Quantum electrodynamics corrections to the 2P fine splitting in Li

Mariusz Puchalski

Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

Krzysztof Pachucki

Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

Abstract

We consider quantum electrodynamics (QED) corrections to the fine splitting $E(2P_{3/2}) - E(2P_{1/2})$ in the Li atom. We derive complete formulas for the $m \alpha^6$ and $m \alpha^7 \ln \alpha$ contributions and calculate them numerically using highly optimized, explicitly correlated basis functions. The obtained results are in agreement with the most recent measurement, helping to resolve discrepancies between former ones and lay the foundation for investigation of QED effects in light, many-electron atoms.

PACS numbers: 31.15.ac, 31.15.aj, 31.30.J-

INTRODUCTION

The inclusion of relativistic effects and correlations between electrons in atomic systems gives rise to some fundamental problems related to the many-electron Dirac equation. This equation has to include two and more electron-positron pairs to be in accordance with Quantum Electrodynamics (QED). From the numerical point of view it suffers from instabilities, like that in achieving the correct nonrelativistic limit for the energy difference between states of the same orbital momentum [1]. For example the relativistic calculation of the lithium $2P_{3/2} - 2P_{1/2}$ splitting has reached the precision of only one significant digit so far [2].

For light atomic systems the best approach relies on nonrelativistic QED theory, where relativistic and QED effects are treated perturbatively, while the nonrelativistic Hamiltonian is solved using explicitly correlated basis sets. This approach has been successfully applied to helium [3, 4], lithium [5, 6], and beryllium atoms [7]. The helium fine structure is a very good example; it was calculated to the $m \alpha^7$ order and currently serves as one of the most precise QED tests in few-electron systems [8]. Conversely, theoretical results for lithium fine structure are much less accurate, and the various experiments are not always in agreement with each other and with the theory [11]. For example, long standing discrepancies in the isotope shift of the fine structure have been resolved only recently, and it would appear that the results from previous experiments and theoretical predictions were both incorrect [11, 12]. In this work we aim to significantly improve theoretical prediction of the lithium fine structure $2P_{3/2} - 2P_{1/2}$ by the complete calculation of the $m\,\alpha^6$ and $m\,\alpha^7\,\ln\alpha$ contributions. We derive closed formulas for QED corrections and perform numerical calculations using explicitly correlated basis sets with Hylleraas and Gaussian functions. Such calculations have been performed by Douglas and Kroll for the helium fine structure of ${}^{3}P_{J}$ levels in Ref. [14]. It took 40 years to extend their two-electron $m\alpha^{6}$ result to an atom with three electrons, indicating that accurate calculations of QED effects in many electron systems is a challenging task. Here, in addition we develop a general perturbative approach based on QED theory, which can be used in an arbitrary few electron atomic and molecular systems, provided one can solve the Schrödinger equation with the sufficient accuracy. No other approach developed in the literature, allows one for consistent inclusion of relativistic and QED effects in light atomic and molecular systems.

LITHIUM FINE STRUCTURE

The fine structure $E_{\rm fs}$ can be expanded in powers of the fine structure constant α

$$E_{\rm fs} = E_{\rm fs}^{(4)} + E_{\rm fs}^{(6)} + E_{\rm fs}^{(7)} + \dots,$$
(1)

where $E_{\rm fs}^{(n)}$ is of the order of $m \alpha^n$. The leading order contribution $E_{\rm fs}^{(4)}$, including the all-order electron g-factor, is obtained from the fine-structure Hamiltonian [13]

$$E_{\rm fs}^{(4)} = \langle \phi | H_{\rm fs}^{(4)} | \phi \rangle \tag{2}$$

where

$$H_{\rm fs}^{(4)} = \sum_{a} \frac{Z \alpha}{4 r_a^3} \vec{\sigma}_a \left[(g-1) \vec{r}_a \times \vec{p}_a \right] + \sum_{a \neq b} \frac{\alpha}{4 r_{ab}^3} \vec{\sigma}_a \left[g \vec{r}_{ab} \times \vec{p}_b - (g-1) \vec{r}_{ab} \times \vec{p}_a \right]$$
(3)

and g is the electron g-factor, and we employ natural units $\hbar = c = m = 1$. The wave function ϕ in Eq. (2) is a solution of the nonrelativistic stationary Schrödinger equation corresponding to the 2^2P state

$$(H - E)\phi = 0 \tag{4}$$

where

$$H = \sum_{a} \frac{\vec{p}_{a}^{2}}{2} + V$$
$$V = \sum_{a} -\frac{Z\alpha}{r_{a}} + \sum_{b < a} \frac{\alpha}{r_{ab}}$$
(5)

