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 Zα, 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 Zα, 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, mα4 (where m is the electron mass). Furthermore, at the next-to-leading order mα5, 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 mα6 [30, 31], while for other energy intervals of three-electron systems the mα6 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 ≥ 5. To this end, we will match the Zα 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 ≈ 8–20, in which the both above-mentioned methods do not work well.

The relativistic units (ℏ = 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_{struc}, the radiative QED correction E_{rad}, and the nuclear recoil correction E_{rec},

\[ E = E_{struc} + E_{rad} + E_{rec}. \]  

(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_{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_{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, \((1s)^2p_{3/2}\) and \((1s)^2p_{1/2}\). In the following, we will denote by \(E_i(v)\) corrections to the ionization energy of the valence electron state \(v\) and by \(E_i(\text{fns})\) corrections to the fns splitting, \(E_i(\text{fns}) = E_i(2p_{3/2}) - E_i(2p_{1/2})\). We note that the energy contributions involving interactions only between the core electrons do not contribute neither to the ionization energy or the fns 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,

\[
E_{\text{struc}}(v) = E_D + E_{1\text{phot}} + E_{2\text{phot}} + E_{3\text{phot}} + E_{\geq 4\text{phot}},
\]

where \(E_D\) is the Dirac one-electron energy; \(E_{1\text{phot}}\), \(E_{2\text{phot}}\), and \(E_{3\text{phot}}\) are corrections due to the exchange of one, two, and three virtual photons, respectively, and \(E_{\geq 4\text{phot}}\) 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

\[
E_D(v) = \left[ 1 + \left( \frac{Z\alpha}{n_v - |\kappa_v| + \sqrt{\kappa_v^2 - (Z\alpha)^2}} \right)^2 \right]^{-1/2} - 1,
\]

where \(n_v\) and \(\kappa_v\) 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 \(\omega\) and is given, in the Feynman gauge, by

\[
I_{\text{Feyn}}(\omega) = \alpha \left( 1 - \alpha_1 \cdot \alpha_2 \right) e^{i|x_1 x_2|} x_{12},
\]

where \(\alpha_1\) and \(\alpha_2\) are vectors of Dirac matrices acting on the coordinate \(x_1\) and \(x_2\), respectively, and \(x_{12} = |x_{12}| = |x_1 - x_2|\). The electron-electron interaction operator in the Coulomb gauge is

\[
I_{\text{Coul}}(\omega) = \alpha \left[ \frac{1}{x_{12}} - \frac{\alpha_1 \cdot \alpha_2}{x_{12}^3} + \frac{(\alpha_1 \cdot \nabla_1)(\alpha_2 \cdot \nabla_2)}{\omega^2} e^{i|x_1 x_2|} - 1 \right].
\]

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, \(E_{1\text{phot}}\) and \(E_{2\text{phot}}\). 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,

\[
I_{abcd}(\Delta) \equiv \langle ab | I(\Delta) | cd \rangle, \quad I_{abcd} \equiv \langle ab | I_{\text{Coul}}(0) | cd \rangle.
\]

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

\[
E_{1\text{phot}}(v) = \sum_{\mu_c} (\Delta P) I_{\text{cc}}(\mu_c, \Delta P_{cc}) \equiv \sum_{\mu_c} \left[ I_{\text{cc}}(0) - I_{\text{cc}}(\Delta_{cc}) \right],
\]

where \(P\) is the permutation operator interchanging the one-electron states, \((PcPc) = \langle vc \rangle\) 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 \(\mu_c\) 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]

$$E_{\text{2phot}}(v) = \sum_{\mu_e} \sum_{P} (-1)^P \sum_{n_1n_2} \sum_{(+)} \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \left[ \frac{I_{\mu_e} \mu_n n_2 \mu_1 (\omega - \Delta P_{\text{ee}})}{(\epsilon_{\mu_e} - \omega - u_{e_1,n_1} \epsilon_{\mu_1} \epsilon_{\mu_1} + \omega - u_{e_1,n_2} \epsilon_{\mu_1} \epsilon_{\mu_1})} + \frac{I_{\mu_n} \mu_n n_2 \mu_1 (\omega - \Delta P_{\text{ee}})}{(\epsilon_{\mu_n} - \omega - u_{e_1,n_1} \epsilon_{\mu_1} \epsilon_{\mu_1} + \omega - u_{e_1,n_2} \epsilon_{\mu_1} \epsilon_{\mu_1})} \right] + \sum_{PQ} (-1)^{P+Q} \sum_{n} \left[ \frac{I_{\mu_2} \mu_3 \mu_4 (\Delta P_{\text{3ph}})}{(\epsilon_{\mu_1} + \epsilon_{\mu_2} - \epsilon_{\mu_1} - \epsilon_{\mu_1} - \epsilon_{\mu_1})} \right] + + E_{\text{red}}(v), \quad (9)$$

