QED calculation of the $2p$ fine structure in Li-like ions

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Large-scale *ab initio* QED calculations are performed for the $2p_{3/2}$–$2p_{1/2}$ fine-structure interval of Li-like ions with nuclear charges $Z = 5-92$. Improved theoretical predictions are obtained by combining together two complementary theoretical methods, namely, the approach that accounts for all orders in the binding nuclear strength and the nonrelativistic QED approach that accounts for all orders in the nonrelativistic electron-electron interaction. The resulting unified approach provides theoretical predictions which are more accurate than the available experimental results across the interval of the nuclear charges considered.

Three-electron atoms, namely, Li and Li-like ions, are among the simplest many-electron systems. They can be calculated *ab initio* within quantum electrodynamics (QED) and measured with a very high precision. Investigations of such atoms enable precision tests of bound-state QED of many-body systems and allow studies of nuclear properties probed by atomic electrons [1]. The spectacular experimental progress achieved during the past decades in spectroscopy of Li-like atoms [2–11] motivated large efforts devoted to QED calculations of energy levels in these systems.

There are presently two main *ab initio* methods that systematically describe various atomic properties within QED. The first method, described in Ref. [12], accounts for all orders in the nuclear binding strength (i.e., the parameter $Z\alpha$, where Z is the nuclear charge number and α is the fine-structure constant) but expands in the number of virtual photons exchanged between the electrons (i.e., in the parameter $1/Z$). Such calculations were performed by a number of authors, most notably, by the Notre-Dame [13–15] and the St. Petersburg [16–22] group. This method yields very accurate results for high-Z ions, providing one of the best tests of QED in the strong-field regime [23]. In the low-Z region, however, the applicability of this method diminishes, since the relative contribution of the electron correlation increases as Z goes down and the convergence of the $1/Z$ expansion deteriorates.

For light atoms, the best results are obtained with the second method, based on the nonrelativistic quantum electrodynamics (NRQED) [24]. This method expands the energy levels of a bound system in powers of α and $Z\alpha$, but accounts for all orders in $1/Z$. High-precision NRQED calculations were performed for energy levels of Li and Be^+ in Refs. [25–30]. For heavier systems, however, the accuracy of the NRQED results deteriorates as Z increases, since the omitted higher-order effects become enhanced by high powers of Z.

The fine structure (fs) of energy levels is particularly favourable for theoretical calculations by the NRQED method, offering numerous simplifications. For example, only a few operators explicitly depending on the electron spin contribute to the fs splitting at the leading order of the NRQED expansion, $m\alpha^4$ (where m is the electron mass). Furthermore, at the next-to-leading order $m\alpha^5$, the leading QED contribution comes only from the anomalous magnetic moment of the electron. Owing to these and other theoretical simplifications, the $2p$ fs interval in Li and Be^+ is presently calculated up to order $m\alpha^6$ [30, 31], while for other energy intervals of three-electron systems the $m\alpha^6$ effects remain uncalculated so far.

In the present investigation we will combine the $1/Z$-expansion method and the NRQED approach and obtain the most accurate theoretical predictions for the $2p_{3/2}-2p_{1/2}$ fs interval through the lithium isoelectronic atomic sequence with $Z \geq 5$. To this end, we will match the $Z\alpha$ expansion of numerical results obtained by the $1/Z$-expansion method and the $1/Z$ expansion of the NRQED results. The main improvement will be achieved in the region of medium nuclear charges, $Z \approx 8-20$, in which the both above-mentioned methods do not work well.

The relativistic units ($\hbar = c = m = 1$) will be used throughout this paper, unless explicitly specified otherwise.

I. $1/Z$-EXPANSION QED

In the present work, theoretical contributions to the energy of a Li-like atom are separated into three parts, namely, the electron-structure part $E_{\rm struc}$, the radiative QED correction $E_{\rm rad}$, and the nuclear recoil correction $E_{\rm rec}$,

$$E = E_{\rm struc} + E_{\rm rad} + E_{\rm rec}\,. \tag{1}$$

We note that we distinguish between the QED effects of the self-energy and vacuum-polarization type (termed as the radiative QED effects, $E_{\rm rad}$) and the QED effects originating from the frequency-dependence of the electron-electron interaction (termed as the electron-structure QED effects and included into $E_{\rm struc}$).

The $2p$ fs splitting of Li-like atoms is obtained as a difference of energies of the $2p$ states with different

values of the total angular momentum, $(1s)^2 2p_{3/2}$ and $(1s)^2 2p_{1/2}$. In the following, we will denote by $E_i(v)$ corrections to the ionization energy of the valence electron state v and by $E_i(\mathrm{fs})$ corrections to the fs splitting, $E_i(\mathrm{fs}) = E_i(2p_{3/2}) - E_i(2p_{1/2})$. We note that the energy contributions involving interactions only between the core electrons do not contribute neither to the ionization energy or the fs interval, so they are not considered in this work.

A. Electronic structure

The electronic-structure part of the energy is represented by an expansion in the number of virtual photons exchanged between the electrons,

$$E_{\mathrm{struc}}(v) = E_{\mathrm{D}} + E_{1\mathrm{phot}} + E_{2\mathrm{phot}} + E_{3\mathrm{phot}} + E_{\geq 4\mathrm{phot}}\,, \tag{2}$$

where E_{D} is the Dirac one-electron energy; $E_{1\mathrm{phot}}$, $E_{2\mathrm{phot}}$, and $E_{3\mathrm{phot}}$ are corrections due to the exchange of one, two, and three virtual photons, respectively, and $E_{\geq 4\mathrm{phot}}$ corresponds to the exchange by four and more photons.

The Dirac ionization energy of the valence state v, for the point nuclear model, is given by the well-known formula

$$E_{\mathrm{D}}(v) = \left[1 + \left(\frac{Z\alpha}{n_v - |\kappa_v| + \sqrt{\kappa_v^2 - (Z\alpha)^2}}\right)^2\right]^{-1/2} - 1\,, \tag{3}$$

where n_v and κ_v are the principal and the relativistic angular quantum numbers of the state v, respectively. The point-nucleus Dirac energy receives a correction from the finite nuclear size (fns), which is very small for low-Z ions but becomes increasingly important as Z increases. The fns correction can be easily calculated numerically, by solving the Dirac equation with a suitable nuclear binding potential.

The electron-structure corrections to the Dirac energy arise through the electron-electron interaction. The relativistic operator of the electron-electron interaction depends on the energy of the exchanged virtual photon ω and is given, in the Feynman gauge, by

$$I_{\mathrm{Feyn}}(\omega) = \alpha\left(1 - \boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\right)\frac{e^{i|\omega|x_{12}}}{x_{12}}\,, \tag{4}$$

where $\boldsymbol{\alpha}_1$ and $\boldsymbol{\alpha}_2$ are vectors of Dirac matrices acting on the coordinate $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$, respectively, and $x_{12} = |\boldsymbol{x}_{12}| = |\boldsymbol{x}_1 - \boldsymbol{x}_2|$. The electron-electron interaction operator in the Coulomb gauge is

$$I_{\mathrm{Coul}}(\omega) = \alpha\left[\frac{1}{x_{12}} - \boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\,\frac{e^{i|\omega|x_{12}}}{x_{12}} + \frac{\left(\boldsymbol{\alpha}_1\cdot\boldsymbol{\nabla}_1\right)\left(\boldsymbol{\alpha}_2\cdot\boldsymbol{\nabla}_2\right)}{\omega^2}\,\frac{e^{i|\omega|x_{12}} - 1}{x_{12}}\right]. \tag{5}$$

Despite the dependence of the electron-electron interaction operator I on the choice of the gauge, all terms of the expansion (2) are gauge invariant, when calculated rigorously within QED. In the present work, we perform QED calculations of the corrections due to exchange by one and two virtual photons, $E_{1\mathrm{phot}}$ and $E_{2\mathrm{phot}}$. The corrections induced by an exchange of three or more photons are calculated within the Breit approximation, which is equivalent to choosing the Coulomb gauge in the photon propagator and setting $\omega \to 0$.

In the following, we will extensively use the following short-hand notations for the matrix elements of the electron-electron interaction operator,

$$I_{abcd}(\Delta) \equiv \langle ab|I(\Delta)|cd\rangle\,, \tag{6}$$

$$I_{abcd} \equiv \langle ab|I_{\mathrm{Coul}}(0)|cd\rangle\,. \tag{7}$$

The leading electron-structure correction comes from the exchange of one virtual photon between the electrons. The correction due to one-photon exchange between a valence electron v and a closed shell of electron states c is given by

$$E_{1\mathrm{phot}}(v) = \sum_{\mu_c}\sum_{P}(-1)^P I_{PvPcvc}(\Delta_{Pcc}) \equiv \sum_{\mu_c}\Big[I_{vcvc}(0) - I_{cvvc}(\Delta_{vc})\Big]\,, \tag{8}$$

where P is the permutation operator interchanging the one-electron states, $(PvPc) = (vc)$ or (cv), $(-1)^P$ is the sign of the permutation, $\Delta_{ab} = \varepsilon_a - \varepsilon_b$ is the difference of one-electron energies, and the summation over μ_c runs over the angular momentum projections of the core electrons. The one-photon exchange correction is relatively simple and can be calculated to very high numerical accuracy.

The effects caused by the exchange of two photons are much more complicated than the one-photon contribution. First rigorous QED calculations of the two-photon exchange correction started in 1990th and were performed for He-like ions [32–35]. For Li-like ions, analogous calculations were accomplished in Refs. [15, 18–20, 22]. In the present work, we extend the previous calculations described in Refs. [18–20] to a greater numerical accuracy and a larger interval of nuclear charges.

The correction induced by the two-photon exchange between a valence electron v and a closed shell of electron

states c is given by [19]

$$E_{2\rm phot}(v) = \sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1 n_2}{}' \frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega \left[\frac{I_{PcPvn_1n_2}(\omega)\, I_{n_1n_2cv}(\omega-\Delta_{Pcc})}{(\varepsilon_{Pc}-\omega-u\varepsilon_{n_1})(\varepsilon_{Pv}+\omega-u\varepsilon_{n_2})} + \frac{I_{Pcn_2n_1v}(\omega)\, I_{n_1Pvcn_2}(\omega-\Delta_{Pcc})}{(\varepsilon_{Pc}-\omega-u\varepsilon_{n_1})(\varepsilon_{v}-\omega-u\varepsilon_{n_2})}\right]$$
$$+\sum_{PQ}(-1)^{P+Q}\sum_{n}{}' \frac{I_{P2P3nQ3}(\Delta_{P3Q3})\, I_{P1nQ1Q2}(\Delta_{Q1P1})}{\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_n} + E_{\rm red}(v)\,, \tag{9}$$

where P and Q are the permutation operators, $u \equiv 1 - i0$, and the prime on the sum symbol means that some terms are excluded from the summation (the excluded terms are ascribed to the reducible part $E_{\rm red}$ and evaluated separately, see Refs. [19, 20] for details). In Eq. (9), the first part on the right-hand side is the irreducible two-electron contribution, the second part is the irreducible three-electron contribution (with "1", "2", and "3" numerating the three electrons, in arbitrary order), and the third part $\Delta E_{\rm red}$ is the reducible contribution. The explicit expression for $\Delta E_{\rm red}$ can be found in Refs. [19, 20].

The two-photon exchange correction can be greatly simplified in the MBPT approximation, which assumes that (i) the electron-electron interaction is taken in the Breit approximation, $I(\omega) \to I_{\rm Coul}(0)$ and (ii) the summations are performed over the positive-energy part of the Dirac spectrum. Within this approximation, the integration over ω is performed by the Cauchy theorem and the crossed-photon and reducible contributions vanish, yielding the result

$$E^{\rm MBPT}_{2\rm phot}(v) = \sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1 n_2}{}'^{(+)} \frac{I_{PcPvn_1n_2}\, I_{n_1n_2cv}}{\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_2}} + \sum_{PQ}(-1)^{P+Q}\sum_{n}{}'^{(+)} \frac{I_{P2P3nQ3}\, I_{P1nQ1Q2}}{\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_n}\,, \tag{10}$$

where the prime on the summation symbol means that terms with vanishing denominator are omitted and "(+)" means that the summation is extended over the positive-energy part of the Dirac spectrum.