The higher-order relativistic correction $E^{(6)}$ is the subject of the present work. It can be expressed as the sum of the first- and second-order terms

$$E_{\rm fs}^{(6)} = \langle \phi | H^{(4)} \frac{1}{(E-H)'} H^{(4)} | \phi \rangle_{\rm fs} + \langle \phi | H_{\rm fs}^{(6)} | \phi \rangle, \tag{6}$$

where [13]

$$H^{(4)} = H_A^{(4)} + H_B^{(4)} + H_C^{(4)}$$
(7)

$$H_{A}^{(4)} = \sum_{a} \left\{ -\frac{\vec{p}_{a}^{4}}{8} + \frac{\pi Z}{2} \,\delta^{3}(r_{a}) \right\}$$

$$+ \sum_{b < a} \left\{ \pi \,\delta^{3}(r_{ab}) - \frac{1}{2} \,p_{a}^{i} \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^{i} \,r_{ab}^{j}}{r_{ab}^{3}} \right) \,p_{b}^{j} \right\}.$$
(8)

$$H_B^{(4)} = \sum_{a} \frac{Z}{4 r_a^3} \vec{\sigma}_a \cdot \vec{r}_a \times \vec{p}_a + \sum_{a \neq b} \frac{1}{4 r_{ab}^3} \vec{\sigma}_a \left(2 \vec{r}_{ab} \times \vec{p}_b - \vec{r}_{ab} \times \vec{p}_a \right).$$
(9)

$$H_C^{(4)} = \sum_{b < a} \frac{\sigma_a^i \, \sigma_b^j}{4 \, r_{ab}^3} \left(\delta^{ij} - 3 \, \frac{r_{ab}^i \, r_{ab}^j}{r_{ab}^2} \right) \tag{10}$$

and where $H_{\rm fs}^{(6)}$ is an effective Hamiltonian of order $m \alpha^6$. $H_B^{(4)}$ above coincides with $H_{\rm fs}^{(4)}$ in Eq. (3) for g = 2. The first derivation of $H_{\rm fs}^{(6)}$ was performed for helium fine structure by Douglas and Kroll in [14] using the Salpeter-like approach. Numerical evaluation of this splitting has been performed to a high degree of precision in [15] and [16]. In this work we obtain $H_{\rm fs}^{(6)}$ for lithium fine structure using a different approach, where nonrelativistic expansion is performed in the beginning at the Lagrangian level [17].

In order to further improve theoretical predictions, the higher-order $m \alpha^7$ contribution is not neglected but instead is approximated by the numerically dominating logarithmic part. This part is obtained from the analogous result for helium fine structure [16, 18] by dropping the $\sigma^i \sigma^j$ terms because they do not contribute for states with total electron spin S = 1/2,

$$E_{\rm fs,log}^{(7)} = \langle H_{\rm fs,log}^{(7)} \rangle + 2 \left\langle H_B^{(4)} \frac{1}{(E_0 - H_0)'} H_{\rm log}^{(5)} \right\rangle$$
(11)

$$H_{\log}^{(5)} = \alpha^2 \ln[(Z\alpha)^{-2}] \left[\frac{4Z}{3} \sum_{a} \delta^3(r_a) - \frac{7}{3} \sum_{b < a} \delta^3(r_{ab}) \right]$$
(12)

$$H_{\rm fs,log}^{(7)} = \alpha^2 \ln[(Z \alpha)^{-2}] \left[\frac{Z}{3} \sum_a i \vec{p}_a \times \delta^3(r_a) \vec{p}_a \cdot \vec{\sigma}_a - \frac{3}{4} \sum_{b \neq a} i \vec{p}_a \times \delta^3(r_{ab}) \vec{p}_a \cdot \vec{\sigma}_a \right].$$
(13)

The neglected higher-order corrections are the nonlogarithmic $m \alpha^7$ term and the finite nuclear mass corrections to the $m \alpha^6$ contribution. Corresponding uncertainties are 40 kHz and 15 kHz, what together with numerical uncertainties leads to about 6 ppm accuracy in the Li fine structure.