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 $E_{\text{red}}$ 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 $\Delta E_{\text{red}}$ is the reducible contribution. The explicit expression for $\Delta E_{\text{red}}$ 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, $I(\omega) \rightarrow I_{\text{Coul}}(0)$ and (ii) the summations are performed over the positive-energy part of the Dirac spectrum. Within this approximation, the integration over $\omega$ is performed by the Cauchy theorem and the crossed-photon and reducible contributions vanish, yielding the result

$$E_{\text{MBPT}}^{\text{2phot}}(v) = \sum_{\mu_e} \sum_{P} (-1)^P \sum_{n_1n_2} \sum_{(+)} \frac{I_{\mu_e} \mu_n n_2 \mu_1 (\omega - \Delta P_{\text{ee}})}{(\epsilon_{\mu_e} + \epsilon_{\mu_1} - \epsilon_{\mu_1} - \epsilon_{\mu_1})} + \sum_{PQ} (-1)^{P+Q} \sum_{n} \left[ \frac{I_{\mu_2} \mu_3 \mu_4 (\Delta P_{\text{3ph}})}{(\epsilon_{\mu_1} + \epsilon_{\mu_2} - \epsilon_{\mu_1} - \epsilon_{\mu_1} - \epsilon_{\mu_1})} \right], \quad (10)$$

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]

$$\Delta E_{\text{3ph}}^{\text{MBPT}}(v) = \sum_{\mu_e} \sum_{P} (-1)^P \sum_{n_1n_2n_4} \sum_{(+)} \frac{I_{\mu_e} \mu_n n_2 \mu_1 (\omega - \Delta P_{\text{ee}})}{(\epsilon_{\mu_e} + \epsilon_{\mu_2} - \epsilon_{\mu_1} - \epsilon_{\mu_1} - \epsilon_{\mu_1})} + \sum_{PQ} (-1)^{P+Q} \sum_{n_1n_2n_3n_4} \left[ \frac{2 I_{\mu_2} \mu_3 \mu_4 (\Delta P_{\text{3ph}})}{(\epsilon_{\mu_1} + \epsilon_{\mu_2} - \epsilon_{\mu_1} - \epsilon_{\mu_1} - \epsilon_{\mu_1})} \right] + + I_{\mu_1} \mu_2 \mu_3 \mu_4 (\Delta P_{\text{3ph}}) \frac{1}{(\epsilon_{\mu_1} + \epsilon_{\mu_2} - \epsilon_{\mu_1} - \epsilon_{\mu_1} - \epsilon_{\mu_1})} \right], \quad (11)$$

where the operator $\Xi_1$ acts on energy denominators $\Delta_1$, $\Delta_2$ as following

$$\Xi_1 = \begin{cases} 1, & \text{if } \Delta_1 \neq 0, \Delta_2 \neq 0, \\ \frac{X}{\Delta_1 \Delta_2}, & \text{if } \Delta_1 \neq 0, \Delta_2 = 0, \\ -\frac{X}{\Delta_1 \Delta_2}, & \text{if } \Delta_1 = 0, \Delta_2 \neq 0, \\ -\frac{X}{\Delta_1}, & \text{if } \Delta_1 = 0, \Delta_2 = 0. \end{cases} \quad (12)$$

The correction induced by the exchange of four and more photons, $E_{\text{4phot}}$, 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 $1/Z$),

$$E_{\text{rad}} = E_{\text{QEDhydr}} + E_{\text{QEDscr1}} + E_{\text{QEDscr2}} + E_{\text{QEDscr3}}, \quad (13)$$

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

The one-electron QED contribution $E_{\text{QEDhydr}}$ is presently well established, see, e.g., a recent review [36]; it will be taken from the literature in this work. The
first-order $1/Z^{1}$ screening QED correction $E_{QEDscr1}$ 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 $E_{QEDscr2}$. 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],

$$H_{amm,1} = \frac{\kappa}{4} Z\alpha (1-i) \sum_a \beta_a \frac{\alpha_a \cdot r_a}{r_a^3}, \quad (14)$$

$$H_{amm,2} = \frac{\alpha}{4} \sum_{a<b} \beta_a \left( \frac{i \alpha_a \cdot r_{ab}}{r_{ab}^3} - \sum_a \frac{\beta_a \cdot r_{ab}}{r_{ab}^3} \right), \quad (15)$$

where $a$ and $b$ numerate the electrons in the atom, $\kappa = g_e^2 - 2 = \alpha^2 + O(\alpha^3)$, $g_e$ is the g-factor of the free electron, $\beta_a$ and $\alpha_a$ are the Dirac matrices acting on ath electron, and

$$\Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & -\sigma \end{pmatrix}, \quad (16)$$

with $\sigma$ being a vector of Pauli matrices.

The effective amm Hamiltonian $H_{amm} = H_{amm,1} + H_{amm,2}$ 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 $h_{\text{MQED}}$ introduced in Ref. [40]. In order to avoid double counting, we subtract from $h_{\text{MQED}}$ the part already accounted for by the amm Hamiltonian. Specifically, we make the replacement

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

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 $h'_{\text{MQED}}$.