The three-photon exchange correction cannot be presently calculated rigorously within QED. In the present work we evaluate it within the MBPT approximation, where it is represented as [21]

$$\Delta E^{\rm MBPT}_{3\rm ph}(v) = \sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1\ldots n_4}{}^{(+)} \Xi_1 \frac{I_{PvPcn_1n_2}\, I_{n_1n_2n_3n_4}\, I_{n_3n_4vc}}{(\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_2})(\varepsilon_c+\varepsilon_v-\varepsilon_{n_3}-\varepsilon_{n_4})}$$
$$+\sum_{PQ}(-1)^{P+Q}\sum_{n_1n_2n_3}{}^{(+)} \Xi_1 \left[\frac{2\, I_{P2P3n_1Q3}\, I_{P1n_1n_2n_3}\, I_{n_2n_3Q1Q2}}{(\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_{n_1})(\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{n_2}-\varepsilon_{n_3})}\right.$$
$$\left.+\frac{I_{P1P2n_1n_2}\, I_{n_2P3n_3Q3}\, I_{n_1n_3Q1Q2}}{(\varepsilon_{P1}+\varepsilon_{P2}-\varepsilon_{n_1}-\varepsilon_{n_2})(\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{n_1}-\varepsilon_{n_3})} + \frac{I_{P2P3n_1n_2}\, I_{P1n_1n_3Q2}\, I_{n_3n_2Q1Q3}}{(\varepsilon_{P2}+\varepsilon_{P3}-\varepsilon_{n_1}-\varepsilon_{n_2})(\varepsilon_{Q1}+\varepsilon_{Q3}-\varepsilon_{n_2}-\varepsilon_{n_3})}\right], \tag{11}$$

where the operator Ξ_1 acts on energy denominators Δ_1, Δ_2 as following

$$\Xi_1 \frac{X}{\Delta_1\,\Delta_2} = \begin{cases} \dfrac{X}{\Delta_1\,\Delta_2}\,, & \text{if } \Delta_1 \neq 0\,, \Delta_2 \neq 0\,, \\ -\dfrac{X}{2\,\Delta_1^2}\,, & \text{if } \Delta_1 \neq 0\,, \Delta_2 = 0\,, \\ -\dfrac{X}{2\,\Delta_2^2}\,, & \text{if } \Delta_1 = 0\,, \Delta_2 \neq 0\,, \\ 0\,, & \text{if } \Delta_1 = 0\,, \Delta_2 = 0\,. \end{cases} \tag{12}$$

The correction induced by the exchange of four and more photons, $E_{\geq 4\rm phot}$, is too complicated to be calculated by perturbation theory. In the present work we extract this correction from the NRQED results, which account for all orders in $1/Z$ but only the leading order in $Z\alpha$; the corresponding calculation is described in Sec. II.

B. Radiative QED

The radiative QED contribution to the fs splitting is represented as an expansion in the number of virtual photons exchanged between the electrons (with the expansion parameter $1/Z$),

$$E_{\rm rad} = E_{\rm QEDhydr} + E_{\rm QEDscr1} + E_{\rm QEDscr2} + E_{\rm QEDscr3+}\,, \tag{13}$$

where $E_{\rm QEDhydr}$ is the hydrogenic QED correction, $E_{\rm QEDscr1}$ is the screening QED correction with one electron-electron interaction, $E_{\rm QEDscr2}$ is the screening QED correction with two electron-electron interactions, and $E_{\rm QEDscr3+}$ contains three and more electron-electron interactions.

The one-electron QED contribution $E_{\rm QEDhydr}$ is presently well established, see, e.g., a recent review [36]; it will be taken from the literature in this work. The

TABLE I. Comparison of different approximate methods with the rigorous QED calculations [16, 17, 37] of the first-order $1/Z^1$ QED screening correction, in units $\alpha^2(Z\alpha)^3$.

Z	amm	MQED	amm+MQED	Full QED
12	−0.0658	−0.0362	−0.0618	−0.0616 (14)
16	−0.0664	−0.0341	−0.0601	−0.0590 (9)
18	−0.0667	−0.0330	−0.0592	−0.0579 (4)
20	−0.0671	−0.0319	−0.0582	−0.0566 (3)
30	−0.0699	−0.0253	−0.0529	−0.0501 (3)
32	−0.0706	−0.0238	−0.0517	−0.0486 (4)
40	−0.0741	−0.0173	−0.0465	−0.0422 (2)
50	−0.0803	−0.0075	−0.0387	−0.0325 (2)
54	−0.0835	−0.0029	−0.0350	−0.0281 (2)
60	−0.0893	0.0049	−0.0285	−0.0202 (2)
66	−0.0967	0.0142	−0.0209	−0.0113 (2)
70	−0.1028	0.0213	−0.0149	−0.0041 (1)
74	−0.1101	0.0294	−0.0080	0.0037 (2)
80	−0.1241	0.0439	0.0043	0.0182 (1)
83	−0.1329	0.0523	0.0115	0.0266 (1)
90	−0.1601	0.0761	0.0319	0.0501 (1)
92	−0.1702	0.0842	0.0389	0.0581 (1)
100	−0.2277	0.1240	0.0728	0.0974 (1)

first-order $1/Z^1$ screening QED correction $E_{\rm QEDscr1}$ was calculated for Li-like ions in Refs. [14–17, 22, 37]; numerical results for this correction will also be taken from the literature.

We now concentrate on the second-order $1/Z^2$ screening QED contribution $E_{\rm QEDscr2}$. At present, it is not possible to calculate this correction rigorously to all orders in $Z\alpha$. In this work, we will calculate it by an approximate relativistic method which is exact to the leading order in $Z\alpha$ and accounts for the dominant part of the higher-order $Z\alpha$ terms.

It is well-known [38] that, to the leading order in $Z\alpha$, the radiative QED effects in the fs splitting are described by the electron anomalous magnetic moment (amm). In the absence of external fields, the electron amm induces the following two additions to the Dirac Hamiltonian of a few-electron atom [38, 39],

$$H_{\rm amm,1} = \kappa\,\frac{Z\alpha}{4}\,(-i)\sum_a \beta_a\,\frac{\boldsymbol{\alpha}_a\cdot\boldsymbol{r}_a}{r_a^3}\,, \tag{14}$$

$$H_{\rm amm,2} = \kappa\,\frac{\alpha}{4}\sum_{a<b}\beta_a\left(i\,\frac{\boldsymbol{\alpha}_a\cdot\boldsymbol{r}_{ab}}{r_{ab}^3} - \boldsymbol{\Sigma}_a\cdot\frac{\boldsymbol{\alpha}_b\times\boldsymbol{r}_{ab}}{r_{ab}^3}\right), \tag{15}$$

where a and b numerate the electrons in the atom, $\kappa = g_e-2 = {}^{\alpha}\!/_{\pi}+O(\alpha^2)$, g_e is the g-factor of the free electron, β_a and $\boldsymbol{\alpha}_a$ are the Dirac matrices acting on ath electron, and

$$\boldsymbol{\Sigma} = \begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix}, \tag{16}$$

with $\boldsymbol{\sigma}$ being a vector of Pauli matrices.

The effective amm Hamiltonian $H_{\rm amm} = H_{\rm amm,1} + H_{\rm amm,2}$ yields a good description of the radiative QED effects for low-Z ions, but the accuracy deteriorates quickly when Z increases. We will correct this with help of the model QED (MQED) operator $h_{\rm MQED}$ introduced in Ref. [40]. In order to avoid double counting, we subtract from $h_{\rm MQED}$ the part already accounted for by the amm Hamiltonian. Specifically, we make the replacement

$$\frac{1}{2}\langle\psi_j|\Sigma(\varepsilon_j)+\Sigma(\varepsilon_l)|\psi_l\rangle \to \frac{1}{2}\langle\psi_j|\Sigma(\varepsilon_j)+\Sigma(\varepsilon_l)|\psi_l\rangle - \langle\psi_j|H_{\rm amm,1}|\psi_l\rangle \tag{17}$$

in the definition of the MQED operator (where $\Sigma(\varepsilon)$ is the self-energy operator), see Eq. (17) of Ref. [40]. We will denote the amm-subtracted MQED operator by $h'_{\rm MQED}$.

In this work we will calculate the second-order QED screening correction $E_{\rm QEDscr2}$ by using the standard Rayleigh-Schrödinger perturbation theory to the second order in the electron-electron interaction and to first order in the effective Hamiltonian $H_{\rm amm+MQED}$,

$$H_{\rm amm+MQED} = H_{\rm amm,1} + H_{\rm amm,2} + h'_{\rm MQED} \equiv U + W\,. \tag{18}$$

The operators U and W introduced in the right-hand-side of the above equation incorporate the one-electron part ($H_{\rm amm,1} + h'_{\rm MQED}$) and the two-electron part ($H_{\rm amm,2}$) of the effective Hamiltonian, respectively.

Before calculating the second-order screening QED effect, we need to check the accuracy of the approximate method we devised. We do this by applying this approximation to the first-order screening QED correction and comparing the obtained results with those delivered by the rigorous QED calculations.

The $1/Z^1$ correction induced by the one-electron operator U is obtained as a first-order (in U) perturbation of the one-photon exchange correction (8), which is (after dropping the frequency-dependent terms)

$$E_{\rm 1phot,\,U} = 2\sum_{\mu_c}\sum_P (-1)^P\left(I_{PvPc\delta vc} + I_{PvPcv\delta c}\right)\,, \tag{19}$$

where

$$|\delta a\rangle = {\sum_n}'\,\frac{|n\rangle\,U_{na}}{\varepsilon_a-\varepsilon_n}\,, \tag{20}$$

and $U_{ab}\equiv\langle a|U|b\rangle$. The $1/Z^1$ correction induced by the two-electron operator W is just

$$E_{\rm 1phot,\,W} = \sum_{\mu_c}\sum_P (-1)^P W_{PvPcvc}\,, \tag{21}$$

where $W_{abcd}\equiv\langle ab|W|cd\rangle$.

Table I presents results of our test calculations of the first-order $1/Z^1$ QED screening correction performed by three approximate methods and compares them with results obtained by the full QED treatment. The column "amm" lists results obtained with the amm operator $H_{\rm amm}$, the column "MQED" displays results obtained

with the standard MQED operator $h_{\rm MQED}$, whereas the column "amm+MQED" shows results obtained with the combined operator (18).

We observe that the approach based on the amm Hamiltonian works well only in the low-Z region but fails for high values of Z, not reproducing even the overall sign of the effect. The standard MQED operator yields the order of magnitude and the sign of the exact QED screening correction, but the quantitative agreement is not very good. In contrast, the combined "amm+MQED" approach demonstrates a significantly improved agreement with the rigorous QED treatment as compared to the both other methods.