SPIN-ORBIT HAMILTONIAN OF ORDER $m \, \alpha^6$

Various approaches are possible to derive $m \alpha^6$ correction, and here we use a variant of nonrelativistic QED, where the effective NRQED Lagrangian is obtained by the Foldy-Wouthuysen (FW) transformation of a Dirac equation.

$$H_D = \vec{\alpha} (\vec{p} - e \vec{A}) + e A^0$$

$$H_{FW} = e^{iS} (H_D - i \partial_t) e^{-iS}$$

$$= H_D + i[S, H_D] - \frac{\partial S}{\partial t} + \dots$$
(14)

FW transformation at the level of leading relativistic corrections is well described in many textbooks. At higher orders however, it is not unique [17], and we take advantages of this flexibility to simplify the further derivation of $m \alpha^6$ operators. The H_{FW} obtained is

$$H_{FW} = e A^{0} + \frac{1}{2} \left(\vec{\pi}^{2} - e \vec{\sigma} \cdot \vec{B} \right) - \frac{1}{8} \left(\vec{\pi}^{4} - e \vec{\sigma} \cdot \vec{B} \vec{\pi}^{2} - \vec{\pi}^{2} e \vec{\sigma} \cdot \vec{B} \right) - \frac{1}{8} \left(e \vec{\nabla} \cdot \vec{E}_{\parallel} + e \vec{\sigma} \cdot \left(\vec{E}_{\parallel} \times \vec{p} - \vec{p} \times \vec{E}_{\parallel} \right) \right) + \frac{e^{2}}{2} \vec{\sigma} \cdot \vec{E}_{\parallel} \times \vec{A} + \frac{i e}{16} \left[\vec{\sigma} (\vec{A} \times \vec{p} - \vec{p} \times \vec{A}), p^{2} \right] + \frac{e^{2}}{8} \vec{E}_{\parallel}^{2} + \frac{3}{32} \left\{ p^{2}, \vec{E}_{\parallel} \times \vec{p} \cdot \vec{\sigma} \right\} + \frac{5}{128} \left[p^{2}, \left[p^{2}, e A^{0} \right] \right] - \frac{3}{64} \left\{ p^{2}, \nabla^{2} (e A^{0}) \right\} + \frac{p^{6}}{16}$$
(15)

where $\vec{E}_{\parallel} = -\vec{\nabla}A^0$ and $\vec{\pi} = \vec{p} - e \vec{A}$. H_{FW} can be used to derive $H^{(4)}$ as well as $H^{(6)}$ [17]. Here we rederive $H_{\rm fs}^{(6)}$ with the use of H_{FW} in Eq. (15). Let \mathcal{E}_a denote the static electric field at the position of particle a

$$e\,\vec{\mathcal{E}}_a \equiv -\nabla_a V = -Z\,\alpha\,\frac{\vec{r}_a}{r_a^3} + \sum_{b\neq a}\alpha\,\frac{\vec{r}_{ab}}{r_{ab}^3} \tag{16}$$

The vector potential at the position of particle a, which is produced by all other particles, is

$$e \mathcal{A}_{a}^{i} \equiv \sum_{b \neq a} \frac{\alpha}{2 r_{ab}} \left(\delta^{ij} + \frac{r_{ab}^{i} r_{ab}^{j}}{r_{ab}^{2}} \right) p_{b}^{j} + \frac{\alpha}{2} \frac{\left(\vec{\sigma}_{b} \times \vec{r}_{ab}\right)^{i}}{r_{ab}^{3}} , \qquad (17)$$

Using Eqs. (16,17) and following the derivation in Ref. [17], the higher-order contributions which result from H_{FW} in Eq. (15) are