In this work we will calculate the second-order QED screening correction $E_{QEDscr2}$ 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 $H_{amm+MQED}$,

$$H_{amm+MQED} = H_{amm,1} + H_{amm,2} + h'_{\text{MQED}} \equiv U + W. \quad (18)$$

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

$$E_{1\text{phot},U} = 2 \sum_{\mu} \sum_{P} (-1)^P \left( I_{P_{\nu}P_{\nu}\text{vec}} + I_{P_{\nu}P_{\nu}\text{vec}} \right), \quad (19)$$

where

$$|\delta a\rangle = \sum_{n} \frac{|n\rangle}{\varepsilon_a - \varepsilon_n} U_{na}, \quad (20)$$

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

$$E_{1\text{phot},W} = \sum_{\mu} \sum_{P} (-1)^P W_{P_{\nu}P_{\nu}\text{vec}}, \quad (21)$$

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 $H_{amm}$, the column “MQED” displays results obtained...
with the standard MQED operator $h_{\text{MQED}}$, 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.

$$E_{2\text{phot},U} = E_{2\text{phot},\text{wf}} + E_{2\text{phot},\text{en}} + E_{2\text{phot},\text{ver}}.$$  \hspace{2cm} (22)

The corresponding parts are given by

$$E_{2\text{phot},\text{wf}} = 2 \sum_{\mu_1} \sum_P (-1)^P \sum_{n_1 n_2} \epsilon^{(+)} I_{P1\mu_1 n_2} \sum_{I_{n_1 n_2} = 1} \frac{I_{P1\mu_1 n_2} (I_{n_1 n_2} + I_{n_1 n_2} b e)}{\epsilon_c + \epsilon_v - \epsilon_{n_1} - \epsilon_{n_2}}$$

$$+ 2 \sum_{PQ} (-1)^{P+Q} \sum_n \epsilon^{(+)} I_{P2\mu_1 n_2} \sum_{Q_{n_1 n_2} = 1} \frac{I_{P2\mu_1 n_2} (I_{n_1 n_2} Q_{n_1 n_2} + I_{n_1 n_2} Q_{n_1 n_2} + I_{P1\mu_1 n_2} Q_{n_1 n_2})}{\epsilon_v + \epsilon_{Q_{n_1 n_2}} - \epsilon_{n_1} - \epsilon_{n_2}}$$  \hspace{2cm} (23)

$$E_{2\text{phot},\text{en}} = -(U_{1 v e} + U_{c c}) \sum_{\mu_1} \sum_P (-1)^P \sum_{n_1 n_2} \epsilon^{(+)} I_{P1\mu_1 n_2} \sum_{I_{n_1 n_2} = 1} \frac{I_{P1\mu_1 n_2} I_{n_1 n_2} v}{(\epsilon_c + \epsilon_v - \epsilon_{n_1} - \epsilon_{n_2}^2)}$$

$$- \sum_{PQ} (-1)^{P+Q} (U_{P Q 1 Q 2} + U_{Q 2 P 1} - U_{P 1 P 1}) \sum_n \epsilon^{(+)} I_{P2\mu_1 n_2} \sum_{Q_{n_1 n_2} = 1} \frac{I_{P2\mu_1 n_2} I_{n_1 n_2} Q_{n_1 n_2}}{(\epsilon_v + \epsilon_{Q_{n_1 n_2}} - \epsilon_{n_1} - \epsilon_{n_2})^2},$$  \hspace{2cm} (24)

$$E_{2\text{phot},\text{ver}} = \sum_{\mu_1} \sum_P (-1)^P \sum_{n_1 n_2 n_3} \sum_{\Xi_2} \epsilon^{(+)} I_{P1\mu_1 n_2} \sum_{n_{n_1 n_2} = 1} \frac{I_{P1\mu_1 n_2} I_{n_{n_1 n_2} v}}{(\epsilon_{n_1} + \epsilon_{n_2})^2 (\epsilon_{n_1} - \epsilon_{n_2})^2}$$

$$+ \sum_{PQ} (-1)^{P+Q} \sum_{n_1 n_2} \sum_{\Xi_2} \sum_{n_{n_1 n_2}} \epsilon^{(+)} I_{P2\mu_1 n_2} U_{P1\mu_1 n_2} \sum_{n_{n_1 n_2} = 1} \frac{I_{P2\mu_1 n_2} I_{n_{n_1 n_2} v}}{(\epsilon_v + \epsilon_{Q_{n_1 n_2}} - \epsilon_{n_1} - \epsilon_{n_2})},$$  \hspace{2cm} (25)

where the operator $\Xi_2$ acts on energy denominators $\Delta_1$, $\Delta_2$ as following:

$$\Xi_2 \frac{X}{\Delta_1 \Delta_2} = \begin{cases} 
\frac{X}{\Delta_1 \Delta_2}, & \text{if } \Delta_1 \neq 0, \Delta_2 \neq 0, \\
\frac{X}{\Delta_1}, & \text{if } \Delta_1 \neq 0, \Delta_2 = 0, \\
\frac{X}{\Delta_2}, & \text{if } \Delta_1 = 0, \Delta_2 \neq 0, \\
0, & \text{if } \Delta_1 = 0, \Delta_2 = 0. 
\end{cases}$$  \hspace{2cm} (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

$$E_{2\text{phot},W} = \sum_{\mu_1} \sum_P (-1)^P \sum_{n_1 n_2} \epsilon^{(+)} I_{P1\mu_1 n_2} W_{n_1 n_2} + W_{P1\mu_1 n_2} I_{n_1 n_2} v$$

$$+ \sum_{PQ} (-1)^{P+Q} \sum_n \epsilon^{(+)} I_{P2\mu_1 n_2} W_{P1\mu_1 n_2} + W_{P2\mu_1 n_2} I_{n_1 n_2} v,$$  \hspace{2cm} (27)