We now turn to the second-order $1/Z^2$ screening QED effect. The $1/Z^2$ correction induced by the one-electron operator U can be derived as a first-order (in U) perturbation of the two-photon exchange correction in the MBPT approximation, given by Eq. (10). It consists of 3 parts that are induced by perturbations of the wave functions ("wf"), binding energies ("en"), and propagators ("ver"), respectively,

$$E_{\rm 2phot,U} = E_{\rm 2phot,wf} + E_{\rm 2phot,en} + E_{\rm 2phot,ver}\,. \tag{22}$$

The corresponding parts are given by

$$\begin{aligned} E_{\rm 2phot,wf} = {}& 2\sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1 n_2}{}'^{(+)} \frac{I_{PvPcn_1n_2}\left(I_{n_1n_2\delta vc} + I_{n_1n_2v\delta c}\right)}{\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_2}} \\ & + 2\sum_{PQ}(-1)^{P+Q} \sum_{n}{}'^{(+)} \frac{I_{P2P3nQ3}\left(I_{\delta P1nQ1Q2} + I_{P1n\delta Q1Q2} + I_{P1nQ1\delta Q2}\right)}{\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_n}\,, \end{aligned} \tag{23}$$

$$\begin{aligned} E_{\rm 2phot,en} = {}& -(U_{vv}+U_{cc})\sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1 n_2}{}'^{(+)} \frac{I_{PvPcn_1n_2}\, I_{n_1n_2vc}}{(\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_2})^2} \\ & - \sum_{PQ}(-1)^{P+Q}\left(U_{Q1Q1}+U_{Q2Q2}-U_{P1P1}\right) \sum_{n}{}'^{(+)} \frac{I_{P2P3nQ3}\, I_{P1nQ1Q2}}{(\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_n)^2}\,, \end{aligned} \tag{24}$$

$$\begin{aligned} E_{\rm 2phot,ver} = {}& \sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1 n_2 n_3}{}^{(+)} \Xi_2 \frac{I_{PvPcn_1n_2}}{\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_2}} \left(\frac{U_{n_1n_3}\, I_{n_3n_2vc}}{\varepsilon_c+\varepsilon_v-\varepsilon_{n_3}-\varepsilon_{n_2}} + \frac{U_{n_2n_3}\, I_{n_1n_3vc}}{\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_3}}\right) \\ & + \sum_{PQ}(-1)^{P+Q} \sum_{n_1 n_2}{}^{(+)} \Xi_2 \frac{I_{P2P3n_1Q3}\, U_{n_1n_2}\, I_{P1n_2Q1Q2}}{(\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_{n_1})(\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_{n_2})}\,, \end{aligned} \tag{25}$$

where the operator Ξ_2 acts on energy denominators Δ_1, Δ_2 as following:

$$\Xi_2 \frac{X}{\Delta_1\,\Delta_2} = \begin{cases} \dfrac{X}{\Delta_1\,\Delta_2}\,, & \text{if } \Delta_1\neq 0\,, \Delta_2\neq 0\,, \\ -\dfrac{X}{\Delta_1^2}\,, & \text{if } \Delta_1\neq 0\,, \Delta_2 = 0\,, \\ -\dfrac{X}{\Delta_2^2}\,, & \text{if } \Delta_1 = 0\,, \Delta_2\neq 0\,, \\ 0\,, & \text{if } \Delta_1 = 0\,, \Delta_2 = 0\,. \end{cases} \tag{26}$$

We note that similar formulas appeared in a slightly different context in Ref. [21] (*cf.* Eqs. (32)-(35) of that work).

The $1/Z^2$ correction induced by the two-electron operator W is given by

$$\begin{aligned} E_{\rm 2phot,W} = {}& \sum_{\mu_c}\sum_{P}(-1)^P \sum_{n_1 n_2}{}'^{(+)} \frac{I_{PvPcn_1n_2}\, W_{n_1n_2vc} + W_{PvPcn_1n_2}\, I_{n_1n_2vc}}{\varepsilon_c+\varepsilon_v-\varepsilon_{n_1}-\varepsilon_{n_2}} \\ & + \sum_{PQ}(-1)^{P+Q} \sum_{n}{}'^{(+)} \frac{I_{P2P3nQ3}\, W_{P1nQ1Q2} + W_{P2P3nQ3}\, I_{P1nQ1Q2}}{\varepsilon_{Q1}+\varepsilon_{Q2}-\varepsilon_{P1}-\varepsilon_n}\,. \end{aligned} \tag{27}$$

C. Nuclear recoil

The nuclear recoil contribution is represented in this work as a sum of two parts,

$$E_{\rm rec} = E_{\rm rec}^{\rm oneel} + E_{\rm rec}^{\rm fewel}\,, \tag{28}$$

where the first part is the one-electron (hydrogenic) contribution and the second part is the few-body contribu-

tion. The one-electron contribution is presently well established, see, e.g., a recent review [36], and is taken from the literature. The few-body recoil contribution will be evaluated to the leading order in $Z\alpha$ within the NRQED approach in next Section.

II. NON-RELATIVISTIC QED

In the nonrelativistic quantum electrodynamics (NRQED) framework, the fs splitting of light atoms is represented by an expansion in powers of the fine-structure constant α and the electron-to-nucleus mass ratio m/M [29, 30],

$$E_{\rm NRQED} = \alpha^4 \left[\mathcal{E}^{(4,0)} + \frac{m}{M}\,\mathcal{E}^{(4,1)} + \alpha\,\mathcal{E}^{(5,0)} + \ldots\right] . \tag{29}$$

Here, the first superscript of the expansion terms $\mathcal{E}^{(i,j)}$ indicates the order in α, whereas the second superscript shows the order in m/M. Each term of the NRQED expansion is represented as an expectation value of some effective Hamiltonian on the nonrelativistic atomic wave function and thus accounts for the nonrelativistic electron-electron interaction (i.e., the parameter $1/Z$) to all orders.

The leading term of the NRQED expansion of the fs interval is given by the difference of the expectation values of the spin-dependent Breit Hamiltonian, $\mathcal{E}^{(4,0)} = \langle H^{(4,0)}\rangle_{J=3/2} - \langle H^{(4,0)}\rangle_{J=1/2}$. The spin-dependent part of the Breit Hamiltonian is (in atomic units)

$$H^{(4,0)} = \sum_a \frac{Z}{2\,r_a^3}\,\vec{s}_a\cdot\vec{r}_a\times\vec{p}_a + \sum_{a\neq b}\frac{1}{2\,r_{ab}^3}\,\vec{s}_a\cdot\vec{r}_{ab}\times\left(2\vec{p}_b-\vec{p}_a\right), \tag{30}$$

where a and b numerate electrons in the atom, $\vec{r}_{ab} = \vec{r}_a - \vec{r}_b$, $\vec{p}_a$ is the electron momentum, and $\vec{s}_a$ is the electron-spin operator.

The spin-dependent $m\alpha^4$ recoil correction for a state with the total angular momentum J is given by (in atomic units)

$$\mathcal{E}_J^{(4,1)} = \left\langle H^{(4,0)}\,\frac{1}{(E-H)'}\,H^{(2,1)}\right\rangle_J + \left\langle \sum_{ab}\frac{Z}{r_a^3}\,\vec{s}_a\cdot\vec{r}_a\times\vec{p}_b\right\rangle_J , \tag{31}$$

where $H^{(2,1)}$ is the recoil operator of order $m\alpha^2$,

$$H^{(2,1)} = \frac{1}{2}\,\vec{P}^2 = \frac{1}{2}\left(-\sum_a\vec{p}_a\right)^2 , \tag{32}$$

and $\vec{P}$ is the nuclear momentum.

The leading QED contribution to the fs interval is induced by the Hamiltonian $H^{(5,0)}$, $\mathcal{E}^{(5,0)} = \langle H^{(5,0)}\rangle_{J=3/2} - \langle H^{(5,0)}\rangle_{J=1/2}$, where (in atomic units)

$$H^{(5,0)} = \sum_a \frac{Z}{2\pi\,r_a^3}\,\vec{s}_a\cdot\vec{r}_a\times\vec{p}_a + \sum_{a\neq b}\frac{1}{2\pi\,r_{ab}^3}\,\vec{s}_a\cdot\vec{r}_{ab}\times\left(\vec{p}_b-\vec{p}_a\right). \tag{33}$$

In the present work we calculate the corrections $\mathcal{E}^{(4,0)}$, $\mathcal{E}^{(5,0)}$, and $\mathcal{E}^{(4,1)}$ for the series of nuclear charges $Z =$ 3–13. The computational scheme and numerical details are described in Ref. [29, 30]. Our numerical results are presented in Table II.

In order to combine the NRQED results with those obtained within the $1/Z$-exansion method in Sec. I, we represent the numerical results listed in Table II in the form of the $1/Z$ expansion,

$$\mathcal{E}^{(4,0)} = Z^4\sum_{i=0}^{\infty}\frac{C_{i,4}}{Z^i}\,, \tag{34}$$

$$\mathcal{E}^{(5,0)} = Z^4\sum_{i=0}^{\infty}\frac{D_{i,5}}{Z^i}\,, \tag{35}$$

$$\mathcal{E}^{(4,1)} = Z^4\sum_{i=0}^{\infty}\frac{R_{i,4}}{Z^i}\,. \tag{36}$$

Here and in what follows, we adopt the following notations for the expansion coefficients $C_{i,j}$, $D_{i,j}$, $R_{i,j}$: the first index i corresponds to the order in $1/Z$, whereas the second index j indicates the order in α.

The first coefficients of the expansions are known analytically,

$$C_{0,4} = \frac{1}{32}\,, \quad D_{0,5} = \frac{1}{32\pi}\,, \tag{37}$$

$$R_{0,4} = -\frac{1}{32} + \frac{2^8}{3^9}\left(3\ln\frac{3}{2} - 2\right), \tag{38}$$

where $C_{0,4}$ comes from the $Z\alpha$ expansion of the Dirac energy (3), $D_{0,5}$ comes from the one-loop self-energy (see, e.g., Eq. (38) of Ref. [41]), whereas the $R_{0,4}$ coefficient was derived in Ref. [42]. The coefficients $C_{1,4}$ and $C_{2,4}$ will be numerically evaluated in the next Section, by calculating the one-photon and two-photon exchange corrections and fitting their $Z\to 0$ and $\alpha\to 0$ limit. The other coefficients in Eqs. (34)-(36) are approximately obtained by fitting the numerical results from Table II.

III. CALCULATIONAL DETAILS AND RESULTS

A. Electronic structure

Table III presents results of our numerical calculations of individual electron-structure contributions. The column labeled "Dirac" shows the Dirac one-electron energies E_D. The uncertainties of E_D, appearing for high-Z

TABLE II. Numerical results for the α^4, α^5, and $\alpha^4(m/M)$ corrections to the fine structure of the $2P$ state of Li-like ions. $\mathcal{E}^{(i,j)}$ are defined by Eq. (29).

Z	$\mathcal{E}^{(4,0)}/Z^4$	$\mathcal{E}^{(5,0)}/Z^4$	$\mathcal{E}^{(4,1)}/Z^4$
3	0.000 353 014 9 (1)	0.000 169 064 948 (1)	−0.001 074 97 (2)
4	0.002 190 425 2 (5)	0.000 865 489 89 (10)	−0.003 891 58 (4)
5	0.004 653 760 1 (3)	0.001 713 290 95 (7)	−0.007 034 07 (2)
6	0.007 054 738 0 (2)	0.002 505 289 60 (3)	−0.010 032 02 (2)
7	0.009 196 952 5 (7)	0.003 195 699 19 (15)	−0.012 717 88 (4)
8	0.011 057 748 2 (1)	0.003 786 733 68 (2)	−0.015 068 04 (1)
9	0.012 664 475 3 (1)	0.004 292 004 93 (4)	−0.017 111 05 (1)
10	0.014 054 569 0 (1)	0.004 725 993 9 (2)	−0.018 888 65 (2)
11	0.015 263 384 0 (1)	0.005 101 316 3 (3)	−0.020 441 55 (1)
12	0.016 321 112 5 (1)	0.005 428 312 6 (2)	−0.021 805 51 (1)
13	0.017 252 626 (3)	0.005 715 289 (8)	−0.023 010 5 (5)

ions, are due to the finite nuclear size effect. The $Z\alpha$ expansion of the Dirac fs splitting follows from Eq. (3),

$$E_D = (Z\alpha)^4 \left[C_{0,4} + (Z\alpha)^2\, C_{0,6} + (Z\alpha)^4\, C_{0,8} + \ldots\right], \tag{39}$$

where $C_{0,4} = {}^1\!/_{32}$, $C_{0,6} = {}^5\!/_{256}$, etc.