$$H_{\rm fs}^{(6)} = \sum_{a} \left\{ \frac{3}{16} p_{a}^{2} e \,\vec{\mathcal{E}}_{a} \times \vec{p}_{a} \cdot \vec{\sigma}_{a} + \frac{e}{4} \left(2 \, p_{a}^{2} \, \vec{p}_{a} \cdot \vec{\mathcal{A}}_{a} + p_{a}^{2} \, \vec{\sigma}_{a} \cdot \nabla_{a} \times \vec{\mathcal{A}}_{a} \right) + \frac{e^{2}}{2} \, \vec{\sigma}_{a} \cdot \vec{\mathcal{E}}_{a} \times \vec{\mathcal{A}}_{a} \\ + \frac{i \, e}{16} \left[\vec{\mathcal{A}}_{a} \times \vec{p}_{a} \cdot \vec{\sigma}_{a} - \vec{\sigma}_{a} \cdot \vec{p}_{a} \times \vec{\mathcal{A}}_{a} , p_{a}^{2} \right] + \frac{e^{2}}{2} \,\vec{\mathcal{A}}_{a}^{2} \right\} + \sum_{b \neq a} \left\{ -\frac{i \, \pi \, \alpha}{8} \, \vec{\sigma}_{a} \cdot \vec{p}_{a} \times \delta^{3}(r_{ab}) \, \vec{p}_{a} \\ + \frac{\alpha}{4} \left(-i \left[\vec{\sigma}_{a} \times \frac{\vec{r}_{ab}}{r_{ab}}, \frac{p_{a}^{2}}{2} \right] e \, \vec{\mathcal{E}}_{b} + \left[\frac{p_{b}^{2}}{2}, \left[\vec{\sigma}_{a} \times \frac{\vec{r}_{ab}}{r_{ab}}, \frac{p_{a}^{2}}{2} \right] \right] \vec{p}_{b} \right\} \right\}$$
(18)

Most of the terms in $H_{\rm fs}^{(6)}$ are obtained in the nonretardation approximation, which corresponds to replacing the electromagnetic fields in H_{FW} for the particle a with fields that come from all other particles, called b. The last two are exceptions. The first term under the sum over a and b comes from a Coulomb interaction between electrons, where both electron vertices, instead of $e A^0$, are of the form $-\left[e\vec{\nabla}\cdot\vec{E}_{\parallel}+e\vec{\sigma}\cdot\left(\vec{E}_{\parallel}\times\vec{p}-\vec{p}\times\vec{E}_{\parallel}\right)\right]/8$, and the second term comes from the single transverse photon exchange with the electron vertices of the form $-e\vec{p}\vec{A}-e\vec{\sigma}\cdot\vec{B}/2$.

TABLE I: $m \alpha^6$ and $m \alpha^7 \ln \alpha$ contributions to Li 2P fine splitting, in units $m \alpha^6$ and $m \alpha^7$ correspondingly, 1_X is a projection operator into states of the type X, $E_{\rm fs}^{(6)}$ is a sum of all preceding terms.

$$\begin{split} &\langle \phi | H_{\rm fs}^{(6)} | \phi \rangle & -0.202 \, 1(16) \\ &\langle \phi | H_B^{(4)} \frac{1_{2S_o}}{E - H} H_B^{(4)} | \phi \rangle & 0.293 \, 49 \\ &\langle \phi | H_B^{(4)} \frac{1_{4S_o}}{E - H} H_B^{(4)} | \phi \rangle & -0.295 \, 94(2) \\ 2 \, \langle \phi | H_B^{(4)} \frac{1_{2P}}{(E - H)'} H_A^{(4)} | \phi \rangle & 0.195 \, 3(17) \\ &\langle \phi | H_B^{(4)} \frac{1_{2P}}{(E - H)'} H_B^{(4)} | \phi \rangle & 0.539 \, 7(5) \\ &\langle \phi | H_B^{(4)} \frac{1_{4P}}{E - H} H_B^{(4)} | \phi \rangle & -0.450 \, 6(2) \\ &\langle \phi | H_C^{(4)} \frac{1_{4P}}{E - H} H_C^{(4)} | \phi \rangle & 0.006 \, 23 \\ 2 \, \langle \phi | H_B^{(4)} \frac{1_{2D_o}}{E - H} H_C^{(4)} | \phi \rangle & 0.020 \, 90 \\ &\langle \phi | H_B^{(4)} \frac{1_{2D_o}}{E - H} H_C^{(4)} | \phi \rangle & 0.733 \, 27(2) \\ &\langle \phi | H_B^{(4)} \frac{1_{4D_o}}{E - H} H_C^{(4)} | \phi \rangle & 0.000 \, 08 \\ 2 \, \langle \phi | H_B^{(4)} \frac{1_{4D_o}}{E - H} H_C^{(4)} | \phi \rangle & -0.000 \, 01 \\ &\langle \phi | H_C^{(4)} \frac{1_{4D_o}}{E - H} H_C^{(4)} | \phi \rangle & -0.002 \, 13 \\ & E_{\rm fs}^{(6)} & 0.087 \, 1(24) \\ &\langle \phi | H_B^{(4)} \frac{1_{2P}}{E - H''} H_{\rm log}^{(5)} | \phi \rangle & 1.783 \, 9(4) \\ &E_{\rm fs,\log}^{(7)} & 1.047 \, 5(4) \\ \end{split}$$