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 \( \alpha \) and the electron-to-nucleus mass ratio \( m/M \) [29, 30],

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

(29)

Here, the first superscript of the expansion terms \( \mathcal{E}^{(i,j)} \) indicates the order in \( \alpha \), 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)

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

(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 \( ma^4 \) recoil correction for a state with the total angular momentum \( J \) is given by (in atomic units)

\[
\mathcal{E}^{(4,1)}_J = \left( \langle H^{(4,0)} \rangle \frac{1}{(E - H)^2} \langle H^{(2,1)} \rangle_J \right) + \left( \sum_{a,b} \frac{Z}{r_a^3} \vec{s}_a \cdot \vec{r}_{ab} \times \vec{p}_b \right)_J,
\]

(31)

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

\[
H^{(2,1)} = \frac{1}{2} \vec{p}^2 = \frac{1}{2} \left( - \sum_a \vec{p}_a \right)^2,
\]

(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)

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

(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 \( 1/Z \)-expansion method in Sec. I, we represent the numerical results listed in Table II in the form of the \( 1/Z \) expansion,

\[
\mathcal{E}^{(4,0)} = Z^4 \sum_{i=0}^{\infty} \frac{C_{i,4}}{Z^i},
\]

(34)

\[
\mathcal{E}^{(5,0)} = Z^4 \sum_{i=0}^{\infty} \frac{D_{i,5}}{Z^i},
\]

(35)

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

(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 \( \alpha \).

The first coefficients of the expansions are known analytically,

\[
C_{0,4} = \frac{1}{32}, \quad D_{0,5} = \frac{1}{32 \pi},
\]

(37)

\[
R_{0,4} = -\frac{1}{32} + \frac{2^8}{3^5} (3 \ln \frac{3}{2} - 2),
\]

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

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

(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

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

(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

\[
C_{1,4} = -0.21810912 \quad \text{and} \quad C_{1,6} = -0.194777.
\]

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 \( |\kappa_{\text{max}}| = 20 \), 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,

\[
E_{2\text{phot}} = a^2 (Z\alpha)^2 \left[ C_{2,4} + (Z\alpha)^2 C_{2,6} + \ldots \right].
\]

(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 \( ma^4 \) NRQED results obtained in Sec. II. Second, we get it by fitting the \( Z \rightarrow 0 \) and \( \alpha \rightarrow 0 \) limit of the two-photon exchange correction in the MBPT approximation (10). Both methods yield consistent results, but the second is more accurate. We therefore fix the coefficient as \( C_{2,4} = 0.49788 \). 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 \( Z \leq 13 \), 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 \( Z \geq 20 \). 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

\[
E_{3\text{phot}} = a^3 (Z\alpha) \left[ C_{3,4} + (Z\alpha)^2 C_{3,6} + \ldots \right].
\]

(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 $E_{\geq 4\text{phot}}$ 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 $E_{\geq 4\text{phot}}$ by subtracting the first terms of the $1/Z$ expansion from the $ma^4$ NRQED contribution listed in Table II,

$$E_{\geq 4\text{phot}} = \alpha^4 E^{(4,0)} - (Z\alpha)^4 \left[ C_{0.4} + \frac{C_{1.4}}{2} + \frac{C_{2.4}}{Z^2} + \frac{C_{3.4}}{Z^3} \right].$$

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 $E_{\geq 4\text{phot}}$ by fitting the $1/Z$ expansion of numerical results for $E^{(4,0)}$ listed in Table II.

Our results for $E_{\geq 4\text{phot}}$ are presented in Table III, in the column labeled “$\geq 4\text{-ph}$”. The indicated numerical uncertainty takes into account uncalculated QED effects of order $ma^6$ 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 $ma^4$ 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 $2p_{1/2}-2p_{1/2}$ 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 $ma^4$ 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), $E_{\text{QEDhydr}}$, is due to one-electron QED effects. They were recently reviewed in Ref. [36], so we obtain $E_{\text{QEDhydr}}$ from data tabulated in that work, adding together the one-loop and two-loop QED effects. The $Z\alpha$ expansion of this contribution is

$$E_{\text{QEDhydr}} = \alpha(Z\alpha)^4 \left[ D_{0.5} + (Z\alpha)^2 \ln(Z\alpha) D_{0.7} + (Z\alpha)^2 D_{0.7} + \ldots \right],$$

where $D_{0.5} = 1/32\pi$, $D_{0.7} = 1/16\pi$ [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 $E_{\text{QEDscr1}}$ 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]),

$$
\begin{align*}
E_{(1s)^22p_{1/2}} &= \frac{1}{2} E_{(1s)^22p_{3/2}} + \frac{3}{2} E_{(1s)^22p_{1/2}}; \\
E_{(1s)^22p_{3/2}} &= \frac{3}{4} E_{(1s)^22p_{3/2}} + \frac{5}{4} E_{(1s)^22p_{1/2}}.
\end{align*}
$$

