from 2 to 6. The value $g = 9$ is chosen to optimize the rate of convergence.

A further important subtlety in building the basis set is to include the $j_2 = 0$ term for the p electron. This is one power of r more singular than the usual $r\cos\theta$ behavior for p electrons at the origin, but terms of this type are

TABLE I. Convergence study for the Bethe logarithm for the ground state of lithium. N is the number of terms in the basis set.

Ω	N	$\beta^{(0)}$	Difference	Ratio	$2\pi Z\sum_i\langle\delta(\mathbf{r}_i)\rangle$
2	87	2.846 5271			260.4295
3	207	2.964 2629	0.117 735 7		260.8115
4	459	2.978 9857	0.014 722 8	8.00	260.8878
5	937	2.980 7196	0.001 733 9	8.49	260.9097
6	1763	2.980 9043	0.000 184 7	9.39	260.9176
Extrapolation		2.980 925(3)	0.000 021(3)		260.924(2)
Exact [3]					260.927 045

known to be part of the exact analytic solution for a hydrogen atom with a $\delta(\mathbf{r})$ perturbation [12].

Table I shows the pattern of convergence of the Bethe logarithm for the $2\,^2S_{1/2}$ state of lithium, calculated in the acceleration gauge. The numbers in the fourth column are the differences between successive calculations, and the numbers in the fifth column are the ratios of differences. As in the hydrogenic case [5], the series converges approximately as a geometric series that can readily be extrapolated to infinity. Assuming that the ratios for Li similarly remain approximately constant, the extrapolated value for infinite nuclear mass is $\beta^{(0)} = 2.980\,925(3)$, with k_0 in units of Z^2 Ry. For comparison, the values for $\mathrm{Li}^+(1s^2\,^1S)$ and $\mathrm{Li}^{++}(1s)$ are 2.982 624 56 and 2.984 128 56, respectively [5], indicating that an accuracy of 0.06% in $\beta^{(0)}$ is needed just to get the first figure correct in the contribution to the ionization energy.

As a check on the accuracy, the last column of Table I shows the value of the denominator $\mathcal{D}$ in Eq. (8), which by an exact sum rule is equal to the matrix element $\mathcal{D} \rightarrow 2\pi Z\sum_i\langle\delta(\mathbf{r}_i)\rangle$ if the sum over intermediate states is complete. The good agreement for the extrapolated value indicates that the pseudospectrum provides an adequate representation of the intermediate states.

Similar calculations were performed for the $1s^2 3s\,^2S_{1/2}$ state, and then all the calculations were repeated for the finite nuclear mass case in order to calculate the coefficient of the mass-dependent correction (due to mass polarization) by differencing. The determination of this quantity is of key importance for applications to isotope shifts and the determination of the nuclear charge radius. The results of all the calculations are summarized in Table II.

TABLE II. Summary of results for the lithium Bethe logarithm, expressed in the form $\beta = \beta^{(0)} + (\mu/M)\beta^{(1)} + \ln(Z^2\mu/m_e)$.

State	$\beta(0)$	$\beta^{(1)}$
$\mathrm{Li}(1s^2 2s\,^2S_{1/2})$	2.980 925(3)	0.1136(2)
$\mathrm{Li}(1s^2 3s\,^2S_{1/2})$	2.982 40(4)	0.111(1)
$\mathrm{Li}^+(1s^2\,^1S_0)$	2.982 624 55(4)[a]	0.109 55(4)[a]

[a] Drake and Goldman [5].

With these results in hand, it is now possible to perform a complete calculation of the ionization energy for the $2\,^2S_{1/2}$ state, and the $3\,^2S_{1/2}$–$2\,^2S_{1/2}$ transition energy, complete through terms of order α^3 Ry. Also, the dominant one-electron part of the higher-order QED corrections can be included, as shown in Eq. (7). The results shown in Table III combine the present QED terms with previous results for the lower order terms [3]. The mass-dependent expansion coefficients are displayed explicitly, with the superscripts being the powers of μ/M as shown in Eq. (2). With these results, the transition energies and isotope shifts can be calculated for any of the isotopes of lithium.

As an example, the contributions to the $3\,^2S_{1/2}$–$2\,^2S_{1/2}$ transition frequency and the ionization potential for the $2\,^2S_{1/2}$ state of ^{7}Li are listed in Table IV, and compared with the recent high precision measurement of Radziemski [13] for the transition frequency, and the older value from Moore [14] for the ionization potential.

TABLE III. Mass-dependent expansion coefficients for contributions to the lithium $1s^2 3s\,^2S$–$1s^2 2s\,^2S$ transition energy and $1s^2 2s\,^2S$ ionization potential (I.P.). For the finite nuclear size correction, the form is $E_{\mathrm{nuc}} = [C^{(0)}_{r^2_{\mathrm{rms}}} + (\mu/M)C^{(1)}_{r^2_{\mathrm{rms}}}]r^2_{\mathrm{rms}}$ with r_{rms} in units of the Bohr radius. Units are $2R_\infty$.