The second-order contribution in Eq. (6) is split into parts coming from intermediate states of the specified angular momentum and the spin. These parts are defined in Table I. Most of them can be calculated as they stand. Only the matrix elements involving $H_A^{(4)}$ and $\delta^3(r_a)$ need special treatment due to the high singularity of these operators.

SPIN REDUCTION OF MATRIX ELEMENTS

The wave function of the ²P state in the three-electron system is represented as

$$\Phi^{i} = \frac{1}{\sqrt{6}} \mathcal{A} \left[\phi^{i}(\vec{r_{1}}, \vec{r_{2}}, \vec{r_{3}}) \left[\alpha(1) \beta(2) - \beta(1) \alpha(2) \right] \alpha(3) \right],$$
(19)

where \mathcal{A} denotes antisymmetrization and $\phi^i(\vec{r_1}, \vec{r_2}, \vec{r_3})$ is a spatial function with Cartesian index *i* that comes from any of the electrons coordinate, $\phi^i = r_a^i \phi$. The normalization we assume is

$$1 = \sum_{i} \langle \Phi'^{i} | \Phi^{i} \rangle$$

= $\sum_{i} \langle \phi'^{i}(r_{1}, r_{2}, r_{3}) | \mathcal{P}[c_{123} \phi^{i}(r_{1}, r_{2}, r_{3})] \rangle$ (20)

where \mathcal{P} denotes a sum of all permutations of 1,2,3 subscripts. The ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ wave functions are constructed using Clebsch-Gordon coefficients. Expectation values with these wave functions can be reduced to spatial expectation values with algebraic prefactor for J = 1/2, 3/2, accordingly; i.e. the first-order matrix elements take the form

$$\langle \Phi' | O | \Phi \rangle = \{1, 1\} \left\langle \phi'^{i}(r_{1}, r_{2}, r_{3}) | Q \mathcal{P}[c_{123} \phi^{i}(r_{1}, r_{2}, r_{3})] \right\rangle$$
(21)

$$\langle \Phi' | \sum_{a} \vec{\sigma}_{a} \cdot \vec{Q}_{a} | \Phi \rangle = \{ 1, -1/2 \} i \, \epsilon^{ijk} \langle \phi'^{i}(r_{1}, r_{2}, r_{3}) | \sum_{a} Q_{a}^{j} \mathcal{P} \Big[c_{123}^{Fa} \phi^{k}(r_{1}, r_{2}, r_{3}) \Big] \rangle$$
(22)

$$\langle \Phi' | \sum_{a \neq b} \vec{\sigma}_a \times \vec{\sigma}_b \cdot \vec{Q}_{ab} | \Phi \rangle = \{ 1, -1/2 \} (-2 \epsilon^{ijk}) \langle \phi'^i(r_1, r_2, r_3) |$$

$$\sum_{ab=12,23,31} (Q^j_{ab} - Q^j_{ba}) \mathcal{P} \Big[c^{F_1}_{123} \phi^k(r_1, r_2, r_3) \Big] \rangle$$

$$(23)$$

The second-order matrix elements can also been reduced to the spatial ones, with different prefactors similarly to those above.

(k,l,m)	c_{klm}	$c_{klm}^{F_1}$	$c_{klm}^{F_2}$	$c_{klm}^{F_3}$
(1,2,3)	2	0	0	2
(1, 3, 2)	-1	1	-1	-1
(2, 1, 3)	2	0	0	2
(2, 3, 1)	-1	-1	1	-1
(3, 1, 2)	-1	1	-1	-1
(3, 2, 1)	-1	-1	1	-1

TABLE II: Symmetrization coefficients in spatial matrix elements

NUMERICAL CALCULATIONS

The spatial function is represented as a linear combination of the Hylleraas [19]

$$\phi = e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3} r_{23}^{n_1} r_{23}^{n_2} r_{23}^{n_3} r_1^{n_4} r_2^{n_5} r_3^{n_6}$$
(24)

or of the Gaussian functions [20]

$$\phi = e^{-\alpha_1 r_1^2 - \alpha_2 r_2^2 - \alpha_3 r_3^2 - \alpha_{12} r_{12}^2 - \alpha_{13} r_{13}^2 - \alpha_{23} r_{23}^2} \tag{25}$$