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

$$E_{\text{QEDscr1}} = \alpha^2(Z\alpha)^3 \left[ D_{1.5} + (Z\alpha)^2 \ln(Z\alpha) D_{1.7} + (Z\alpha)^2 D_{1.7} + \ldots \right],$$

using the accurate value for the leading coefficient $D_{1.5} = -0.065060$, obtained in Sec. II from fitting the NRQED results for the $E^{(5,0)}$ correction. Numerical results for $E_{\text{QEDscr1}}$ 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, $E_{\text{QEDscr2}}$, 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 annihilation operators was carried out according to formulas presented in Appendix A. The $Z\alpha$ expansion of $E_{\text{QEDscr}2}$ is

$$E_{\text{QEDscr}2} = \alpha^3(Z\alpha)^2 D_{2,5} + \ldots$$

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 annihilation contributions 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 $E_{\text{QEDscr}3+}$ was obtained from the NRQED calculations described in Sec. II. For $Z \leq 13$, we obtain $E_{\geq4\text{phot}}$ by subtracting the first terms of the $1/Z$ expansion from the $ma5^5$ NRQED contribution listed in Table II,

$$E_{\text{QEDscr}3+} = \alpha^5\mathcal{E}^{(5,0)} - \alpha(Z\alpha)^4 \left[ D_{0,5} + \frac{D_{1,5}}{Z} + \frac{D_{2,5}}{Z^2} \right].$$

For $Z > 13$, we evaluate $E_{\text{QEDscr}3+}$ by fitting the $1/Z$ expansion of numerical results for $\mathcal{E}^{(5,0)}$ listed in Table II. Our results for $E_{\text{QEDscr}3+}$ are listed in Table III, in the last four columns. 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 $ma5^5$ 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 $E_{\text{oneel}}$ was calculated rigorously within QED to all orders in $Z\alpha$ in Refs. [45, 46]. In this work we take numerical results for $E_{\text{oneel}}$ from the recent tabulation presented in Ref. [36].

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

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

where the second term in braces subtracts the one-electron contribution already taken into account by $E_{\text{rec}1}$. For $Z \leq 13$, 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 $ma5^5$ 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 “$(r^2)^{1/2}$” 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 $Z \leq 10$, 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 steady growing deviation between their values and our results.

For $Z \geq 10$, 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 $2p_{1/2} - 2s$ 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 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 ann operator [given by Eqs. (14) and (15)] with the Dirac wave functions, after angular integrations. The matrix element of the one-electron ann operator is evaluated as

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

(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]; $\kappa_n$ and $\mu_n$ are the relativistic angular-momentum quantum number and the angular-momentum projection, correspondingly.

The matrix element of the two-electron ann 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]),

$$
\langle ab | H_{\text{amm},2} | cd \rangle = \frac{\alpha \kappa}{4} \sum_L J_L(abcd) R_{L}^{\text{amm},2}(abcd),
$$

(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 $R_{L}^{\text{amm},2}$ is the radial integral evaluated as

$$
R_{L}^{\text{amm},2}(abcd) = (-1)^L \left( 2L + 1 \right) \int_0^\infty r_1^2 dr_1 \left[ \sqrt{\frac{L+1}{2L+1}} C_L(\kappa_b, \kappa_d) \frac{1}{r_1^L} X_{ac,LL+1}(r_1) \int_0^{r_1} r_2^2 dr_2 \frac{1}{r_2^L} W_{bd}(r_2) 
+ \sqrt{\frac{L}{2L+1}} C_L(\kappa_b, \kappa_d) \frac{1}{r_1^{L+1}} W_{bd}(r_1) \int_0^{r_1} r_2^2 dr_2 \frac{1}{r_2^{L+1}} X_{ac,LL-1}(r_2) 
+ \sum_{l=L-1}^L \sqrt{6(l+1)} \left\{ \begin{array}{ccc} 1 & 1 & 1 \\ L & l & l+1 \end{array} \right\} \frac{1}{r_1^{L+2}} Y_{ac,LL+1}(r_1) \int_0^{r_1} r_2^2 dr_2 \frac{1}{r_2^{L+2}} Z_{bd,LL}(r_2) \right].
$$

(A3)
### TABLE III. The electron structure corrections to the 2p_{3/2}-2p_{1/2} fine structure splitting, in eV.

