Bethe logarithm for lithium atom from exponentially correlated Gaussian functions

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Abstract

The calculation of Bethe logarithm for the ground state of the lithium atom is presented. The Bethe logarithm is the main QED effect coming from the electron self-interaction, which has not been obtained yet. Both results for the infinite nuclear mass, $\ln k_0 = 5.178\,17(3)$, and the mass polarization correction, $\Delta \ln k_0 = 0.114(3)$, significantly improve the hitherto theoretical values for the lithium ground state energy. They allow from one side, to test the theory against precise measurements of transition frequencies and from the other side, to improve the accuracy of determination of the difference in the square of nuclear charge radii from the isotope-shift measurements. The applied calculational method is based on the well adapted explicitly correlated Gaussian basis set and can be extended to other few-electron atoms and molecules.

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I. INTRODUCTION

The calculation of the influence of the electron self-energy on energy levels in few-electron atoms is a nontrivial task. Several approaches have been developed, depending on the charge of the nucleus and the number of electrons. For alkali metals QED effects are calculated within the approximation which relies on some effective potential to account for screening of the electron-nucleus interactions. This approach is pursued by Sapirstein and coworkers in [1] and several promising results have been obtained for radiative energy shift and hyperfine splitting. The limitation of this method is the lack of incorporation of electron correlations. In few-electron heavy ions QED effects are studied systematically in powers of the fine structure constant, where the electron-electron interaction is treated perturbatively as the electron self-energy [2]. For atoms with more complicated electronic structure, the QED effects are obtained in an approximate way by scaling the hydrogenic result [3]. However, for light atoms with only a few electrons, the calculation of the electron self-energy is possible within the so-called $Z\,\alpha$ expansion. In the simplest case of the hydrogen atom, calculations of the QED effects, as initiated by Bethe in [4], have reached at present the accuracy of 10^{-7} [5], where uncertainties from the nuclear structure become dominant. The leading QED effects in helium have been derived by Araki [6] and by Sucher [7]. Since their original derivation based on the Bethe-Salpeter equation has been quite complicated, a simplified derivation has been presented in [8]. Apart from the effects which are similar to that in hydrogen, for example the electron self-energy, there is an electron-electron interaction beyond the Coulomb one, which contributes to the energy shift. Although the derivation requires a relativistic formalism, the final formula makes use of some nonrelativistic but singular operators acting on the nonrelativistic Schrödinger wave function. The result can be easily extended to any light atom and takes the form

$$
\begin{aligned}
E_L \;=\; & \sum_{i>j}\biggl\{\left[\frac{164}{15}+\frac{14}{3}\,\ln\alpha\right]\,\frac{\alpha^2}{m^2}\,\langle\delta(\boldsymbol{r}_{ij})\rangle \\
& -\frac{14}{3}\,m\,\alpha^5\,\left\langle\frac{1}{4\,\pi}\,P\left(\frac{1}{(m\,\alpha\,r_{ij})^3}\right)\right\rangle\biggr\} \\
& +\left[\frac{19}{30}+\ln(\alpha^{-2})-\ln k_0\right]\,\frac{4\,\alpha^2\,Z}{3\,m^2}\,\Bigl\langle\sum_i\delta(\boldsymbol{r}_i)\Bigr\rangle.
\end{aligned}
\tag{1}
$$

Here, Z is the atomic number, α the fine-structure constant, m the mass of the electron, $\boldsymbol{\sigma}_i$ Pauli matrices corresponding to the ith electron, and δ means the Dirac delta function.

The distribution P is defined as the limit

$$\left\langle \phi \left| P\left(\frac{1}{r^3}\right) \right| \psi \right\rangle \equiv \qquad (2)$$
$$\lim_{a\to 0} \int d\boldsymbol{r}\, \phi^*(\boldsymbol{r})\, \psi(\boldsymbol{r}) \left[\frac{1}{r^3}\, \Theta(r-a) + 4\,\pi\, \delta(\boldsymbol{r})\,(\gamma + \ln a)\right] ,$$

with Θ and γ being the step function and the Euler constant, respectively. The n-electron Bethe logarithm, ln k_0, is defined by ($\boldsymbol{\nabla} = \sum_i \boldsymbol{\nabla}_i$)

$$\ln k_0 \;=\; -\frac{1}{D} \left\langle \boldsymbol{\nabla}\,(H-E)\, \ln\left[\frac{2\,(H-E)}{m\,\alpha^2}\right] \boldsymbol{\nabla} \right\rangle, \qquad (3)$$
$$D \;=\; 2\,\pi\,\alpha\, Z \left\langle \sum_i \delta(\boldsymbol{r}_i) \right\rangle. \qquad (4)$$