In the Hylleraas basis we use 6 sectors with different values of nonlinear parameters w_i and a maximum value of $\Omega = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 = 13$, details are in [9, 10]. In Gaussian basis we use N = 256, 512, 1024, and 2048 functions with well-optimized nonlinear parameters for each basis function, separately. The accuracy achieved for nonrelativistic energies is about 10^{-113} in Hylleraas and 10^{-111} in Gaussian bases. The first-order matrix elements involving the Dirac δ -function are calculated with Hylleraas basis; all other operators are calculated using Gaussians. Numerical results for the extrapolated value of $\langle H_{\rm fs}^{(6)} \rangle$ are presented in Table I, and the achieved precision is about 10^{-3} . The evaluation of second-order matrix elements is much more demanding. They are obtained using the Gaussian basis, as follows. The resolvent 1/(E - H) for each angular momentum is represented in terms of functions with the appropriate Cartesian prefactor. Nonlinear parameters for intermediate states are optimized for each symmetric matrix element. For the asymmetric matrix elements, the basis is combined from two corresponding symmetric ones. The most computationally demanding matrix elements were these, which involve $H_A^{(4)}$ and

 $H_{log}^{(5)}$ operators, and they are transformed to the regular form by the following transformations

$$H_A^{(4)} = [H_A^{(4)}]_r + \left\{ \sum_a \frac{Z}{4r_a} - \sum_{b < a} \frac{1}{2r_{ab}}, E - H \right\},$$
(26)

$$4\pi\,\delta^3(r_a) = 4\pi\,[\delta^3(r_a)]_r - \left\{\frac{2}{r_a}, E - H\right\}.$$
(27)

The resulting second order matrix elements became less singular and can readily be evaluated. Numerical results for matrix elements are summarized in Table I. The achieved precision is of order 10^{-3} and better; similarly to the first-order matrix elements. Moreover, we observed significant cancellations between S = 1/2 and S = 3/2 intermediate states, and between the first-and second-order terms. The final numerical result for the $m \alpha^6$ contribution $E_{\rm fs}^{(6)}$ in Table I is quite small but larger than the hydrogenic value 5/256 = 0.019531, as it should be. Regarding the $m \alpha^7$ contribution, the second-order term is numerically dominant, and the contribution from $H_{\rm fs,log}^{(7)}$ is more than twice smaller. Altogether, this correction is only 10 times smaller than the $m \alpha^6$ contribution and is significant in comparison to the accuracy of experimental values.

SUMMARY

We have performed accurate calculations of the fine structure in Li using the nonrelativistic QED approach. Relativistic and QED corrections are represented in terms of effective operators and are calculated using a highly accurate nonrelativistic wave function. Numerical results are summarized in Table III. The obtained theoretical predictions for the ^{6,7}Li fine structure are in an agreement with the recent experimental values of Ref. [11] and also with Refs. [21, 22], but are in disagreement with all the other ones. This demonstrates the capability of NRQED theory and the numerical approach based on explicitly correlated functions in achieving high-precision predictions for energies and energy splittings in light, few-electron atoms.

Acknowledgments

The authors acknowledge the support of NCN grants 2012/04/A/ST2/00105, 2011/01/B/ST4/00733, and by PL-Grid Infrastructure.

^[1] P. Indelicato, E. Lindroth, and J.P. Desclaux, Phys. Rev. Lett. 94, 013002 (2005).

	actes of $D_{\rm fs}$ and from the neglect $D_{\rm fs,nolog}$, which is estimated by 2070 of $D_{\rm fs,log}$				
	⁶ Li	⁷ Li	Ref.		
$E_{\rm fs}^{(4)}$	10053.7072(83)	10053.7072(83)	[9, 10]		
$E_{\rm fs,rec}^{(4)}$	-2.7868(6)	-2.3891(5)	[9, 10]		
$E_{\rm fs}^{(6)}$	1.63(5)	1.63(5)			
$E_{\rm fs,log}^{(7)}$	0.15	0.15			
$\delta E_{\rm fs}$	0.01217	0.15916	[10]		
$E_{\rm fs}$ (theo)	10052.72(6)	10053.25(6)			
$E_{\rm fs}(\exp)$	10052.779(17)	10053.310(17)	Brown [11]		
	10052.76(22)	10053.24(22)	Brog [21]		
		10053.184(58)	Orth [22]		
	10052.964(50)	10053.119(58)	Noble [23]		
	10052.044(91)	10052.37(11)	Walls [24]		
	10052.862(41)	10051.999(41)	Das [25]		