The next column labeled "1-ph" contains results for the one-photon exchange correction. Its calculation is relatively straightforward and can be preformed up to arbitrary numerical accuracy. The $Z\alpha$ expansion of the one-photon exchange correction for the fs splitting is of the form

$$E_{\rm 1phot} = \alpha(Z\alpha)^3 \left[C_{1,4} + (Z\alpha)^2\, C_{1,6} + (Z\alpha)^4\, C_{1,8} + \ldots\right]. \tag{40}$$

While our numerical calculation accounts for all orders in $Z\alpha$, we also determine values of the first two expansion coefficients by fitting our all-order results, obtaining $C_{1,4} = -0.218\,109\,12$ and $C_{1,6} = -0.194\,777$.

The two-photon exchange correction is calculated in the present work rigorously within QED, by the method described in the previous investigations [19, 20]. The Dirac spectrum is represented by using the dual kinetic balance (DKB) method [43] with $N = 85$ B-spline basis functions. The partial-wave expansion was extended up to $|\kappa_{\rm max}| = 20$, with the remaining tail of the expansion estimated by a least-square fitting in $1/|\kappa|$. The direct numerical calculations were performed for $Z > 13$.

In order to obtain results for the two-photon exchange correction in the low-Z region, we fit our numerical values to the form of the $Z\alpha$ expansion,

$$E_{\rm 2phot} = \alpha^2\,(Z\alpha)^2 \Big[C_{2,4} + (Z\alpha)^2\, C_{2,6} + \ldots\Big]. \tag{41}$$

The leading expansion coefficient $C_{2,4}$ is evaluated separately, by two different methods. First, we obtain it by fitting the $1/Z$ expansion of the $m\alpha^4$ NRQED results obtained in Sec. II. Second, we get it by fitting the $Z \to 0$ and $\alpha \to 0$ limit of the two-photon exchange correction in the MBPT approximation (10). Both methods yield consisting results, but the second is more accurate. We therefore fix the coefficient as $C_{2,4} = 0.497\,88$. With the leading coefficient $C_{2,4}$ fixed in this way, the higher-order coefficients are obtained by fitting our numerical all-order results. In particular, we obtain the next-order coefficient as $C_{2,6} = 0.75$.

Our numerical results for the two-photon exchange correction are presented in Table III. For convenience, we separate them into two parts. The first, dominant part is delivered by the MBPT approximation, see Eq. (10). The second, much smaller part is the deviation of the full QED result from the MBPT value. For $Z > 13$, the listed QED values are obtained by a direct calculation. For $Z \le 13$, the listed values are obtained by fitting.

The three-photon exchange correction is evaluated within the MBPT approximation, according to Eq. (11). The scheme of the calculation mainly follows that of Ref. [21]. However, Ref. [21] included the Breit interaction up to first order only, whereas here we include in addition the exchange by two and three Breit photons. The reason is that the inclusion of the second-order Breit exchange significantly improves the agreement between MBPT and QED for the two-photon exchange correction to the fs splitting.

The summations over the Dirac spectrum in the three-photon exchange correction was performed by using the DKB method [43] with B-spline basis functions. The number of B-splines in the basis was $N = 50$ for the three-electron part and $N = 40$ for the two-electron part. The extrapolation of the double partial wave expansion was performed as described in Ref. [21], with the number of partial waves $l_1 = 8$ for the first summation and $l_2 = 12$ for the second summation.

Direct numerical calculations of the three-photon exchange correction were performed for $Z \ge 20$. For lower values of Z, the accuracy of the numerical evaluation gradually deteriorates, so we obtain results for this correction by fitting. Specifically, we fit our numerical results to the form of the $Z\alpha$-expansion

$$E_{\rm 3phot} = \alpha^3\,(Z\alpha)\left[C_{3,4} + (Z\alpha)^2\, C_{3,6} + \ldots\right], \tag{42}$$

with the leading coefficient $C_{3,4} = -0.3681$ obtained by fitting the $1/Z$ expansion of the NRQED results in Sec. II. We obtain the next-order coefficient (in the MBPT approximation) as $C_{3,6} = -1.4$.

Numerical results for the three-photon exchange correction are presented in Table III, in the column labeled "3-ph". The uncertainty of this correction comes mainly from unknown QED effects beyond the MBPT approximation. We estimate it by taking the relative value of the QED-MBPT difference for the two-photon exchange correction and multiplying it by the extension factor of 4.

The correction induced by the exchange of four and more photons $E_{\geq 4\mathrm{phot}}$ is obtained from the NRQED calculations described in Sec. II. Direct NRQED calculations were performed for $Z \leq 13$. For these nuclear charges, we obtain $E_{\geq 4\mathrm{phot}}$ by subtracting the first terms of the $1/Z$ expansion from the $m\alpha^4$ NRQED contribution listed in Table II,

$$E_{\geq 4\mathrm{phot}} = \alpha^4 \mathcal{E}^{(4,0)} - (Z\alpha)^4 \left[C_{0,4} + \frac{C_{1,4}}{Z} + \frac{C_{2,4}}{Z^2} + \frac{C_{3,4}}{Z^3}\right]. \tag{43}$$

We note that numerical uncertainties of the coefficients $C_{2,4}$ and $C_{3,4}$ do not contribute to the uncertainty of the total electron-structure contribution for $Z \leq 13$, since the same coefficients used in Eqs. (41), (42) and (43) cancel each other when the sum of these equations is evaluated. For $Z > 13$, we obtain $E_{\geq 4\mathrm{phot}}$ by fitting the $1/Z$ expansion of numerical results for $\mathcal{E}^{(4,0)}$ listed in Table II.

Our results for $E_{\geq 4\mathrm{phot}}$ are presented in Table III, in the column labeled "≥4-ph". The indicated numerical uncertainty takes into account uncalculated QED effects of order $m\alpha^6$ and higher and the uncertainty of the fit for $Z > 13$. The uncalculated effects are estimated by taking the relative value of the deviation of the full QED results for the two-photon exchange correction from the $m\alpha^4$ contribution induced by the coefficient $C_{2,4}$, and multiplying it by a conservative factor of 2.

Table III summarizes our total numerical values of the electron-structure contribution to the $2p_{3/2}$-$2p_{1/2}$ fs splitting in Li-like ions and compares them with results obtained by other methods. We observe that for $Z \leq 6$, our results essentially coincide with the $m\alpha^4$ NRQED values. The reason is that the $1/Z$ expansion, used in the present work for calculating the higher-order QED effects, breaks down for low Z, with individual $1/Z$-expansion terms cancelling each other to a great extent. For larger values of Z, the convergence of the $1/Z$ expansion improves; the higher-order QED effects also become increasingly more important, moving our results further away from the NRQED values.

For $Z \geq 10$, we compare our results with the previous *ab initio* QED calculation by Kozhedub *et al.* [22]. The agreement between the calculations is excellent, but our results are more accurate, most notably in the low-Z region, due to a more complete inclusion of many-photon exchange effects.

B. Radiative QED

We now turn to the radiative QED part, which is represented by a sum of several terms, as given by Eq. (13). The first term on the right-hand-side of Eq. (13), E_{QEDhydr}, is due to one-electron QED effects. They were recently reviewed in Ref. [36], so we obtain E_{QEDhydr} from data tabulated in that work, adding together the one-loop and two-loop QED effects. The $Z\alpha$ expansion of this contribution is

$$E_{\mathrm{QEDhydr}} = \alpha(Z\alpha)^4 \Big[D_{0,5} + (Z\alpha)^2 \ln(Z\alpha)\, D_{0,7}^{\log} + (Z\alpha)^2\, D_{0,7} + \dots\Big], \tag{44}$$

where $D_{0,5} = 1/32\pi$, $D_{0,7}^{\log} = 1/16\pi$ [41]. The other terms on the right-hand-side of Eq. (13) are due to the electron-electron interaction; they are referred to as the screening QED corrections.

The first-order $1/Z$ screening QED correction E_{QEDscr1} was calculated for Li-like ions in a series of investigations [14–17, 22, 37]. The data reported in these studies are not fully sufficient for our present needs, because of a limited number of nuclear charges for which results are presented. In the present work we use a more complete tabulation from Ref. [44], originally calculated for He-like ions. We convert these results from He-like ions to Li-like ions, using the fact that the following exact relation exists between the $1/Z$ screening QED corrections for Li-like and He-like ions (see Eq. (70) of Ref. [44]),

$$E_{(1s)^2 2p_{1/2}} = \frac{1}{2} E_{(1s\,2p_{1/2})_0} + \frac{3}{2} E_{(1s\,2p_{1/2})_1}, \tag{45}$$

$$E_{(1s)^2 2p_{3/2}} = \frac{3}{4} E_{(1s\,2p_{3/2})_1} + \frac{5}{4} E_{(1s\,2p_{3/2})_2}. \tag{46}$$

Specifically, for nuclear charges $Z \geq 20$, we interpolate the numerical data presented in Ref. [44]. Values for $Z < 20$ were obtained by fitting numerical data for $Z \geq 20$ to the $Z\alpha$-expansion form

$$E_{\mathrm{QEDscr1}} = \alpha^2(Z\alpha)^3 \Big[D_{1,5} + (Z\alpha)^2 \ln(Z\alpha)\, D_{1,7}^{\log} + (Z\alpha)^2\, D_{1,7} + \dots\Big], \tag{47}$$

using the accurate value for the leading coefficient $D_{1,5} = -0.065\,060$, obtained in Sec. II from fitting the NRQED results for the $\mathcal{E}^{(5,0)}$ correction. Numerical results for E_{QEDscr1} are listed in the column "$1/Z$" of Table IV.

The column "$1/Z^2$" of Table IV presents numerical results for the second-order $1/Z^2$ screening QED correction, E_{QEDscr2}, obtained by the amm+MQED approach

described in Sec. I B. The Dirac spectrum is represented by using the DKB method [43] with $N = 85$ B-spline basis functions. The angular integration in radial matrix elements of the amm operators was carried out according to formulas presented in Appendix A. The $Z\alpha$ expansion of $E_{\rm QEDscr2}$ is

$$E_{\rm QEDscr2} = \alpha^3 (Z\alpha)^2 \, D_{2,5} + \dots \,, \tag{48}$$

where $D_{2,5} = 0.1377$ is obtained in Sec. II from fitting the variational NRQED results for the $\mathcal{E}^{(5,0)}$ correction. The uncertainty ascribed to this correction in Table IV estimates the error of the approximation. It was evaluated by taking the difference of the amm+MQED and full-QED results for the $1/Z$ screening correction, scaling it by the ratio $D_{2,5}/(Z\,D_{1,5})$, and multiplying it by a conservative factor of 2.

The higher-order screening QED correction $E_{\rm QEDscr3+}$ was obtained from the NRQED calculations described in Sec. II. For $Z \le 13$, we obtain $E_{\ge 4\rm phot}$ by subtracting the first terms of the $1/Z$ expansion from the $m\alpha^5$ NRQED contribution listed in Table II,

$$E_{\rm QEDscr3+} = \alpha^5 \mathcal{E}^{(5,0)} - \alpha (Z\alpha)^4 \left[D_{0,5} + \frac{D_{1,5}}{Z} + \frac{D_{2,5}}{Z^2} \right] . \tag{49}$$

For $Z > 13$, we evaluate $E_{\rm QEDscr3+}$ by fitting the $1/Z$ expansion of numerical results for $E^{(5,0)}$ listed in Table II. Our results for $E_{\rm QEDscr3+}$ are listed in Table III, in the column labeled "$1/Z^{3+}$". The indicated numerical uncertainty takes into account uncalculated QED effects. We estimate these effects by taking the relative value of the deviation of the full QED results for the $1/Z$ screening correction from the $m\alpha^5$ contribution induced by the coefficient $D_{1,5}$, and multiplying it by a conservative factor of 2.

C. Nuclear recoil

The one-electron nuclear recoil correction $E_{\rm rec}^{\rm oneel}$ was calculated rigorously within QED to all orders in $Z\alpha$ in Refs. [45, 46]. In this work we take numerical results for $E_{\rm rec}^{\rm oneel}$ from the recent tabulation presented in Ref. [36].