| Z  | Dirac  | 1-ph. MBPT | 2-ph. QED | 3-ph. | ≥4-ph. | Sum | Other methods |
|----|--------|------------|-----------|-------|--------|-----|--------------|
| 5  | 0.028325 | 0.018070  | 0.000002 (1) | −0.000681 (2) | 0.000050 | 0.004214 (2) | 0.004215 | a |
| 6  | 0.058757 | 0.026403  | 0.000004 (2) | −0.000322 (2) | 0.000057 | 0.001253 (3) | 0.001249 | b |
| 7  | 0.108901 | 0.035483  | 0.000007 (3) | −0.000371 (3) | 0.000062 | 0.003203 (5) | 0.003198 | a |
| 8  | 0.185873 | 0.046398  | 0.000012 (5) | −0.000423 (5) | 0.000065 (1) | 0.006514 (7) | 0.00653a | |
| 9  | 0.297902 | 0.058798  | 0.000018 (7) | −0.000080 (6) | 0.000067 (1) | 0.120615 (9) | 0.12040a | |
| 10 | 0.454338 | 0.072695  | 0.000027 (9) | −0.000444 (8) | 0.000069 (1) | 0.204128 (12) | 0.20366b | |

1. NRQED, this work; 2. 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 \( ^{4} \) | Sum | NRQED | Kozhedub et al. [22] |
|----|----------------|----------------|----------------|-----|-----|----------------------|
| 5  | −0.0000846 (1) | 0.0000356 (2) | −0.0000048 (2) | −0.0000538 (3) | −0.000054 | |
| 6  | −0.0001454 (2) | 0.0000509 (5) | −0.0000058 (3) | −0.0001003 (6) | −0.000102 | |
| 7  | −0.0002295 (4) | 0.0000686 (8) | −0.0000068 (4) | −0.000108 (1) | −0.000171 | |
| 8  | −0.0003493 (7) | 0.0000887 (13) | −0.0000078 (5) | −0.000250 (2) | −0.000267 | |
| 9  | −0.0004811 (12) | 0.0001120 (20) | −0.0000088 (7) | −0.000379 (2) | −0.000392 | |
| 10 | −0.0006551 (20) | 0.0001360 (29) | −0.0000099 (9) | −0.000529 (4) | −0.000552 | −0.0005 (2) |
| 12 | −0.0011142 (43) | 0.0001961 (54) | −0.0000118 (15) | −0.000935 (7) | −0.000991 | −0.0009 (3) |
| 15 | −0.0012012 (11) | 0.000289 (12) | −0.000015 (3) | −0.000185 (2) | −0.000185 (4) | |
| 18 | −0.003558 (22) | 0.000399 (22) | −0.000018 (4) | −0.000313 (8) | −0.000325 (6) | |
| 20 | −0.004790 (27) | 0.000478 (29) | −0.000020 (5) | −0.000334 (4) | −0.000345 (5) | |
| 26 | −0.00983 (15) | 0.000731 (69) | −0.000026 (10) | −0.00092 (1) | −0.00092 (8) | |
| 30 | −0.01430 (8) | 0.00090 (11) | −0.000030 (14) | −0.0134 (2) | −0.0134 (11) | |
| 32 | −0.0165 (13) | 0.00098 (14) | −0.0000136 (16) | −0.0159 (2) | −0.0160 (12) | |
| 40 | −0.02856 (14) | 0.00122 (31) | −0.000040 (28) | −0.0274 (4) | −0.0279 (18) | |
| 47 | −0.03921 (26) | 0.00125 (55) | −0.000047 (42) | −0.0380 (7) | −0.0387 (24) | |
| 50 | −0.04302 (29) | 0.00118 (69) | −0.000050 (50) | −0.0419 (9) | −0.0428 (27) | |
| 54 | −0.04678 (38) | 0.00099 (89) | −0.000054 (61) | −0.0459 (10) | −0.0470 (32) | |
| 60 | −0.04621 (45) | 0.000513 (6) | −0.000060 (82) | −0.0458 (14) | −0.0480 (42) | |
| 66 | −0.03439 (64) | −0.00004 (19) | −0.00007 (11) | −0.035 (2) | −0.037 (5) | |
| 70 | −0.01483 (47) | −0.0012 (24) | −0.000017 (3) | −0.016 (2) | −0.020 (7) | |
| 74 | 0.01598 (86) | −0.0012 (29) | −0.000017 (6) | 0.014 (3) | 0.010 (8) | |
| 80 | 0.0987 (58) | −0.0023 (40) | −0.000020 (8) | 0.095 (4) | 0.086 (11) | |
| 82 | 0.13813 (63) | −0.0035 (44) | −0.000022 (23) | 0.135 (4) | 0.122 (12) | |
| 90 | 0.38616 (82) | −0.0020 (66) | −0.000093 (32) | 0.384 (7) | 0.359 (17) | |
| 92 | 0.47880 (91) | −0.0030 (73) | −0.000093 (35) | 0.478 (7) | 0.446 (19) | |

