Relativistic configuration-interaction calculations of energy levels of the $1s^2 2l$ and $1s2l2l'$ states in lithium-like ions: carbon through chlorine

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We present systematic calculations of energy levels of the $1s^2 2l$ and $1s2l2l'$ states of ions along the lithium isoelectronic sequence from carbon till chlorine. The calculations are performed by using the relativistic configuration-interaction method adapted to the treatment of autoionizing core-excited states. The relativistic energies are supplemented with the QED energy shifts calculated within the model QED operator approach. A systematic estimation of the theoretical uncertainties is performed for every electronic state and every nuclear charge. The results are in agreement with existing high-precision theoretical and experimental data for the ground and first excited states. For the core-excited states, our theory is much more accurate than the presently available measurements.

I. INTRODUCTION

Lithium-like ions are among the simplest atomic systems. Their spectra can be described in ab initio theoretical calculations very accurately. For light atoms, the presently most powerful calculational approach is based on the non-relativistic quantum electrodynamics (NRQED) expansion of energy levels in powers of $\alpha$ and $Z\alpha$ (where $\alpha$ is the fine-structure constant and $Z$ is the nuclear charge number). High-precision NRQED calculations were performed by Puchalski and Pachucki for the lowest-lying states of Li and $\text{Be}^+$ [1–5]. In the region of heavy ions, the best results are presently obtained within the alternative approach that accounts for all orders in the nuclear binding strength parameter $Z\alpha$ but expands in the electron-electron interaction parameter $1/Z$. Calculations by this method were performed by Shabaev and coworkers [4–7] for the ground and first excited states of Li-like ions with $Z \geq 10$. It is important to point out that both these methods were able to produce predictive results, i.e., their results contain estimates of theoretical errors obtained without referring to experimental data.

For the core-excited states of Li-like ions, there have been no rigorous QED calculations accomplished so far. Previous calculations were performed using various methods, notably, the multi-configurational Dirac-Fock method [8, 9], the variational nonrelativistic approach with inclusion of leading relativistic effects [10], and many-body perturbation theory (MBPT) [11]. None of these calculations were able to provide estimations of theoretical errors.

In our previous investigation [12] we obtained predictive results for energies of the $1s2l2l'$ core-excited states of Li-like ions in the nuclear charge region $Z = 18$ – 36. By combining results obtained by the relativistic configuration-interaction method with the one-loop QED effects calculated in effective screening potentials, we were able to produce theoretical predictions with an accuracy better than what is presently achievable in experiments, see, e.g., the recent measurement of the $K\alpha$ transitions in iron [13]. Such accuracy opens possibilities of using theoretical energies of Li-like ions for calibration of experimental X-ray spectra for ions with a larger number of electrons, for which accurate calculations are presently not possible.

With the range of $Z$ computed in Ref. [12], possible calibrations are restricted to the X-ray energies beyond 3 keV. The energy range of most third- and fourth-generation synchrotron light sources, however, lies in the region of smaller X-ray energies [14]. High-quality calibration sources are urgently needed for the energy range between the carbon and the chlorine $K$-edges.

The present situation with calibration standards in the soft-X-ray regime has recently been examined by Müller and coworkers [15] with emphasis on photon energies near the neon $K$-edge at approximately 870 eV. In numerous experiments performed by various techniques (see Table I of Ref. [15]), the $1s\rightarrow 3p$ dipole transition energy in neutral neon has been measured, with results ranging between 867.05 and 867.69 eV with quoted uncertainties of typically 50 to 80 meV but discrepancies reaching up to 640 meV. This situation clearly shows the need for new and reliable calibration standards in the soft-X-ray energy region.

Precise knowledge of the satellite transition energies are also required for the diagnostics of hot laboratory plasmas, particularly those in the magnetically-confined-fusion research. High-quality theoretical energies are considered to be critical for a proper fit of spectral lines and, accordingly, a better plasma diagnostics [16, 17].