The few-body recoil correction $E_{\rm rec}^{\rm fewel}$ is obtained from the NRQED calculations described in Sec. II. Specifically, we calculate $E_{\rm rec}^{\rm fewel}$ from $\mathcal{E}^{(4,1)}$ as

$$E_{\rm rec}^{\rm fewel} = \alpha^4 \, \frac{m}{M} \left(\mathcal{E}^{(4,1)} + \frac{Z^4}{32} \right) , \tag{50}$$

where the second term in braces subtracts the one-electron contribution already taken into account by $E_{\rm rec}^{\rm oneel}$. For $Z \le 13$, we use the values of $\mathcal{E}^{(4,1)}$ listed in Table II, whereas for larger Z, we get results by fitting the $1/Z$ expansion of $\mathcal{E}^{(4,1)}$. The uncertainty of the few-body recoil contribution was estimated by taking the relative value of the deviation of the one-electron QED recoil correction from the leading-order $m\alpha^4$ term and multiplying it by a conservative factor of 2.

D. Total fine structure

Table VI summarizes results of our calculations of the $2p_{3/2} - 2p_{1/2}$ fine-structure interval in Li-like ions with nuclear chargers $Z = 5-92$. The column labeled "$\langle r^2 \rangle^{1/2}$" contains values for the root-mean-square nuclear charges radii used in the calculation, taken from Ref. [47]. The next column specifies the isotope for which the calculation is performed. The nuclear masses were taken from Ref. [48].

The next three columns display the theoretical results for the electron-structure contribution, the one-electron QED effects, and the recoil correction, respectively. The one-electron QED part was taken from the tabulation [36]; the other contributions are evaluated as described in previous Sections.

Results collected in Table VI indicate that for light ions, the dominant theoretical uncertainty comes from the electron-structure effects, more specifically, from the numerical uncertainty of the two-photon QED correction and the residual three-photon QED effects. In the high-Z region, comparable uncertainties arise from various contributions, including the one-electron QED effects, QED screening, and nuclear charge radii.

IV. DISCUSSION

Table V presents a comparison of our theoretical predictions with previous theoretical and experimental results. For $Z \le 10$, we compare our results with theoretical values by Wang *et al.* [49]. Their calculation accounted for the electron-correlation effects within the Breit-Pauli approximation and added the relativistic and QED effects as delivered by the hydrogenic approximation with an effective nuclear charge. Their approach is reasonably adequate for very low Z. As Z increases, we observe a steadily growing deviation between their values and our results.

For $Z \ge 10$, we compare our results with the two most complete *ab initio* QED calculations, by Kozhedub *et al.* [22] and by Sapirstein and Cheng [15]. In these studies, results were reported for the $2p_{3/2}$–$2s$ and $2p_{1/2}$–$2s$ transition energies; we combine them together to get results for the $2p_{3/2}$–$2p_{1/2}$ interval. Doing this, we assume the uncertainties of the two transitions to be correlated. Specifically, we take the largest of the uncertainties reported for the two intervals, rather than adding them quadratically.

The calculations by Kozhedub *et al.* and by Sapirstein and Cheng provided accurate theoretical predictions for medium- and high-Z ions. For lower-Z ions, however, the relative accuracy of their results diminished, due to a large cancelation of various effects between the $2p_{3/2}$ and the $2p_{1/2}$ states. We observe very good agreement with predictions by Kozhedub *et al.* for all nuclear charges reported in that work, well within their error bars. The agreement with the calculation by Sapirstein and Cheng

is good for high values of Z but moderate in the interval $Z = 20-30$, which might be due to residual electron-correlation effects not accounted for in their work. Our results are significantly more accurate than those of the both previous studies, partly due to a more complete inclusion of many-photon electron-correlation effects and partly due to usage of the advantages offered by the $2p_{3/2}-2p_{1/2}$ interval as compared to the $2p_j-2s$ intervals.

The comparison of our theoretical predictions with the available experimental results is summarized in Table V and shows good agreement in most cases. In several occasions (notably, for $Z = 15$, 39, 82) deviations of about two experimental uncertainties are observed. The reasons behind them are probably on the experimental side, since different calculations agree well with each other on the level of the experimental uncertainties.

Generally, the theoretical predictions for the $2p_{3/2}-2p_{1/2}$ interval are found to be more accurate than the existing experimental results. The only exception in the range of nuclear charges covered in this work is boron ($Z = 5$), where the uncertainty of the experimental result [50] matches the theoretical accuracy. Even more accurate measurements are available for Li and Be^+ [10, 11]. Unfortunately, our present approach is not useful for these lightest atoms, since it is relies on the $1/Z$ expansion for description of QED effects of order $m\alpha^6$ and higher, which fails at very low Z.

In summary, we performed *ab initio* QED calculations of the $2p$ fine-structure interval in Li-like ions with nuclear charges $Z = 5-92$. In order to improve the theoretical accuracy, we combined together two complementary theoretical methods, namely, the $1/Z$-expansion approach, which accounts for all orders in the parameter $Z\alpha$ but expands in $1/Z$, and the NRQED approach, which accounts for all orders in $1/Z$ but expands in $Z\alpha$. In the result, we obtain the currently most accurate theoretical predictions for a wide range of nuclear charges. For $Z \geq 20$, our theoretical predictions have the fractional accuracy of better than 10^{-5}, providing an opportunity for high-precision tests of the interplay of QED and electron-correlation effects.

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Appendix A: Radial integrations in matrix elements of amm operators

In this section we present formulas for the matrix elements of the amm operators [given by Eqs. (14) and (15)] with the Dirac wave functions, after angular integrations. The matrix element of the one-electron amm operator is evaluated as

$$\langle a|H_{\rm amm,1}|b\rangle = -\frac{Z\alpha\kappa}{4}\,\delta_{\kappa_a\kappa_b}\,\delta_{\mu_a\mu_b}\int_0^\infty r^2dr\,\frac{1}{r^2}\left[g_a(r)\,f_b(r)+f_a(r)\,g_b(r)\right], \tag{A1}$$

where $g_n(r)$ and $f_n(r)$ are the upper and the lower radial components of the wave function of the electron state n, defined as in Ref. [66]; κ_n and μ_n are the relativistic angular-momentum quantum number and the angular-momentum projection, correspondingly.

The matrix element of the two-electron amm operator can be written in the form, analogous to that for the matrix element of the electron-electron interaction operator (*cf.* Eq. (38) in Ref. [66]),

$$\langle ab|H_{\rm amm,2}|cd\rangle = \frac{\alpha\kappa}{4}\sum_L J_L(abcd)\,R_L^{\rm amm,2}(abcd)\,, \tag{A2}$$

where $J_L(abcd)$ is the standard function incorporating the dependence of a two-body operator on the angular-momentum projections (see Eq. (39) of Ref. [66]) and $R_L^{\rm amm,2}$ is the radial integral evaluated as

$$\begin{aligned}R_L^{\rm amm,2}(abcd) = (-1)^L\,(2L+1)\int_0^\infty r_1^2dr_1\Bigg[&\sqrt{\frac{L+1}{2L+1}}\,C_L(\kappa_b,\kappa_d)\,\frac{1}{r_1^{L+2}}\,X_{ac,LL+1}(r_1)\int_0^{r_1} r_2^2dr_2\,r_2^L\,W_{bd}(r_2)\\
&+\sqrt{\frac{L}{2L+1}}\,C_L(\kappa_b,\kappa_d)\,\frac{1}{r_1^{L+1}}\,W_{bd}(r_1)\int_0^{r_1} r_2^2dr_2\,r_2^{L-1}\,X_{ac,LL-1}(r_2)\\
&+\sum_{l=L-1}^{L}\sqrt{6(l+1)}\begin{Bmatrix}1&1&1\\L&l&l+1\end{Bmatrix}\frac{1}{r_1^{l+2}}\,Y_{ac,Ll+1}(r_1)\int_0^{r_1} r_2^2dr_2\,r_2^l\,Z_{bd,Ll}(r_2)\end{aligned}$$

TABLE III. The electron structure corrections to the $2p_{3/2}$–$2p_{1/2}$ fine structure splitting, in eV.

Z	Dirac	1-ph.	2-ph. MBPT	2-ph. QED	3-ph.	≥4-ph.	Sum	Other methods
5	0.028 325	−0.039 553	0.018 070	0.000 002 (1)	−0.002 681 (1)	0.000 050	0.004 214 (2)	0.004 215[a]
6	0.058 757	−0.068 384	0.026 043	0.000 004 (2)	−0.003 224 (2)	0.000 057	0.013 253 (3)	0.013 249[a]
7	0.108 901	−0.108 658	0.035 483	0.000 007 (3)	−0.003 771 (3)	0.000 062	0.032 023 (5)	0.031 998[a]
8	0.185 873	−0.162 311	0.046 398	0.000 012 (5)	−0.004 323 (5)	0.000 065 (1)	0.065 714 (7)	0.065 63[a]
9	0.297 902	−0.231 290	0.058 798	0.000 018 (7)	−0.004 880 (6)	0.000 067 (1)	0.120 615 (9)	0.120 40[a]
10	0.454 338	−0.317 558	0.072 695	0.000 027 (9)	−0.005 444 (8)	0.000 069 (1)	0.204 128 (12)	0.203 66[a]
								0.204 1 (6)[b]
15	2.309 735	−1.078 183	0.165 127	0.000 128 (3)	−0.008 373 (26)	0.000 074 (3)	1.388 51 (3)	1.388 4 (3)[b]
20	7.343 045	−2.577 266	0.297 502	0.000 347 (6)	−0.011 556 (54)	0.000 076 (5)	5.052 15 (5)	5.052 4 (3)[b]
26	21.169 98	−5.738 39	0.513 50	0.000 94 (1)	−0.015 84 (12)	0.000 08 (1)	15.930 26 (12)	15.930 9 (3)[b]
28	28.580 10	−7.204 91	0.600 50	0.001 24 (1)	−0.017 41 (14)	0.000 08 (1)	21.959 59 (14)	21.960 5 (3)[b]
30	37.813 57	−8.912 13	0.695 52	0.001 62 (1)	−0.019 07 (18)	0.000 08 (1)	29.579 58 (18)	29.579 6 (3)[b]
36	79.495 27	−15.703 91	1.032 61	0.003 19 (2)	−0.024 61 (30)	0.000 08 (2)	64.802 6 (3)	64.803 3 (5)[b]
40	122.466 49	−21.871 21	1.305 26	0.004 73 (3)	−0.028 87 (42)	0.000 08 (2)	101.876 5 (4)	101.878 4 (11)[b]
47	238.588 48 (1)	−36.594 23	1.890 10	0.008 81 (4)	−0.037 70 (70)	0.000 08 (3)	203.855 5 (7)	203.856 6 (16)[b]
50	308.853 99 (1)	−44.725 25	2.188 88	0.011 19 (4)	−0.042 12 (86)	0.000 08 (4)	266.286 8 (9)	266.288 1 (21)[b]
54	426.722 24 (3)	−57.580 77	2.639 24	0.015 11 (5)	−0.048 7 (11)	0.000 08 (4)	371.747 2 (11)	371.748 7 (29)[b]
60	667.503 4 (1)	−81.929 1	3.443 8	0.022 9 (1)	−0.060 5 (16)	0.000 1 (1)	588.980 6 (16)	588.983 4 (41)[b]
70	1302.156 8 (4)	−139.881 9	5.224 0	0.042 1 (1)	−0.086 5 (28)	0.000 1 (1)	1167.455 (3)	1167.461 (11)[b]
80	2367.736 6 (16)	−228.290 4	7.783 3	0.071 4 (2)	−0.124 4 (46)	0.000 1 (1)	2147.177 (5)	2147.188 (14)[b]
83	2804.106 0 (23)	−262.859 7	8.761 3	0.082 3 (2)	−0.139 0 (52)	0.000 1 (1)	2549.951 (6)	2549.961 (16)[b]
90	4103.324 (12)	−362.755 8	11.560 8	0.110 8 (2)	−0.181 7 (70)	0.000 1 (2)	3752.058 (14)	3752.127 (41)[b]
92	4561.237 4 (47)	−397.245 0	12.523 2	0.119 8 (3)	−0.196 6 (75)	0.000 1 (2)	4176.439 (9)	4176.457 (51)[b]

[a] NRQED, this work; [b] Kozhedub *et al.* [22].