\( ^{1} \) NRQED, this work; \( ^{2} \) Kozhedub et al. [22].
TABLE V. Comparison of different theoretical predictions and experimental results for the $2p_{3/2}\cdot2p_{1/2}$ 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 | 1650.39 (10) | 1649.2 | 1653 (3) | 1653 (8) | 1649 (2) | [52] |
| 11 | 2625.73 (10) | | | 2631 (5) | [52] |
| 12 | 3979.15 (13) | | 3984 (8) | 3985 (3) | [52] |
| 13 | 5797.76 (16) | | 5796 (5) | [52] |
| 14 | 8177.95 (21) | | 8177 (4) | [52] |
| 15 | 11225.35 (25) | 11224 (4) | 11219 (8) | 11253 (15) | [52] |
| 16 | 15055.24 (30) | | | 15054 (1) | [53] |
| 17 | 19792.36 (35) | | | 19770 (15) | [52] |
| 18 | 25571.24 (42) | 25572 (5) | 25560 (8) | 25572 (10) | [52] |
| 20 | 40841.36 (55) | 40843 (6) | 40828 (8) | 40850 (10) | [52] |
| 21 | 50651.62 (70) | 50627 (8) | 50627 (8) | 50627 (8) | [52] |
| 22 | 62141.83 (95) | 62146 (10) | 62146 (10) | 62146 (10) | [52] |
| 24 | 90941.45 (15) | | 90912 (12) | [54] |
| 25 | 108598.5 (16) | | 108634 (40) | [52] |
| 26 | 128769.8 (17) | | 128774 (16) | 128774 (16) | [55] |
| 28 | 177502.2 (17) | 177508 (8) | 177474 (8) | 177524 (20) | [56] |
| 29 | 206557.7 (17) | | 206549 (33) | [57] |

| Z   | This work | Kozhedub 2010 [22] | Sapirstein 2011 [15] | Experiment | Ref. |
|-----|-----------|-------------------|----------------------|-------------|------|
|     | in eV: | | | | |
| 30 | 29.64327 (23) | 29.6436 (12) | 29.641 (1) | 29.6464 (47) | [58] |
| 32 | 39.14230 (30) | 39.14 | 39.1417 (53) | [57] |
| 34 | 50.79946 (38) | 50.799 (23) | 50.799 (23) | [59] |
| 36 | 64.93657 (43) | 64.9367 (17) | 64.93 (17) | 64.955 (37) | [60, 61] |
| 39 | 91.5657 (53) | 91.5657 (53) | 91.5657 (53) | 91.5657 (53) | [62] |
| 40 | 102.08050 (58) | 102.081 (23) | 102.081 (23) | 102.081 (23) | [62] |
| 42 | 125.87940 (70) | 125.88 | 125.88 | 125.841 (73) | [59] |
| 47 | 204.2389 (11) | 204.238 (36) | 204.238 (36) | 204.238 (36) | [63] |
| 50 | 266.7725 (14) | 266.772 (14) | 266.772 (14) | 266.772 (14) | [63] |
| 52 | 316.135 (16) | 316.135 (16) | 316.135 (16) | 316.135 (16) | [63] |
| 54 | 372.3950 (19) | 372.3950 (19) | 372.3950 (19) | 372.3950 (19) | [63] |
| 60 | 589.9285 (30) | 589.928 (6) | 589.928 (6) | 589.928 (6) | [64, 64] |
| 64 | 784.0283 (41) | 784.028 (1) | 784.028 (1) | 784.028 (1) | [64, 64] |
| 66 | 898.7121 (48) | 898.712 (1) | 898.712 (1) | 898.712 (1) | [64, 64] |
| 70 | 1169.031 (3) | 1169.031 (3) | 1169.031 (3) | 1169.031 (3) | [64, 64] |
| 74 | 1502.7150 (65) | 1502.715 (3) | 1502.715 (3) | 1502.715 (3) | [64, 64] |
| 79 | 2027.7569 (93) | 2027.756 (9) | 2027.756 (9) | 2027.756 (9) | [64, 64] |
| 80 | 2149.404 (10) | 2149.404 (10) | 2149.404 (10) | 2149.404 (10) | [64, 64] |
| 82 | 2411.403 (11) | 2411.403 (11) | 2411.403 (11) | 2411.403 (11) | [64, 64] |
| 83 | 2552.326 (11) | 2552.326 (5) | 2552.326 (5) | 2552.326 (5) | [64, 64] |
| 90 | 3754.525 (22) | 3754.525 (22) | 3754.525 (22) | 3754.525 (22) | [64, 64] |
| 92 | 4178.830 (22) | 4178.830 (8) | 4178.830 (8) | 4178.830 (8) | [6, 65] |

\[
\sum_{l=L}^{L+1} \sqrt{6l} \left( \begin{array}{ccc} 1 & 1 & \frac{1}{2} \\ L & l & l-1 \end{array} \right) \frac{1}{\mu_{L+1}} Z_{bd,Ll}(r_1) \int_0^{r_1} r_2^2 dr_2 \int_0^{r_2} \frac{L-1}{Y_{ac,Ll-1}(r_2)} (ac) \leftrightarrow (bd) \ldots,
\]

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

\[
X_{ac,Ll}(r) = g_a(r) f_c(r) S_{Ll}(-\kappa_c, \kappa_a) + f_a(r) g_c(r) S_{Ll}(\kappa_c, -\kappa_a),
\]

where \{\ldots\} denotes the 6j-symbol and
Furthermore, the standard angular coefficients $S_{ll'}$ and $C_I$ are defined by Eqs. (A7)-(A10) of Ref. [66].