Partly motivated by the needs described above, the goal of the present work was to extend our previous calculation of the $n = 2$ valence and core-excited states of Li-like ions [12] to the lower-$Z$ region. This task turned out to be less
straightforward than it seemed and required significant alterations of our original computational approach, for two reasons. First, the interaction of the autoionizing core-excited reference states with closely-lying continuum states became more pronounced for low-$Z$ ions than it was for heavier ions, which led to poor convergence of the results with respect to the basis size. Second, the computation of the QED effects for the nuclear charges as low as $Z = 6$ in the same way as it was done in Ref. [12] turned out to be not possible because of technical difficulties and numerical cancellations, which grow fast as $Z$ is decreased. Our ways for overcoming these problems are discussed in the next two sections.

II. CONFIGURATION-INTERACTION METHOD FOR CORE EXCITED STATES

We start with outlining the main features of the configuration-interaction (CI) method, which is by now one of the standard approaches in atomic structure calculations, see, e.g., Refs. [18, 19]. The CI $N$-electron wave function $\Psi(PJM)$ with a definite parity $P$, total angular momentum $J$, and angular momentum projection $M$ is represented as a finite sum of configuration-state functions (CSFs) with the same $P$, $J$, and $M$,

$$
\Psi(PJM) = \sum_r c_r \Phi(\gamma_r.PJM),
$$

where $\gamma_r$ denotes the set of additional quantum numbers that determine the CSF. The CSFs are constructed as linear combinations of antisymmetrized products of one-electron orbitals $\psi_n$, which are positive-energy eigenfunctions of some one-particle Dirac Hamiltonian (which corresponds to the so-called no-pair approximation). In our implementation of the CI method, we used the one-particle Dirac Hamiltonian with the frozen-core Dirac-Fock potential.

The eigenvalues and eigenfunctions of the Dirac Hamiltonian are constructed by the dual-kinetic-balance (DKB) method [20] from a finite set of $B$-spline basis functions. This approach yields a discrete representation of the continuum part of the Dirac spectrum, in which the density of the continuum states increases as the number of basis functions is enlarged. For a given number of $B$-splines $n_α$, all Dirac eigenstates $\psi_l$ with the energies $0 < \varepsilon_l \leq mc^2(1 + Z\alpha \epsilon)$ and the orbital quantum number $l \leq L_{\text{max}}$ were included into the one-electron basis of our CI calculations. The dependence of the calculated results on the parameters $n_α$, $\epsilon$, and $L_{\text{max}}$ was carefully studied in order to provide estimates of the numerical uncertainty (see Tables I and II of Ref. [12] for examples of the analysis of the basis convergence).

The energies of electronic states and the corresponding expansion coefficients $c_r$ are obtained as the eigenvalues and the eigenvectors of the matrix of the Dirac-Coulomb-Breit (DCB) Hamiltonian in the space of the CSFs,

$$
\{H_{rs}\} \equiv \{\langle\gamma_r.PJM|H_{DCB}|\gamma_s.PJM\rangle\}.
$$

The DCB Hamiltonian is

$$
H_{DCB} = \sum_i h_D(i) + \sum_{i<j}[V_C(i,j) + V_B(i,j)],
$$

where the indices $i, j = 1, \ldots, N$ numerate the electrons, $h_D$ is the one-particle Dirac-Coulomb Hamiltonian, and $V_C$ and $V_B$ are the Coulomb and the Breit parts of the electron-electron interaction. The matrix elements of the Hamiltonian are represented as linear combinations of one- and two-particle radial integrals,

$$
\langle\gamma_r.PJM|H_{DCB}|\gamma_s.PJM\rangle = \sum_{ab} d_{rs}(ab) I(ab) + \alpha \sum_k \sum_{abcd} \psi_{rs}^{(k)}(abcd) R_k(abcd),
$$

where $a$, $b$, $c$, and $d$ numerate the one-electron orbitals, $d_{rs}$ and $\psi_{rs}^{(k)}$ are the angular coefficients, $I(ab)$ are the one-electron radial integrals, and $R_k(abcd)$ are the two-electron radial integrals. We refer the reader to our previous papers for formulas and details of the implementation of the method [12, 21].