This formula gives an exact correction to the energy for the S-states of the order of $m\,\alpha^5$ and thus accounts for electron correlations as long as the wave function does. It means that if one is able to represent accurately the nonrelativistic wave function, as it is possible for few electron atoms and molecules [9], then the QED effects could be precisely calculated. There are additional terms for the P-states which come from the anomalous magnetic moment of the electron [10], they are not presented here, since we concentrate on the S-states only. The most interesting is the Bethe logarithm, $\ln k_0$, since all other terms in Eq. (1) have already been very precisely calculated in [11]. The Bethe logarithm involves the infinite sum over excited states which happens to converge very slowly. Schwartz in [12] has introduced a very effective approach to calculate the Bethe logarithm through the integral representation. Since we followed his approach, we will describe it in details in the next section. The recent progress in the evaluation of the QED effects in helium is due to the use of a well adapted explicitly correlated exponential [13] or Gaussian basis sets [14]. In a different approach Drake and Goldman using the multiple scale Hylleraas basis set obtained a very precise Bethe logarithm value directly through the diagonalization of the large Hamiltonian matrix [15]. While this approach is very suited for helium, the use of the Hylleraas basis set for larger atoms drastically increases the level of the complexity. Our aim is to show that with the well optimized Gaussian basis set one is able to accurately calculate the QED effects in light, few-electron atoms. We demonstrate this approach on two examples of the helium and lithium atoms. Hereinafter we shall use the reduced atomic units.

II. METHOD OF COMPUTATION

A. Schwartz's method

The Bethe logarithm as defined in Eq. (3), using the identity

$$x\,\ln x = \int_0^{\kappa_1}\left(\frac{k}{k+x}-1\right)dk + \int_{\kappa_1}^{\infty}\left(\frac{k}{k+x}-1+\frac{x}{k}\right)dk + x\,\ln\kappa_1\,, \tag{5}$$

can be represented as follows

$$\ln k_0 = (2\pi Z\langle\delta\rangle)^{-1}\left[\int_0^{\kappa_1} k J(k)\,dk + \kappa_1\langle\boldsymbol{\nabla}^2\rangle + \int_{\kappa_1}^{\infty} W(k)/k\,dk\right] + \ln\kappa_1\ , \tag{6}$$

where for the ground state Ψ the following notation was used $\langle\delta\rangle = \langle\Psi\,|\sum_i\delta(\mathbf{r}_i)|\,\Psi\rangle$ and $\langle\boldsymbol{\nabla}^2\rangle = \left\langle\Psi\left|(\sum_i\boldsymbol{\nabla}_i)^2\right|\Psi\right\rangle$, and where the two one-dimensional functions appearing in the integrands are defined as

$$\begin{aligned} J(k) &= \sum_i \frac{|\langle\Psi|\boldsymbol{\nabla}|\Psi_i\rangle|^2}{E_i - E + k}\ , &(7)\\ W(k) &= k^2 J(k) + k\langle\boldsymbol{\nabla}^2\rangle + 2\pi Z\langle\delta\rangle\ . &(8)\end{aligned}$$

The summation in (7) runs over the whole spectrum of the Hamiltonian H, with eigenstates Ψ_i of energy E_i. The advantage of the representation in Eqs. (6)-(8) is the fact that the resulting matrix elements can be calculated very accurately and the large-k asymptotic form is known,

$$W(k) \sim \frac{4\pi Z^2\langle\delta\rangle}{k}\left(\sqrt{2k} - Z\ln k + \sum_{m=0}^{\mathcal{M}} a_m k^{-m/2}\right)\ . \tag{9}$$