TABLE IV. The screened QED corrections to the $2p_{3/2}$–$2p_{1/2}$ fine structure splitting, in eV.

Z	$1/Z^1$	$1/Z^2$	$1/Z^{3+}$	Sum	NRQED	Kozhedub *et al.* [22]
5	−0.000 084 6 (1)	0.000 035 6 (2)	−0.000 004 8 (2)	−0.000 053 8 (3)	−0.000 054	
6	−0.000 145 4 (2)	0.000 050 9 (5)	−0.000 005 8 (3)	−0.000 100 3 (6)	−0.000 102	
7	−0.000 229 5 (4)	0.000 068 6 (8)	−0.000 006 8 (4)	−0.000 168 (1)	−0.000 171	
8	−0.000 340 3 (7)	0.000 088 7 (13)	−0.000 007 8 (5)	−0.000 259 (2)	−0.000 267	
9	−0.000 481 1 (12)	0.000 111 2 (20)	−0.000 008 8 (7)	−0.000 379 (2)	−0.000 392	
10	−0.000 655 1 (20)	0.000 136 0 (29)	−0.000 009 8 (9)	−0.000 529 (4)	−0.000 552	−0.000 5 (2)
12	−0.001 114 2 (43)	0.000 191 6 (54)	−0.000 011 8 (15)	−0.000 935 (7)	−0.000 991	−0.000 9 (3)
15	−0.002 120 (11)	0.000 289 (12)	−0.000 015 (3)	−0.001 85 (2)		−0.001 8 (4)
18	−0.003 558 (22)	0.000 399 (22)	−0.000 018 (4)	−0.003 18 (3)		−0.003 2 (5)
20	−0.004 790 (27)	0.000 478 (29)	−0.000 020 (5)	−0.004 33 (4)		−0.004 3 (5)
26	−0.009 83 (15)	0.000 731 (69)	−0.000 026 (10)	−0.009 1 (2)		−0.009 2 (8)
30	−0.014 30 (8)	0.000 90 (11)	−0.000 030 (14)	−0.013 4 (2)		−0.013 6 (11)
32	−0.016 85 (13)	0.000 98 (14)	−0.000 032 (16)	−0.015 9 (2)		−0.016 0 (12)
40	−0.028 56 (14)	0.001 22 (31)	−0.000 040 (28)	−0.027 4 (4)		−0.027 9 (18)
47	−0.039 21 (26)	0.001 25 (55)	−0.000 047 (42)	−0.038 0 (7)		−0.038 7 (24)
50	−0.043 02 (29)	0.001 18 (69)	−0.000 050 (50)	−0.041 9 (9)		−0.042 8 (27)
54	−0.046 78 (38)	0.000 99 (89)	−0.000 054 (61)	−0.045 9 (10)		−0.047 0 (32)
60	−0.046 21 (45)	0.000 5 (13)	−0.000 060 (82)	−0.045 8 (14)		−0.048 0 (42)
66	−0.034 39 (64)	−0.000 4 (19)	−0.000 07 (11)	−0.035 (2)		−0.037 (5)
70	−0.014 83 (47)	−0.001 2 (24)	−0.000 07 (13)	−0.016 (2)		−0.020 (7)
74	0.015 98 (86)	−0.002 1 (29)	−0.000 07 (16)	0.014 (3)		0.010 (8)
80	0.098 74 (58)	−0.003 3 (40)	−0.000 08 (20)	0.095 (4)		0.086 (11)
82	0.138 13 (63)	−0.003 5 (44)	−0.000 08 (22)	0.135 (4)		0.122 (12)
90	0.386 16 (82)	−0.002 0 (66)	−0.000 09 (32)	0.384 (7)		0.359 (17)
92	0.478 80 (91)	−0.000 3 (73)	−0.000 09 (35)	0.478 (7)		0.446 (19)

TABLE V. Comparison of different theoretical predictions and experimental results for the $2p_{3/2}$–$2p_{1/2}$ fine-structure interval in Li-like ions, in cm^{-1} or eV as indicated, 1 eV = 8065.543 937 cm^{-1}.

Z	This work	Wang 1993 [49]	Kozhedub 2010 [22]	Sapirstein 2011 [15]	Experiment	Ref.
in cm^{-1}:						
5	34.075 (13)	34.04			34.100 (14)	[50]
6	107.166 (23)	107.06			107.3 (3)	[51, 52]
7	258.931 (37)	258.7			259 (1)	[52]
8	531.323 (55)	530.9			531 (1)	[52]
9	975.206 (77)	974.5			976 (2)	[52]
10	1 650.39 (10)	1649.2	1653 (3)	1653 (8)	1649 (2)	[52]
11	2 625.73 (10)				2631 (5)	[52]
12	3 979.15 (13)			3984 (8)	3975 (3)	[52]
13	5 797.76 (16)				5796 (5)	[52]
14	8 177.95 (21)				8177 (4)	[52]
15	11 225.38 (25)		11224 (4)	11219 (8)	11253 (15)	[52]
16	15 055.24 (30)				15054 (1)	[53]
17	19 792.36 (35)				19770 (15)	[52]
18	25 571.24 (42)		25572 (5)	25560 (8)	25572 (10)	[52]
20	40 841.36 (55)		40843 (6)	40828 (8)	40850 (10)	[52]
21	50 651.62 (70)			50627 (8)		
22	62 141.83 (95)				62146 (10)	[52]
24	90 914.5 (15)				90912 (12)	[54]
25	108 598.5 (16)				108634 (40)	[52]
26	128 769.8 (17)		128774 (7)	128750 (8)	128774 (16)	[55]
28	177 502.2 (17)		177508 (8)	177474 (8)	177524 (20)	[56]
29	206 557.7 (17)				206549 (33)	[57]

Z	This work	Kozhedub 2010 [22]	Sapirstein 2011 [15]	Experiment	Ref.
in eV:					
30	29.643 27 (23)	29.643 6 (12)	29.641 (1)	29.646 4 (47)	[58]
32	39.142 30 (30)		39.14	39.141 7 (53)	[57]
34	50.799 46 (38)			50.790 (23)	[59]
36	64.936 53 (43)	64.936 7 (17)	64.93	64.955 (37)	[60, 61]
39	91.565 77 (53)			91.595 (15)	[62]
40	102.080 50 (58)	102.081 7 (23)	102.08		
42	125.879 40 (70)		125.88	125.841 (73)	[59]
47	204.238 9 (11)	204.238 8 (36)	204.26	204.229 (31)	[63]
50	266.772 5 (14)	266.772 1 (46)	266.77		
52	316.135 1 (16)	316.134 (5)	316.11		
54	372.395 0 (19)		372.39	372.354 (53)	[4, 64]
60	589.928 5 (30)	589.929 (6)	589.93 (1)		
64	784.028 3 (41)		784.01 (1)		
66	898.712 1 (48)		898.73 (1)		
70	1 169.031 3 (49)		1 169.03 (2)		
74	1 502.715 0 (65)		1 502.66 (3)		
79	2 027.756 9 (93)		2 027.78 (3)		
80	2 149.404 (10)		2 149.41 (4)		
82	2 411.403 (11)		2 411.41 (4)	2 411.61 (12)	[5, 9]
83	2 552.326 (11)		2 552.32 (5)		
90	3 754.525 (22)		3 754.51 (7)		
92	4 178.830 (22)		4 178.81 (8)	4 178.73 (21)	[6, 65]

$$+\sum_{l=L}^{L+1}\sqrt{6l}\begin{Bmatrix}1 & 1 & 1\\ L & l & l-1\end{Bmatrix}\frac{1}{r_1^{l+1}}\,Z_{bd,Ll}(r_1)\int_0^{r_1} r_2^2 dr_2\, r_2^{l-1}\,Y_{ac,Ll-1}(r_2)+\ldots(ac)\leftrightarrow(bd)\ldots\Bigg], \quad \text{(A3)}$$

where $\{\ldots\}$ denotes the $6j$-symbol and

$$X_{ac,ll'}(r) = g_a(r)\,f_c(r)\,S_{ll'}(-\kappa_c,\kappa_a) + f_a(r)\,g_c(r)\,S_{ll'}(\kappa_c,-\kappa_a)\,, \quad \text{(A4)}$$

$$Y_{ac,ll'}(r) = g_a(r)\, g_c(r)\, S_{ll'}(\kappa_c, \kappa_a) - f_a(r)\, f_c(r)\, S_{ll'}(-\kappa_c, -\kappa_a)\,, \tag{A5}$$

$$Z_{ac,ll'}(r) = g_a(r)\, f_c(r)\, S_{ll'}(-\kappa_c, \kappa_a) - f_a(r)\, g_c(r)\, S_{ll'}(\kappa_c, -\kappa_a)\,, \tag{A6}$$

$$W_{ac}(r) = g_a(r)\, g_c(r) + f_a(r)\, f_c(r)\,. \tag{A7}$$

Furthermore, the standard angular coefficients $S_{ll'}$ and C_l are defined by Eqs. (A7)-(A10) of Ref. [66].