In the present work we would like to use the CI method for computing energy levels of core-excited states with energies above the autoionization threshold. For such states, the interaction of the reference state with the closely-lying continuum $1s^2l^2$ states (with energy $\varepsilon > mc^2$) might be significant and should be properly accounted for. In our previous calculations [12, 21, 22], we addressed this issue by using increasingly large sets of one-electron orbitals and by studying the convergence of the results. In the present work, however, we are interested in the lower-$Z$ ions where the interaction with the continuum states is more significant and the convergence of the results for such a straightforward approach often becomes unsatisfactory.

Let us consider the $1s2s^22S$ state as an example. It is the lowest-lying core-excited state and its energy is significantly influenced by the interaction with the closely-lying continuum $1s^22p_{1/2}$ states. If we increase our basis of one-electron orbitals in a straightforward way, we observe that at a certain level of precision our results stop to converge but start to oscillate instead. We would like to emphasize that this problem reveals itself only when we increase the density of the continuum states in the “problematic” region near the energy of the reference state. If we had not changed the density, we might have not even become aware of this problem.

It turns out that the instabilities of the convergence of energies can be traced back to the situations when a continuum $1s^22p_{1/2}$ state happens to be closely degenerate in energy with the reference state. We found out that the convergence with respect to the basis can be drastically improved if we “balance” our discrete representation of the continuum spectrum in such a way that the energies of the two nearest continuum states are on the same distance from the energy of the reference state (one continuum state below the reference state, and the other above).

The same situation occurs for other core-excited states, but the degree of the coupling to the continuum and, therefore, the
magnitude of instabilities differ for different states. In particular, the $1s2s2p^4P^o$ state is rather insensitive to the interaction with the continuum. On the contrary, the $^2D$ state is very much so. Moreover, the latter couples not only with the $l = 2$ continuum states (as is the case for the $S$ and $P$ states), but also to the $l = 2$ ones. Table I presents a comparison of the convergence of the CI energies of the $1s2p^2^2D_{3/2}$ state for $Z = 6$ and $Z = 17$, as obtained by different methods. The left part of the table contains results obtained with the standard one-electron basis, whereas the right part displays results obtained with the balanced basis. We observe that the proposed balancing of the spectrum of one-electron orbitals significantly improves the convergence of the calculated CI energies, which entails an improvement of the estimated accuracy by up to two orders of magnitude.

Let us now discuss how we produce a balanced discrete representation of the one-electron continuum spectrum. In our approach, the one-electron orbitals are taken from the finite basis set representation of the Dirac Hamiltonian with the frozen-core Dirac-Fock potential, obtained by the DKB $B$-spline method [20]. The $B$-splines are defined on a radial grid, whose form outside of the nucleus is exponential,

$$t_i = t_0 e^{A i/N}, \quad i = 0 \ldots N,$$

where $A = \ln(t_{\text{max}}/t_0)$, $t_{\text{max}}$ is the radial cutoff parameter and $t_0$ is the nuclear radius. In the present work, we introduce a continuous parameter $\gamma$ in the definition of the radial grid,

$$t_i = t_0 e^{A (i/N)\gamma}.$$

After that, the energies of the continuum states of the $B$-spline representation of the one-electron Dirac Hamiltonian spectrum become functions of the parameter $\gamma$, $\varepsilon_n = \varepsilon_n(\gamma)$.

By varying $\gamma$ (typically, by 10-20% from the standard value $\gamma = 1$), we were able to adjust the energy positions of the two nearest continuum states to be symmetrical with respect to the reference-state energy. In practice, we repeated our CI calculations for different values of the parameter $\gamma$, adjusting this parameter until the separation energies of the two closest-lying continuum states from the reference state were equal. In these calculations it was sufficient to restrict the basis by $L_{\text{max}} = 1$ for the $S$ and $P$ states and by $L_{\text{max}} = 2$ for the $D$ states, since the higher-$L$ continuum states do not cause any problems.