TABLE III: Fine splitting of 2P-states in Li isotopes in MHz, $E_{\rm fs,rec}$ is the finite nuclear mass correction, $\delta E_{\rm fs}$ is the hyperfine mixing correction. The uncertainty of $E_{\rm fs}$ (theo) comes mainly from numerical inaccuracies of $E_{\rm fs}^{(6)}$ and from the neglect $E_{\rm fs,nolog}^{(7)}$, which is estimated by 25% of $E_{\rm fs,log}^{(7)}$

- [2] A. Derevianko, S. G. Porsev, and K. Beloy, Phys. Rev. A 78, 010503(R) (2008).
- [3] Z.-T. Lu, P. Mueller, G. W. F. Drake, W. Nörtershäuser, Steven C. Pieper, and Z.-C. Yan, Rev. Mod. Phys. 85, 1383 (2013).
- [4] V. A. Yerokhin and K. Pachucki, Phys. Rev. A 81, 022507 (2010).
- [5] Z.-C. Yan, W. Nörtershäuser, and G. W. F. Drake, Phys. Rev. Lett. 100, 243002 (2008).
- [6] M. Puchalski, D. Kędziera, and K. Pachucki, Phys. Rev. A 87, 032503 (2013).
- [7] M. Puchalski, J. Komasa and K. Pachucki, Phys. Rev. A 87, 030502(R) (2013),
- [8] K. Pachucki and V.A. Yerokhin, Phys. Rev. Lett. 104, 070403 (2010).
- [9] Z.-C. Yan and G.W.F. Drake, Phys. Rev. A 66, 042504 (2002).
- [10] M. Puchalski and K. Pachucki, Phys. Rev. A 79, 032510 (2009).
- [11] R. C. Brown, S. Wu, J. V. Porto, C. J. Sansonetti, C. E. Simien, S. M. Brewer, J. N. Tan, and J. D. Gillaspy, Phys. Rev. A 87, 032504 (2013).
- [12] C. J. Sansonetti, C. E. Simien, J. D. Gillaspy, J. N. Tan, S. M. Brewer, R. C. Brown, S. Wu, and J. V.

Porto, Phys. Rev. Lett. 107, 023001 (2011); 109, 259901(E) (2012).

- [13] H.A. Bethe and E.E. Salpeter, *Quantum Mechanics Of One- And Two-Electron Atoms*, Plenum Publishing Corporation, New York (1977).
- [14] M. Douglas and N.M. Kroll, Ann. Phys. (N.Y) 82, 89 (1974).
- [15] Z.-C. Yan and G.W.F. Drake, Phys. Rev. Lett. 74, 4791 (1995).
- [16] K. Pachucki and V.A. Yerokhin, Phys. Rev. Lett. 104, 070403 (2010).
- [17] K. Pachucki, Phys. Rev. A 71, 012503 (2005).
- [18] T. Zhang, Z.-C. Yan, and G. W. F. Drake, Phys. Rev. Lett. 77, 1715 (1996).
- [19] L.M. Wang, Z.-C. Yan, H.X. Qiao, and G.W.F. Drake, Phys. Rev. A 85, 052513 (2012).
- [20] J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, Rev. Mod. Phys. 85, 693 (2013).
- [21] K.C. Brog, T.G. Eck, H. Wieder, Phys. Rev. 153, 91 (1967).
- [22] H. Orth, H. Ackermann, E. Otten, Z. Phys. A 273, 173 (1975).
- [23] G.A. Noble, B.E. Schultz, H. Ming, W.A. van Wijngaarden, Phys. Rev. A 74, 012502 (2006).
- [24] J. Walls, R. Ashby, J. Clarke, B. Lu, and W. van Wijngaarden, Eur. Phys. J. D 22, 159 (2003).
- [25] D. Das and V. Natarajan, Phys. Rev. A 75, 052508 (2007).