The calculation of the J function does not require the knowledge of the full spectrum. Instead one constructs the perturbed wave function $\tilde{\boldsymbol{\Psi}}$, defined as

$$|\tilde{\boldsymbol{\Psi}}\rangle = \sum_i \frac{|\Psi_i\rangle\,\langle\Psi_i|\boldsymbol{\nabla}|\Psi\rangle}{E - E_i - k} \tag{10}$$

which fulfills the differential equation

$$(E - H - k)\tilde{\boldsymbol{\Psi}} = \boldsymbol{\nabla}\Psi. \tag{11}$$

The unknown function can be obtained by a minimization of the corresponding Hylleraas functional [16, 17]

$$\mathcal{J}_k\left[\tilde{\boldsymbol{\Psi}}\right] = \langle\tilde{\boldsymbol{\Psi}}\,|H - E + k|\,\tilde{\boldsymbol{\Psi}}\rangle + 2\langle\tilde{\boldsymbol{\Psi}}\big|\boldsymbol{\nabla}\big|\Psi\rangle \tag{12}$$

with the energy, E, and the Hamiltonian

$$H = -\sum_i \left\{ \frac{\boldsymbol{\nabla}_i^2}{2} + \frac{Z}{|\boldsymbol{r}_i|} \right\} + \sum_{i>j} \left\{ \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{\mu}{M} \boldsymbol{\nabla}_i \boldsymbol{\nabla}_j \right\}, \tag{13}$$

where M and μ are the nuclear and the reduced mass, respectively. Having $\tilde{\boldsymbol{\Psi}}$, the J function is obtained from

$$J(k) = \langle \Psi | \boldsymbol{\nabla} | \tilde{\boldsymbol{\Psi}} \rangle. \tag{14}$$

B. The wave functions

In this work we employ the method of exponentially correlated Gaussian (ECG) wave functions [9, 18–20]. Both the unperturbed, Ψ, and the first-order correction, $\tilde{\boldsymbol{\Psi}}$, wave functions are expressed in the form of K-term linear combinations of the multi-electron basis functions, $\psi_l(\mathbf{r})$,

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \hat{\mathcal{A}} \left(\Xi_{n,S,M_S}(\boldsymbol{\sigma}) \sum_{l=1}^{K} c_l\, \psi_l(\mathbf{r}) \right). \tag{15}$$

The operator $\hat{\mathcal{A}}$ ensures the antisymmetry of the total wave function with respect to the exchange of the electrons. The $\Xi_{n,S,M_S}(\boldsymbol{\sigma})$ is an n-electron spin eigenfunction with the quantum numbers S and M_S, and $\boldsymbol{\sigma}$ and $\mathbf{r}$ are the n-electron vectors in spin and coordinate spaces. The spatial basis functions, $\psi_l(\mathbf{r})$, are the n-electron atomic Singer functions [21] of the S and P symmetry, respectively:

$$\psi_l(\mathbf{r}) = \exp\left[-\mathbf{r}\, \mathbf{A}_l\, \mathbf{r}^T \right], \tag{16}$$

$$\tilde{\psi}_l(\mathbf{r}) = y_{m_l} \exp\left[-\mathbf{r}\, \tilde{\mathbf{A}}_l\, \mathbf{r}^T \right], \tag{17}$$

with y_{m_l} being the Cartesian component of the coordinate of the electron labeled m_l. The linear, c_l, and the nonlinear, $\mathbf{A}_{l,ij}$, parameters of the unperturbed wave function are determined variationally in an extensive energy minimization process. In the case of the first-order function, the parameters are optimized variationally using the functional given in Eq. (12).

C. Integration over k

The integration domain in Eq. (6) was split into parts by two arbitrarily selected points κ_1 and κ_2, and the contributions to $\ln k_0$ were treated differently in the *low* ($0 \leq k \leq \kappa_1$), *middle* ($\kappa_1 \leq k \leq \kappa_2$), and *high* ($k > \kappa_2$) range of k. The *low* range part of the Bethe logarithm was computed from the expression

$$(2\pi Z\langle\delta\rangle)^{-1}\left(\int_0^{\kappa_1} k\,J(k)\,dk + \kappa_1\langle\boldsymbol{\nabla}^2\rangle\right) + \ln\kappa_1\,. \tag{18}$$