### III. QED EFFECTS

In the present work we evaluated the leading QED effects to the energy levels by means of the model QED operator approach [23]. We used the implementation of this method in the form of the QEDMOD package [24]. Since the published version of the package had a restriction of the nuclear charge $Z \geq 10$, we had to extend it to the lower values of $Z$. We did this by performing numerical calculations of the one-loop self-energy matrix elements for the $ns$, $np_j$, and $nd_j$ states for $Z = 3 - 9$ by the method described in Ref. [23] (extending Tables I - IV of Ref. [23]).

In order to establish the level of accuracy of the model QED operator approach in the region of low nuclear charges, we compared values obtained with the QEDMOD package with results of rigorous QED calculations for the $1s^22s$ and $1s^22p_{1/2}$ states. Such calculations were accomplished for the lightest Li-like atoms within the NRQED approach [1] and for heavier Li-like ions within the all-order $Z\alpha$ method [5, 7]. The comparison is presented in Table II. From this compari-
sults of rigorous QED calculations for the total energies to accuracy of better than 1%.

IV. RESULTS AND DISCUSSION

Numerical results of our calculations of the energy levels for the ground $1s^22s$ state, the first two valence-excited $1s^22p_j$ states and the core-excited $1s2l2l'$ states of Li-like ions are listed in Table III. The results are given for ions along the lithium isoelectronic sequence from carbon ($Z = 6$) and ending with chlorine ($Z = 17$). For the ground state, the table presents ionization energies, i.e., energies relative to the ground state of the corresponding He-like ion. For the valence-excited states, we present energies of the $1s^22p_{1/2}$ state relative to the ground $1s^22s$ state and the $2p_{3/2}-2p_{1/2}$ fine-structure interval, since they usually appear in the literature in this form. For the core-excited levels, the center-of-gravity (cg) energies relative to the ground state and the fine-structure intervals ($J-J'$) are listed.

### TABLE III: Energy levels of Li-like ions, in Rydbergs. The labelling is as follows: “Coul” stands for the Dirac-Coulomb energies, “Breit” denotes the correction due to the Breit interaction, “NMS” is the normal mass shift, “SMS” is the specific mass shift, “QED” denotes the QED correction. Further quantities are: $\mu$, the reduced mass, $R$, the root-mean-square nuclear charge radius, and $cg$, the center-of-gravity energy of the multiplet level.

| Term | $J$ | Coul | Breit | NMS | SMS | QED | Total |
|------|-----|------|-------|-----|-----|-----|-------|
| $C \ (Z = 6)$, $\mu/m = 0.00004573$, $R = 2.470$ fm | $1s^22s$ | $2^S$ | $1/2$ | -4.74074 | 0.00022 | 0.000022 | 0.000001 | 0.000011 | -4.74019 (10) |
| | $1s^22p$ | $2^P$ | $1/2$ | 0.58774 | 0.00013 | -0.00003 | -0.00011 | -0.00012 | 0.58761 (11) |
| | | | $3/2$-1/2 | 0.00118 | -0.00023 | 0.0 | 0.0 | 0 | 0.00096 (8) |
| $1s^22s$ | $2^S$ | $1/2$ | 21.43815 | -0.00387 | -0.00098 | -0.00008 | -0.00124 | 21.4326 (6) |
| | | | $3/2$-1/2 | 0.00070 | -0.00066 | 0.0 | 0.0 | 0 | 0.00004 |
| | | | $5/2$-3/2 | 0.00117 | -0.00029 | 0.0 | 0.0 | 0 | 0.00088 |
| | | | $1s^22s2p$ | $3/2$-1/2 | 0.00082 | 0.00070 | 0.0 | 0.0 | 0 | 0.00089 (5) |
| | | | | $4P$ | $1s^22s2p$ | $3/2$-1/2 | 0.00068 | 0.00002 | 0.0 | 0.0 | 0 | 0.00069 (2) |
| | | | | | $5/2$-3/2 | 0.00112 | -0.00076 | 0.0 | 0.0 | 0 | 0.00036 (2) |
| | | | | | | $1s^22s2p$ | $3/2$-1/2 | 0.00062 | -0.00069 | 0.0 | 0.0 | 0 | -0.0001 (4) |
| $N \ (Z = 7)$, $\mu/m = 0.00003918$, $R = 2.558$ fm | $1s^22s$ | $2^S$ | $1/2$ | -7.19567 | 0.00040 | 0.00028 | 0.00001 | 0.00021 | -7.19476 (11) |
| | $1s^22p$ | $2^P$ | $1/2$ | 0.73336 | 0.00028 | -0.00003 | -0.00016 | -0.00024 | 0.73321 (11) |
| | | | $3/2$-1/2 | 0.00277 | -0.00043 | 0.0 | 0.0 | 0 | 0.00024 (8) |
| | $1s^22s$ | $2^S$ | $1/2$ | 30.21196 | -0.00652 | -0.00118 | -0.00009 | -0.00222 | 30.2020 (6) |
| | | | $3/2$-1/2 | 0.00426 | -0.00146 | 0.0 | 0.0 | 0 | 0.00024 (10) |
| | | | $5/2$-3/2 | 0.00134 | -0.00005 | 0.0 | 0.0 | 0 | 0.00031 |
| | | | $1s^22s2p$ | $3/2$-1/2 | 0.00733 | -0.00058 | 0.0 | 0.0 | 0 | 0.000193 |