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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 = 5896 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 | $(r^2)^{1/2}$ [fm] | Structure | QED,1-el | QED,scr | Recoil | Total |
|-----|---------|---------------------|-----------|----------|---------|--------|-------|
| 5   | 11B     | 2.406 (29)          | 0.004 213.7 (16) | 0.000 065.2 | -0.000 053.8 (3) | -0.000 0003 | 0.004 221.8 (17) |
| 6   | 12C     | 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   | 14N     | 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   | 16O     | 2.6991 (52)         | 0.065 713.6 (67) | 0.000 424.6 (1) | -0.000 259.4 (16) | -0.000 0031 | 0.065 787.7 (68) |
| 9   | 18F     | 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  | 20Ne    | 3.0055 (21)         | 0.204 128.12 | 0.001 031.1 (1) | -0.000 529.0 (36) | -0.000 0076 | 0.204 622.13 |
| 13  | 23Na    | 2.9936 (21)         | 0.324 768.11 | 0.001 505.0 | -0.000 713 (5) | -0.000 0100 | 0.325 549.12 |
| 24  | 24Mg    | 3.0570 (16)         | 0.492 176.16 | 0.002 126.0 | -0.000 934 (7) | -0.000 0150 | 0.493 351.16 |
| 27  | 27Al    | 3.0610 (31)         | 0.717 127.18 | 0.002 919.0 | -0.001 195 (9) | -0.000 0200 | 0.718 831.20 |
| 28  | 28Si    | 3.1224 (24)         | 1.011 548.22 | 0.003 913 (1) | -0.001 498 (12) | -0.000 0270 | 1.013 936.26 |
| 31  | 31P     | 3.1889 (19)         | 1.388 508 (26) | 0.005 140.1 | -0.001 846 (16) | -0.000 0330 | 1.391 770.31 |
| 32  | 32S     | 3.2611 (18)         | 1.862 263.61 | 0.006 632 (1) | -0.002 240 (20) | -0.000 0430 | 1.866 612.37 |
| 35  | 35Cl    | 3.365 (19)          | 2.448 253 (36) | 0.008 422 (2) | -0.002 683 (25) | -0.000 0512 | 2.453 940.44 |
| 40  | 40Ar    | 3.4274 (26)         | 3.163 116 (41) | 0.010 548 (3) | -0.003 177 (31) | -0.000 0580 | 3.170 429.52 |
| 39  | 39K     | 3.4349 (19)         | 4.024 704 (46) | 0.013 047 (4) | -0.003 723 (38) | -0.000 0760 | 4.033 952.59 |
| 40  | 40Ca    | 3.4776 (19)         | 5.052 148 (54) | 0.015 959 (5) | -0.004 331 (40) | -0.000 0930 | 5.063 683.68 |
| 21  | 45Sc    | 3.5459 (25)         | 6.265 777 (63) | 0.019 324 (6) | -0.004 998 (59) | -0.000 1030 | 6.280 001.87 |
| 48  | 48Ti    | 3.5921 (17)         | 7.687 235 (72) | 0.023 186 (9) | -0.005 697 (92) | -0.000 1180 | 7.704 610.12 |
| 51  | 51V     | 3.6002 (22)         | 9.339 469 (83) | 0.027 587 (11) | -0.006 48 (12) | -0.000 1350 | 9.360 44 (15) |
| 52  | 52Cr    | 3.6542 (45)         | 11.246 84 (11) | 0.032 574 (14) | -0.007 30 (15) | -0.000 1600 | 11.271 96 (18) |
| 55  | 55Mn    | 3.7057 (22)         | 13.434 66 (10) | 0.038 194 (18) | -0.008 18 (16) | -0.000 1800 | 13.464 50 (19) |
| 56  | 56Fe    | 3.7377 (16)         | 15.930 26 (12) | 0.044 492 (23) | -0.009 12 (17) | -0.000 2100 | 15.965 42 (21) |
| 59  | 59Co    | 3.7875 (21)         | 18.761 95 (13) | 0.051 517 (29) | -0.010 12 (16) | -0.000 2350 | 18.803 11 (21) |
| 58  | 58Ni    | 3.7757 (20)         | 21.595 59 (14) | 0.059 320 (36) | -0.011 7 (15) | -0.000 2800 | 22.007 46 (21) |
| 63  | 63Cu    | 3.8823 (15)         | 25.554 52 (16) | 0.067 951 (44) | -0.012 29 (14) | -0.000 3000 | 25.699 89 (22) |
| 64  | 64Zn    | 3.9283 (15)         | 29.579 58 (18) | 0.077 46 (5) | -0.013 43 (14) | -0.000 3400 | 29.643 27 (23) |