The contribution from the *middle* range of k was

$$(2\pi Z\langle\delta\rangle)^{-1}\int_{\kappa_1}^{\kappa_2}\left(k\,J(k) + \langle\boldsymbol{\nabla}^2\rangle + 2\pi Z\langle\delta\rangle k^{-1}\right)\,dk, \tag{19}$$

and both integrals were evaluated numerically with the end point corrections according to the Euler-Maclaurin formula. In the *high* range, an asymptotic form of the integrand in (19) was used [12]

$$k\,J(k) + \langle\boldsymbol{\nabla}^2\rangle + 2\pi Z\langle\delta\rangle k^{-1} \sim \frac{4\pi Z^2\langle\delta\rangle}{k^2}\left(\sqrt{2k} - Z\ln k + \sum_{m=0}^{\mathcal{M}} a_m k^{-m/2}\right). \tag{20}$$

The integral arising from the first two terms

$$\int_{\kappa_2}^{\infty}\frac{4\pi Z^2\langle\delta\rangle}{k^2}\left(\sqrt{2k} - Z\ln k\right)\,dk \tag{21}$$

was evaluated analytically. The coefficients a_m appearing under the sum sign in the last term were obtained by fitting the sum (with $\mathcal{M} = 5$) to the points of the following expression

$$k^3 J(k) + k^2\langle\boldsymbol{\nabla}^2\rangle + 2\pi Z\langle\delta\rangle k - 4\pi Z^2\langle\delta\rangle\left(\sqrt{2k} - Z\ln k\right). \tag{22}$$

The contribution from this part was then simply

$$4\pi Z^2\langle\delta\rangle\sum_{m=0}^{\mathcal{M}} a_m\int_{\kappa_2}^{\infty} k^{-m/2-2}\,dk \tag{23}$$

III. RESULTS AND DISCUSSION

In both cases, for the finite and the infinite nuclear mass, the wave functions of the ground state lithium atom have been expanded in a 2000-term ECG basis set. The energy E, and the expectation values $\langle\delta\rangle$ and $\langle\boldsymbol{\nabla}^2\rangle$, computed with these wave functions are listed in Table I. It is known that, in the Gaussian type basis, the expectation value of the Dirac delta computed directly converges to the exact value very slowly. For that reason, the Drachman procedure [22], employing global rather than local operators, has been used after a modification taking into account the mass polarization term. This approach enables

TABLE I: The expectation values (expressed in the reduced atomic units) computed from the 2000-term ECG wave function of the ground state lithium atom and other parameters used in the evaluation of $\ln k_0$.

	$^{\infty}$Li	^{7}Li
κ_1	100	
κ_2	1800	
μ/M	0	$7.820\,202\,3(6) \cdot 10^{-5}$
E	$-7.478\,060\,315(10)$	$-7.478\,036\,719(10)$
	$-7.478\,060\,323\,650\,3(71)^{a}$	$-7.478\,036\,728\,106\,3(71)^{a}$
$\langle\delta\rangle$	$13.842\,606(4)$	$13.842\,568(4)$
	$13.842\,609\,642(55)^{a}$	$13.842\,571\,229(53)^{a}$
$\langle\boldsymbol{\nabla}^2\rangle$	$-15.559\,805\,9(4)$	$-15.559\,242\,5(4)$
	$-15.559\,806\,213\,3(5)^{a}$	

[a]See [23].

obtaining $\langle\delta\rangle$ with a satisfactory relative accuracy of 3 parts per 10^7 in comparison with the recent Yan and Drake results [23].

The basis for the final $\tilde{\Psi}$ function has been obtained by merging 4 bases optimized independently at different values of $k = 0$, 50, 1000, and 10000. The first two optimizations have been performed with 800-term bases, the two latter — with 1600 terms, so that the final first-order function is expanded in a 4800-term basis set. Such a method of the construction of the first-order correction function, described in more detail in [18], ensures that the high accuracy of $J(k)$ is preserved for a wide range of k.

In the *low* range, the $J(k)$ was computed with the interval 0.1 and with this interval the numerical integration has been performed. The *middle*-range values of $J(k)$, of the integrand in (19), and of the expression (22) were sampled with the step 1 likewise the integration step in (19). The parameters of the asymptotic formula (20) have been determined from the fit to the *middle*-range points computed this way. Sample values of the $J(k)$ function are given in Table II. The error introduced by the numerical integration is negligible and the main sources of the uncertainty in the $\ln k_0$ are the accuracy of the $J(k)$ function, the errors

TABLE II: The sample values of the $J(k)$ function.