[1] P. Indelicato, J. Phys. B **52**, 232001 (2019).
[2] J. Schweppe, A. Belkacem, L. Blumenfeld, N. Claytor, B. Feinberg, H. Gould, V. E. Kostroun, L. Levy, S. Misawa, J. R. Mowat, and M. H. Prior, Phys. Rev. Lett. **66**, 1434 (1991).
[3] P. Beiersdorfer, A. L. Osterheld, J. H. Scofield, J. R. Crespo López-Urrutia, and K. Widmann, Phys. Rev. Lett. **80**, 3022 (1998).
[4] D. Feili, P. Bosselmann, K.-H. Schartner, F. Folkmann, A. E. Livingston, E. Träbert, X. Ma, and P. H. Mokler, Phys. Rev. A **62**, 022501 (2000).
[5] C. Brandau, C. Kozhuharov, A. Müller, W. Shi, S. Schippers, T. Bartsch, S. Böhm, C. Böhme, A. Hoffknecht, H. Knopp, N. Grün, W. Scheid, T. Steih, F. Bosch, B. Franzke, P. H. Mokler, F. Nolden, M. Steck, T. Stöhlker, and Z. Stachura, Phys. Rev. Lett. **91**, 073202 (2003).
[6] P. Beiersdorfer, H. Chen, D. B. Thorn, and E. Träbert, Phys. Rev. Lett. **95**, 233003 (2005).
[7] S. W. Epp, J. R. C. López-Urrutia, G. Brenner, V. Mäckel, P. H. Mokler, R. Treusch, M. Kuhlmann, M. V. Yurkov, J. Feldhaus, J. R. Schneider, M. Wellhöfer, M. Martins, W. Wurth, and J. Ullrich, Phys. Rev. Lett. **98**, 183001 (2007).
[8] M. Lestinsky, E. Lindroth, D. A. Orlov, E. W. Schmidt, S. Schippers, S. Böhm, C. Brandau, F. Sprenger, A. S. Terekhov, A. Müller, and A. Wolf, Phys. Rev. Lett. **100**, 033001 (2008).
[9] X. Zhang, N. Nakamura, C. Chen, M. Andersson, Y. Liu, and S. Ohtani, Phys. Rev. A **78**, 032504 (2008).
[10] 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).
[11] W. Nörtershäuser, C. Geppert, A. Krieger, K. Pachucki, M. Puchalski, K. Blaum, M. L. Bissell, N. Frömmgen, M. Hammen, M. Kowalska, J. Krämer, K. Kreim, R. Neugart, G. Neyens, R. Sánchez, and D. T. Yordanov, Phys. Rev. Lett. **115**, 033002 (2015).
[12] V. M. Shabaev, Phys. Rep. **356**, 119 (2002).
[13] S. A. Blundell, Phys. Rev. A **47**, 1790 (1993).
[14] J. Sapirstein and K. T. Cheng, Phys. Rev. A **64**, 022502 (2001).
[15] J. Sapirstein and K. T. Cheng, Phys. Rev. A **83**, 012504 (2011).
[16] V. A. Yerokhin, A. N. Artemyev, T. Beier, G. Plunien, V. M. Shabaev, and G. Soff, Phys. Rev. A **60**, 3522 (1999).
[17] A. N. Artemyev, T. Beier, G. Plunien, V. M. Shabaev, G. Soff, and V. A. Yerokhin, Phys. Rev. A **60**, 45 (1999).
[18] V. A. Yerokhin, A. N. Artemyev, V. M. Shabaev, M. M. Sysak, O. M. Zherebtsov, and G. Soff, Phys. Rev. Lett. **85**, 4699 (2000).
[19] V. A. Yerokhin, A. N. Artemyev, V. M. Shabaev, M. M. Sysak, O. M. Zherebtsov, and G. Soff, Phys. Rev. A **64**, 032109 (2001).
[20] A. N. Artemyev, V. M. Shabaev, M. M. Sysak, V. A. Yerokhin, T. Beier, G. Plunien, and G. Soff, Phys. Rev. A **67**, 062506 (2003).
[21] V. A. Yerokhin, A. N. Artemyev, and V. M. Shabaev, Phys. Rev. A **75**, 062501 (2007).
[22] Y. S. Kozhedub, A. V. Volotka, A. N. Artemyev, D. A. Glazov, G. Plunien, V. M. Shabaev, I. I. Tupitsyn, and T. Stöhlker, Phys. Rev. A **81**, 042513 (2010).
[23] V. A. Yerokhin, P. Indelicato, and V. M. Shabaev, Phys. Rev. Lett. **97**, 253004 (2006).
[24] W. E. Caswell and G. P. Lepage, Phys. Lett. **167 B**, 437 (1986).
[25] Z.-C. Yan and G. W. F. Drake, Phys. Rev. A **52**, 3711 (1995).
[26] Z.-C. Yan and G. W. F. Drake, Phys. Rev. Lett. **81**, 774 (1998).
[27] Z.-C. Yan and G. W. F. Drake, Phys. Rev. A **66**, 042504 (2002).
[28] M. Puchalski and K. Pachucki, Phys. Rev. A **78**, 052511 (2008).
[29] M. Puchalski and K. Pachucki, Phys. Rev. A **79**, 032510 (2009).
[30] M. Puchalski and K. Pachucki, Phys. Rev. Lett. **113**, 073004 (2014).
[31] M. Puchalski and K. Pachucki, Phys. Rev. A **92**, 012513 (2015).
[32] S. A. Blundell, P. J. Mohr, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **48**, 2615 (1993).
[33] I. Lindgren, H. Persson, S. Salomonson, and L. Labzowsky, Phys. Rev. A **51**, 1167 (1995).
[34] P. J. Mohr and J. Sapirstein, Phys. Rev. A **62**, 052501 (2000).
[35] O. Y. Andreev, L. N. Labzowsky, G. Plunien, and G. Soff, Phys. Rev. A **64**, 042513 (2001).
[36] V. A. Yerokhin and V. M. Shabaev, J. Phys. Chem. Ref. Data **44**, 033103 (2015).
[37] V. A. Yerokhin, A. N. Artemyev, V. M. Shabaev, G. Plunien, and G. Soff, Optics and Spectroscopy **99**, 12 (2005).
[38] R. A. Hegstrom, Phys. Rev. A **7**, 451 (1973).
[39] D. A. Glazov, V. M. Shabaev, I. I. Tupitsyn, A. V. Volotka, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. A **70**, 062104 (2004).
[40] V. M. Shabaev, I. I. Tupitsyn, and V. A. Yerokhin, Phys. Rev. A **88**, 012513 (2013).
[41] P. J. Mohr, D. B. Newell, and B. N. Taylor, Rev. Mod. Phys. **88**, 035009 (2016).
[42] V. M. Shabaev and A. N. Artemyev, J. Phys. B **27**, 1307

(1994).
[43] V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. Lett. **93**, 130405 (2004).
[44] A. N. Artemyev, V. M. Shabaev, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. A **71**, 062104 (2005).
[45] A. N. Artemyev, V. M. Shabaev, and V. A. Yerokhin, Phys. Rev. A **52**, 1884 (1995).
[46] A. N. Artemyev, V. M. Shabaev, and V. A. Yerokhin, J. Phys. B **28**, 5201 (1995).
[47] I. Angeli and K. Marinova, At. Dat. Nucl. Dat. Tabl. **99**, 69 (2013).
[48] M. Wang, G. Audi, A. H. Wapstra, F. G. Kondev, M. MacCormick, X. Xu, and B. Pfeiffer, Chin. Phys. C **36**, 1603 (2012).
[49] Z.-W. Wang, X.-W. Zhu, and K. T. Chung, Phys. Scr. **47**, 65 (1993).
[50] U. Litzén and R. Kling, J. Phys. B **31**, L933L936 (1998).
[51] J. C. Boyce and C. A. Rieke, Phys. Rev. **47**, 653 (1935).
[52] B. Edlén, Phys. Scr. **28**, 51 (1983).
[53] R. J. Thomas and W. M. Neupert, Astrophys. J. Suppl. **91**, 461 (1994).
[54] J. Sugar, V. Kaufman, and W. L. Rowan, J. Opt. Soc. Am. B **10**, 13 (1993).
[55] J. Reader, J. Sugar, N. Acquista, and R. Bahr, J. Opt. Soc. Am. B **11**, 1930 (1994).
[56] J. Sugar, V. Kaufman, and W. L. Rowan, J. Opt. Soc. Am. B **9**, 344 (1992).
[57] R. J. Knize, Phys. Rev. A **43**, 1637 (1991).
[58] U. Staude, P. Bosselmann, R. Büttner, D. Horn, K.-H. Schartner, F. Folkmann, A. E. Livingston, T. Ludziejewski, and P. H. Mokler, Phys. Rev. A **58**, 3516 (1998).
[59] E. Hinnov, the TFTR Operating Team, B. Denne, and the JET Operating Team, Phys. Rev. A **40**, 4357 (1989).
[60] S. Madzunkov, E. Lindroth, N. Eklow, M. Tokman, A. Paal, and R. Schuch, Phys. Rev. A (2002).
[61] Y. A. Podpaly, J. D. Gillaspy, J. Reader, and Y. Ralchenko, J. Phys. B **47**, 095702 (2014).
[62] R. Silwal, E. Takacs, J. Dreiling, J. Gillaspy, and Y. Ralchenko, Atoms **5**, 30.
[63] P. Bosselmann, U. Staude, D. Horn, K.-H. Schartner, F. Folkmann, A. E. Livingston, and P. H. Mokler, Phys. Rev. A **59**, 1874 (1999).
[64] D. Bernhardt, C. Brandau, Z. Harman, C. Kozhuharov, S. Böhm, F. Bosch, S. Fritzsche, J. Jacobi, S. Kieslich, H. Knopp, F. Nolden, W. Shi, Z. Stachura, M. Steck, T. Stöhlker, S. Schippers, and A. Müller, Phys. Rev. A **91**, 012710 (2015).
[65] P. Beiersdorfer, D. Knapp, R. E. Marrs, S. R. Elliott, and M. H. Chen, Phys. Rev. Lett. **71**, 3939 (1993).
[66] V. A. Yerokhin and A. V. Maiorova, Symmetry **12**, 800 (2020).

TABLE VI: Individual effects and total theoretical predictions for the $2p_{3/2}$–$2p_{1/2}$ fine-structure interval in Li-like ions. Units are eV, 1 eV = 8065.543 937 cm^{-1}. In the case when an entry is given with two uncertainties, the first one is the estimation of the theoretical error and the second is due to the nuclear charge radius. In the case when one uncertainty is given, it is the estimation of the theoretical error and the uncertainty due to the nuclear radius is negligible.

Z	Isotope	$\langle r^2\rangle^{1/2}$ [fm]	Structure	QED,1-el	QED,scr	Recoil	Total
5	^{11}B	2.406 (29)	0.004 213 7 (16)	0.000 065 2	−0.000 053 8 (3)	−0.000 0003	0.004 224 8 (17)
6	^{12}C	2.4702 (22)	0.013 253 2 (28)	0.000 135 0	−0.000 100 3 (6)	−0.000 0009	0.013 286 9 (29)
7	^{14}N	2.5582 (70)	0.032 023 3 (45)	0.000 249 5	−0.000 167 7 (10)	−0.000 0018	0.032 103 4 (46)
8	^{16}0	2.6991 (52)	0.065 713 6 (67)	0.000 424 6 (1)	−0.000 259 4 (16)	−0.000 0031	0.065 875 7 (68)
9	^{19}F	2.8976 (25)	0.120 615 2 (93)	0.000 678 4 (1)	−0.000 378 7 (24)	−0.000 0048	0.120 910 1 (96)
10	^{20}Ne	3.0055 (21)	0.204 128 (12)	0.001 031 1 (1)	−0.000 529 0 (36)	−0.000 0076	0.204 622 (13)
11	^{23}Na	2.9936 (21)	0.324 768 (11)	0.001 505	−0.000 713 (5)	−0.000 010	0.325 549 (12)
12	^{24}Mg	3.0570 (16)	0.492 176 (14)	0.002 126	−0.000 934 (7)	−0.000 015	0.493 351 (16)
13	^{27}Al	3.0610 (31)	0.717 127 (18)	0.002 919	−0.001 195 (9)	−0.000 020	0.718 831 (20)
14	^{28}Si	3.1224 (24)	1.011 548 (22)	0.003 913 (1)	−0.001 498 (12)	−0.000 027	1.013 936 (26)
15	^{31}P	3.1889 (19)	1.388 508 (26)	0.005 140 (1)	−0.001 846 (16)	−0.000 033	1.391 770 (31)
16	^{32}S	3.2611 (18)	1.862 263 (31)	0.006 632 (1)	−0.002 240 (20)	−0.000 043	1.866 612 (37)
17	^{35}Cl	3.365 (19)	2.448 253 (36)	0.008 422 (2)	−0.002 683 (25)	−0.000 052	2.453 940 (44)
18	^{40}Ar	3.4274 (26)	3.163 116 (41)	0.010 548 (3)	−0.003 177 (31)	−0.000 058	3.170 429 (52)
19	^{39}K	3.4349 (19)	4.024 704 (46)	0.013 047 (4)	−0.003 723 (38)	−0.000 076	4.033 952 (59)
20	^{40}Ca	3.4776 (19)	5.052 148 (54)	0.015 959 (5)	−0.004 331 (40)	−0.000 093	5.063 683 (68)
21	^{45}Sc	3.5459 (25)	6.265 777 (63)	0.019 324 (6)	−0.004 998 (59)	−0.000 103	6.280 001 (87)
22	^{48}Ti	3.5921 (17)	7.687 235 (72)	0.023 186 (9)	−0.005 697 (92)	−0.000 118	7.704 60 (12)
23	^{51}V	3.6002 (22)	9.339 469 (83)	0.027 587 (11)	−0.006 48 (12)	−0.000 135	9.360 44 (15)
24	^{52}Cr	3.6452 (42)	11.246 84 (11)	0.032 574 (14)	−0.007 30 (15)	−0.000 160	11.271 96 (18)
25	^{55}Mn	3.7057 (22)	13.434 66 (10)	0.038 194 (18)	−0.008 18 (16)	−0.000 180	13.464 50 (19)
26	^{56}Fe	3.7377 (16)	15.930 26 (12)	0.044 492 (23)	−0.009 12 (17)	−0.000 210	15.965 42 (21)
27	^{59}Co	3.7875 (21)	18.761 95 (13)	0.051 517 (29)	−0.010 12 (16)	−0.000 235	18.803 11 (21)
28	^{58}Ni	3.7757 (20)	21.959 59 (14)	0.059 320 (36)	−0.011 17 (15)	−0.000 280	22.007 46 (21)
29	^{63}Cu	3.8823 (15)	25.554 52 (16)	0.067 951 (44)	−0.012 29 (14)	−0.000 300 (1)	25.609 89 (22)
30	^{64}Zn	3.9283 (15)	29.579 58 (18)	0.077 46 (5)	−0.013 43 (14)	−0.000 34	29.643 27 (23)