Term	$3\,^2S_{1/2}$–$2\,^2S_{1/2}$	$2\,^2S_{1/2}$ I.P.
$E^{(0)}_{\mathrm{NR}}$	0.123 961 902 501(19)	0.198 146 910 981(7)
$E^{(1)}_{\mathrm{NR}}$	−0.133 764 851 4(3)	−0.211 013 907 61(25)
$E^{(2)}_{\mathrm{NR}}$	0.123 648 10(29)	0.235 286 29(17)
$E^{(0)}_{\mathrm{rel}}$	0.000 009 518 3(18)	0.000 012 809 37(6)
$E^{(1)}_{\mathrm{rel}}$	−0.000 002 2(6)	−0.000 000 6(5)
$E^{(0)}_{L,1}$	−0.000 000 904 9(22)	−0.000 001 177 01(16)
$E^{(1)}_{L,1}$	0.000 000 772(7)	0.000 001 025(6)
$E^{(0)}_{L,2}$	0.000 000 048 61(12)	0.000 000 062 80(12)
$E^{(1)}_{L,2}$	−0.000 000 131(24)	−0.000 000 167(24)
$E^{(0)}_{\mathrm{HO}}$	−0.000 000 024(3)	−0.000 000 032(3)
$C^{(0)}_{r^2_{\mathrm{rms}}}$	−0.666 646(5)	−0.870 791 5(3)
$C^{(1)}_{r^2_{\mathrm{rms}}}$	1.980 1(19)	2.576 23(19)

TABLE IV. Contributions to the ^{7}Li $1s^23s\,^2S$–$1s^22s\,^2S$ transition energy and $1s^22s\,^2S$ ionization potential (I.P.), in units of cm^{-1}.

Term	$3\,^2S_{1/2}$–$2\,^2S_{1/2}$	$2\,^2S_{1/2}$ I.P.
$E_{\rm NR}^{(0)}$	27 206.492 856(4)	43 488.220 244 9(16)
$E_{\rm NR}^{(1)}\mu/M$	−2.295 854 30(16)	−3.621 707 668(4)
$E_{\rm NR}^{(2)}(\mu/M)^2$	0.000 165 962	0.000 315 803
$E_{\rm rel}^{(0)}$	2.089 0(4)	2.811 33(2)
$E_{\rm rel}^{(1)}\mu/M$	−0.000 04(1)	−0.000 011(9)
$E_{L,1}^{(0)}$	−0.198 6(3)	−0.258 32(3)
$E_{L,2}^{(0)}$	0.010 747	0.013 884
$E_{\rm HO}^{(0)}$	−0.005 4(4)	−0.007 0(4)
$E_{\rm nuc}$	−0.000 298(8)	−0.000 389(10)
Total	27 206.092 6(9)	43 487.158 3(6)
Experiment	27 206.095 2(10)[a]	43 487.150(5)[b]
Difference	−0.002 6(19)	0.008(5)

[a] Radziemski *et al.* [13].
[b] Moore [14].

The values of the fundamental constants and physical data used for ^{6}Li and ^{7}Li are

$$\begin{aligned} R_\infty &= 109\,737.315\,685\,49(83)\ \text{cm}^{-1}, \\ \alpha &= 1/137.035\,999\,76(50), \\ \mu/M(^6\text{Li}) &= 9.121\,676\,23(76)\times 10^{-5}, \\ \mu/M(^7\text{Li}) &= 7.820\,202\,24(56)\times 10^{-5}, \\ r_{\rm rms}(^6\text{Li}) &= 2.55(4)\ \text{fm}, \\ r_{\rm rms}(^7\text{Li}) &= 2.39(3)\ \text{fm}, \end{aligned}$$

where $r_{\rm rms}$ is the rms nuclear charge radius. The comparison for the transition frequency shows a marginal disagreement of $-0.0026(19)$ cm^{-1}, but the agreement is certainly good enough to indicate that the calculated ionization potential of 43 487.1583(6) cm^{-1} is considerably more accurate than the experimental value. The dominant uncertainty is due to $E_{\rm HO}$ in Table IV.

The calculated ^{7}Li–^{6}Li isotope shift of 11 454.25(5) MHz for the $3\,^2S_{1/2}$–$2\,^2S_{1/2}$ transition agrees with the recently measured value 11 453.734(30) MHz [15] to within the ±0.4 MHz ($\pm 1.3\times 10^{-5}$ cm^{-1}) uncertainty in the calculated value due to the nuclear size correction [3]. Thus, the comparison between theory and experiment for the $3\,^2S_{1/2}$–$2\,^2S_{1/2}$ transition in ^{6}Li shows exactly the same marginal disagreement of $-0.0026(19)$ cm^{-1} as in ^{7}Li. The cause of the discrepancy must therefore be either a mass independent term in the theory or a systematic frequency shift in the measurements.

In summary, the results illustrate the use of a novel discrete basis set method that spans a huge range of energy scales within a single calculation. Similar techniques may prove to be useful in a wide variety of other applications in which many different distance or energy scales must be taken into account simultaneously. The results for the QED shift provide a standard of reference to check approximation methods that can be applied to more complex systems. For example, estimates based on the hydrogenic Lamb shift with a screened nuclear charge [16] tend to seriously underestimate the QED shift [17]. The particular significance of the results for lithium is that the accurately calculated Bethe logarithms, and their mass dependence, remove the main source of uncertainty in calculating the QED contribution to the isotope shift. This opens the way to the use of isotope shifts as a reliable method of measuring the nuclear charge radius in exotic nuclei such as ^{11}Li [15].

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Note added.—Similar results for the Bethe logarithm of the $2\,^2S$ state of lithium have recently been reported by Pachucki and Komasa [18].

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