k	$^{\infty}$Li	^{7}Li
0	4.499 994 111	4.499 290 481
1	2.569 745 832	2.569 528 053
5	1.391 873 540	1.391 786 761
10	0.919 080 419	0.919 030 732
50	0.262 650 328	0.262 639 282
100	0.140 989 612	0.140 984 031
500	0.030 343 214	0.030 342 089
1000	0.015 350 155	0.015 349 592

in $\langle\delta\rangle$ and $\langle\boldsymbol{\nabla}^2\rangle$ parameters, and the fitting procedure. The absolute accuracy of $J(k)$ for $^{\infty}$Li can be assessed at $k = 0$ at which it is known a priori to be equal 9/2. Our procedure yields $J(0)$ with an error of $6 \cdot 10^{-6}$. For growing k the convergence improves and the error diminishes. The final values of the Bethe logarithm for the lithium atom are presented in Table III, where also a comparison with results obtained by other methods is made. As our expectation values, in particular $\langle\boldsymbol{\nabla}^2\rangle$, are not as accurate as those given by Yan and Drake, we have repeated the evaluation of $\ln k_0$ for the infinite mass using their expectation values and we obtained 5.178 15 in full agreement with [24]. The mass polarization or recoil effect has been obtained from

$$\Delta \ln k_0 = \left(\frac{M}{\mu}\right)\left[\ln k_0(^{7}\mathrm{Li}) - \ln k_0(^{\infty}\mathrm{Li})\right]. \tag{24}$$

TABLE III: Comparison of the Bethe logarithm, $\ln k_0$, and the mass polarization effect, $\Delta \ln k_0$, obtained in this work with other sources.

References	$\ln k_0(^{\infty}\mathrm{Li})$	$\ln k_0(^{7}\mathrm{Li})$	$\Delta \ln k_0$
Yan, Drake [25]	5.176 82		0.110 4
Yan, Drake [24]	5.178 15(3)		
This work	5.178 17(3)	5.178 18(3)	0.114(3)

To test the procedure described above we have performed simplified computations for the ground state of the helium atom, for which the Bethe logarithm and the recoil correction to it are known [15]. In the computations a 600-term unperturbed [26] and a 2640-term perturbed ECG wave functions were employed. The values computed using the ECG method are collected in Table IV where they are confronted with the reference results. This comparison shows that our approach enables recovery of at least 6 significant digits for $\ln k_0$.

TABLE IV: The test results (in the reduced atomic units) for the ground states of He computed from the 600-term unperturbed and 2640-term first-order ECG wave functions. For comparison, we have calculated and present here results with the exponential basis set.

	$^{\infty}$He		^{4}He
E	$-2.903\,724\,377\,022$		$-2.903\,702\,581\,481$
Exponential basis	$-2.903\,724\,377\,034$		$-2.903\,702\,581\,507$
$\langle\delta\rangle$	$3.620\,858\,62(2)$		$3.620\,833\,62(2)$
Exponential basis	$3.620\,858\,63(1)$		$3.620\,833\,64(1)$
$\langle\boldsymbol{\nabla}^2\rangle$	$-6.125\,587\,704\,18(6)$		$-6.125\,242\,629\,2(2)$
Exponential basis	$-6.125\,587\,704\,239\,924$		$-6.125\,242\,629\,041\,468$
$\ln k_0$	$4.370\,158(3)$		$4.370\,171(3)$
[15]	$4.370\,160\,218(3)$		$4.370\,173\,155(3)$
μ/M	0		$1.370\,745\,67(2)\cdot 10^{-4}$
$\Delta\ln k_0$		$0.094\,1(3)$	
[15]		$0.094\,38(1)$	

IV. SUMMARY

The purpose of this work was the development of a numerical method for calculation of the QED effects in light atoms. We presented the Bethe logarithm for He which, for the first time, has been obtained using the Gaussian type wave functions and a new result for Li atom. We show that with the well optimized Gaussian basis set one can obtain high accuracy results for Bethe logarithms, as well as for other QED effects. The results allow for improved theoretical predictions for the ground state energy and the isotope shifts between ^{6}Li and ^{7}Li. However, to compare them with the available measurements we need similarly accurate results for P or other excited states of the Li atom, which have not been obtained yet. At present, the tests of QED on the lithium atom are much less accurate compared to hydrogen or helium. The reason for this is the lack of the complete result for the $m\,\alpha^6$ relativistic and QED corrections. Although they can be derived in a closed form, as for helium [27], the calculation of matrix elements is quite difficult from the numerical point of view.

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