31	^{69}Ga	3.9973 (17)	34.069 17 (20)	0.087 90 (7)	−0.014 64 (16)	−0.000 37	34.142 06 (26)
32	^{74}Ge	4.0742 (12)	39.059 27 (21)	0.099 32 (8)	−0.015 90 (19)	−0.000 39	39.142 30 (30)
33	^{75}As	4.0968 (20)	44.587 54 (24)	0.111 78 (10)	−0.017 24 (22)	−0.000 44	44.681 63 (34)
34	^{80}Se	4.1400 (18)	50.693 19 (26)	0.125 32 (12)	−0.018 57 (25)	−0.000 47	50.799 46 (38)
35	^{79}Br	4.1629 (21)	57.417 02 (25)	0.140 00 (9)	−0.019 98 (27)	−0.000 54	57.536 49 (38)
36	^{84}Kr	4.1884 (22)	64.802 64 (31)	0.155 86 (11)	−0.021 40 (29)	−0.000 58 (1)	64.936 53 (43)
37	^{85}Rb	4.2036 (24)	72.893 76 (33)	0.172 97 (13)	−0.022 87 (30)	−0.000 64 (1)	73.043 22 (46)
38	^{88}Sr	4.2240 (18)	81.737 18 (36)	0.191 38 (15)	−0.024 36 (31)	−0.000 69 (1)	81.903 50 (49)
39	^{89}Y	4.2430 (21)	91.381 29 (39)	0.211 12 (18)	−0.025 87 (32)	−0.000 77 (1)	91.565 77 (53)
40	^{90}Zr	4.2694 (10)	101.876 49 (42)	0.232 25 (21)	−0.027 39 (34)	−0.000 85 (1)	102.080 50 (58)
41	^{93}Nb	4.3240 (17)	113.275 21 (45)	0.254 82 (24)	−0.028 97 (37)	−0.000 91 (2)	113.500 14 (63)
42	^{98}Mo	4.4091 (18)	125.632 01 (49)	0.278 87 (28)	−0.030 52 (41)	−0.000 96 (2)	125.879 40 (70)
43	^{98}Tc	4.424 (44)	139.003 39 (50)(4)	0.304 45 (32)	−0.032 07 (45)	−0.001 07 (2)	139.274 71 (74)(4)
44	^{102}Ru	4.4809 (18)	153.449 50 (58)	0.331 60 (36)	−0.033 60 (49)	−0.001 14 (3)	153.746 36 (84)
45	^{103}Rh	4.4945 (23)	169.030 26 (61)	0.360 35 (42)	−0.035 12 (53)	−0.001 24 (3)	169.354 24 (91)
46	^{106}Pd	4.5318 (29)	185.810 18 (66)(1)	0.390 74 (48)	−0.036 59 (57)	−0.001 33 (4)	186.163 00 (99)(1)
47	^{107}Ag	4.5454 (31)	203.855 55 (70)(1)	0.422 80 (54)	−0.038 01 (61)	−0.001 45 (4)	204.238 9 (11)
48	^{112}Cd	4.5944 (24)	223.235 19 (75)(1)	0.456 56 (62)	−0.039 38 (65)	−0.001 52 (5)	223.650 9 (12)
49	^{115}In	4.6156 (26)	244.020 82 (81)(1)	0.492 05 (70)	−0.040 67 (69)	−0.001 62 (6)	244.470 6 (13)
50	^{120}Sn	4.6519 (21)	266.286 79 (86)(1)	0.529 28 (79)	−0.041 89 (75)	−0.001 70 (6)	266.772 5 (14)
51	^{121}Sb	4.6802 (26)	290.110 47 (92)(1)	0.568 27 (89)	−0.043 08 (80)	−0.001 84 (7)	290.633 8 (15)
52	^{130}Te	4.7423 (25)	315.572 13 (98)(2)	0.609 0 (10)	−0.044 14 (85)	−0.001 87 (8)	316.135 1 (16)
53	^{127}I	4.7500 (81)	342.755 5 (10)	0.651 5 (11)	−0.045 08 (91)	−0.002 08 (10)	343.359 9 (18)
54	^{132}Xe	4.7859 (48)	371.747 2 (11)	0.695 8 (12)	−0.045 85 (98)	−0.002 18 (11)	372.395 0 (19)
55	^{133}Cs	4.8041 (46)	402.637 5 (12)	0.741 8 (14)	−0.046 4 (10)	−0.002 35 (12)	403.330 5 (21)
56	^{138}Ba	4.8378 (46)	435.520 0 (13)	0.789 6 (16)	−0.046 8 (11)	−0.002 45 (14)	436.260 3 (23)
57	^{139}La	4.8550 (49)	470.492 2 (13)(1)	0.839 0 (17)	−0.047 0 (12)	−0.002 64 (15)	471.281 7 (25)(1)
58	^{140}Ce	4.8771 (18)	507.655 5 (14)	0.890 1 (19)	−0.046 9 (13)	−0.002 84 (18)	508.495 9 (27)
59	^{141}Pr	4.8919 (50)	547.115 2 (15)(1)	0.942 8 (21)	−0.046 5 (13)	−0.003 05 (20)	548.008 4 (29)(1)
60	^{142}Nd	4.9123 (25)	588.980 6 (16)(1)	0.997 0 (21)	−0.045 8 (14)	−0.003 30 (23)	589.928 5 (30)(1)
61	^{145}Pm	4.962 (50)	633.365 4 (17)(8)	1.052 7 (23)	−0.045 1 (15)	−0.003 46 (25)	634.369 5 (32)(8)
62	^{152}Sm	5.0819 (60)	680.387 2 (18)(1)	1.109 7 (25)	−0.044 0 (16)	−0.003 56 (28)	681.449 4 (35)(1)
63	^{153}Eu	5.1115 (62)	730.171 6 (19)(2)	1.167 9 (28)	−0.042 4 (17)	−0.003 81 (31)	731.293 3 (38)(2)
64	^{158}Gd	5.1569 (43)	782.845 4 (20)(2)	1.227 3 (31)	−0.040 4 (18)	−0.003 98 (34)	784.028 3 (41)(2)
65	^{159}Tb	5.06 (15)	838.545 6 (21)(43)	1.287 7 (34)	−0.037 9 (19)	−0.004 3 (4)	839.791 1 (44)(43)
66	^{162}Dy	5.207 (17)	897.402 5 (23)(6)	1.348 9 (37)	−0.034 9 (20)	−0.004 5 (4)	898.712 1 (48)(6)
67	^{165}Ho	5.202 (31)	959.570 4 (24)(12)	1.410 8 (41)	−0.031 2 (21)	−0.004 7 (5)	960.945 2 (52)(12)
68	^{166}Er	5.2516 (31)	1025.194 8 (25)(2)	1.473 1 (44)	−0.026 9 (22)	−0.005 0 (5)	1 026.635 9 (56)(2)
69	^{169}Tm	5.2256 (35)	1094.437 3 (27)(3)	1.535 6 (49)	−0.021 9 (23)	−0.005 3 (6)	1 095.945 7 (60)(3)
70	^{174}Yb	5.3108 (60)	1167.454 8 (28)(4)	1.598 1 (31)	−0.016 1 (24)	−0.005 6 (6)	1 169.031 3 (49)(4)
71	^{175}Lu	5.370 (30)	1244.423 2 (29)(21)	1.660 3 (34)	−0.010 0 (26)	−0.005 9 (7)	1 246.067 7 (52)(21)
72	^{180}Hf	5.3470 (32)	1325.525 1 (31)(5)	1.721 9 (37)	−0.003 0 (27)	−0.006 1 (8)	1 327.237 9 (56)(5)
73	^{181}Ta	5.3507 (34)	1410.941 1 (33)(5)	1.782 5 (41)	0.004 9 (29)	−0.006 5 (9)	1 412.722 0 (60)(5)
74	^{184}W	5.3658 (23)	1500.866 3 (34)(6)	1.841 7 (45)	0.013 8 (30)	−0.006 9 (10)	1 502.715 0 (65)(6)
75	^{187}Re	5.370 (17)	1595.505 7 (36)(21)	1.899 2 (49)	0.024 2 (32)	−0.007 2 (11)	1 597.421 8 (69)(21)
76	^{192}Os	5.4126 (15)	1695.066 7 (38)(8)	1.954 4 (53)	0.035 7 (33)	−0.007 5 (12)	1 697.049 2 (74)(8)
77	^{193}Ir	5.40 (11)	1799.781 (4)(16)	2.006 8 (58)	0.048 5 (35)	−0.008 0 (14)	1 801.828 (8)(16)
78	^{196}Pt	5.4307 (27)	1909.870 6 (42)(11)	2.056 0 (64)	0.062 6 (37)	−0.008 7 (14)	1 911.980 5 (86)(11)
79	^{197}Au	5.4371 (38)	2025.586 5 (44)(14)	2.101 2 (70)	0.078 2 (38)	−0.009 0 (17)	2 027.756 9 (92)(14)
80	^{202}Hg	5.4648 (33)	2147.176 7 (46)(16)	2.141 8 (76)	0.095 4 (40)	−0.009 7 (17)	2 149.404 1 (99)(16)
81	^{205}Tl	5.4759 (26)	2274.914 3 (48)(17)	2.177 1 (83)	0.114 0 (43)	−0.009 8 (20)	2 277.196 (11)(2)
82	^{208}Pb	5.5012 (13)	2409.073 3 (50)(19)	2.206 3 (90)	0.134 5 (45)	−0.010 9 (20)	2 411.403 (11)(2)
83	^{209}Bi	5.5211 (26)	2549.951 0 (52)(23)	2.228 6 (76)	0.157 2 (47)	−0.010 9 (25)	2 552.326 (11)(2)
84	^{209}Po	5.527 (18)	2697.858 7 (55)(71)	2.242 8 (84)	0.182 1 (51)	−0.011 6 (28)	2 700.272 (12)(7)
85	^{210}At	5.539 (55)	2853.114 (6)(24)	2.248 1 (92)	0.209 1 (55)	−0.012 3 (32)	2 855.559 (13)(24)
86	^{222}Rn	5.691 (20)	3016.003 (6)(11)	2.243 (10)	0.238 (6)	−0.012 (3)	3 018.472 (14)(11)
87	^{223}Fr	5.695 (18)	3186.992 (6)(11)	2.227 (11)	0.270 (6)	−0.013 (4)	3 189.476 (15)(11)
88	^{226}Ra	5.721 (29)	3366.393 (6)(19)	2.199 (12)	0.305 (6)	−0.014 (4)	3 368.883 (16)(19)
89	^{227}Ac	5.670 (57)	3554.660 (7)(42)	2.156 (14)	0.343 (6)	−0.014 (5)	3 557.145 (17)(42)
90	^{232}Th	5.785 (12)	3752.058 (7)(12)	2.098 (15)	0.384 (7)	−0.016 (4)	3 754.525 (19)(12)
91	^{231}Pa	5.700 (57)	3959.276 (7)(56)	2.023 (17)	0.430 (7)	−0.016 (6)	3 961.712 (21)(56)
92	^{238}U	5.8571 (33)	4176.439 (8)(5)	1.928 (18)	0.478 (7)	−0.016 (6)	4 178.830 (21)(5)