We conclude that the QEDMOD package reproduces results of rigorous QED calculations for the total energies to accuracy of better than 1%.
| Energy Level | 3s 2s | 2p 2s | 4p 2s | 5s 2s | 6s 2s |
|-------------|-------|-------|-------|-------|-------|
| 1s(\(2S\))2p(\(3P\)) 4P |       |       |       | 3/2-1/2 | 0.00171 | 0.00012 | 0.0 | 0.0 | 0.0 |
|             |       |       |       | 3/2-1/2 | 0.00142 | 0.00002 | 0.0 | 0.0 | 0.0 |
|             |       |       |       | 5/2-3/2 | 0.00235 | -0.00132 | 0.0 | 0.0 | 0.0 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00126 | 0.000119 | 0.0 | 0.0 | 0.0 |
|             |       |       |       | 5/2-3/2 | 0.00038 | -0.00191 | 0.0 | 0.0 | 0.0 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00284 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1s(\(2S\))2p(\(3S\)) 2S |       |       |       | 1/2 | 32.10533 | -0.00612 | -0.00126 | -0.00221 | -0.00269 |

**0 (Z = 8), 1 - \(\mu/m\) = 0.00003431, R = 2.701 fm**

| Energy Level | 2s 2s | 2p 2s | 4p 2s | 5s 2s | 6s 2s |
|-------------|-------|-------|-------|-------|-------|
| 1s(\(2S\))2p(\(3P\)) 4P |       |       |       | 3/2-1/2 | 0.0 | -10.15293 | 0.00068 | 0.00035 | 0.00001 | 0.00037 |
|             |       |       |       | 3/2-1/2 | 0.00554 | -0.00073 | 0.0 | 0.0 | 0.00002 |
| 1s(\(2S\))2p(\(3D\)) 2D |       |       |       | 3/2-1/2 | 0.00269 | 0.0181 | 0.0 | 0.0 | 0.0001 |
|             |       |       |       | 5/2-3/2 | 0.00453 | -0.00080 | 0.0 | 0.0 | 0.00001 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00265 | 0.00003 | 0.0 | 0.0 | 0.0 |
|             |       |       |       | 5/2-3/2 | 0.00436 | -0.00211 | 0.0 | 0.0 | 0.00001 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00229 | -0.00188 | 0.0 | 0.0 | 0.00001 |
|             |       |       |       | 5/2-3/2 | 0.00034 | -0.00304 | 0.0 | 0.0 | 0.00001 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00532 | 0.0 | 0.0 | 0.0 | 0.00001 |
| 1s(\(2S\))2p(\(3S\)) 2S |       |       |       | 1/2 | 42.73366 | -0.00947 | -0.00147 | -0.00225 | -0.00445 |

**F (Z = 9), 1 - \(\mu/m\) = 0.00002888, R = 2.898 fm**

| Energy Level | 2s 2s | 2p 2s | 4p 2s | 5s 2s | 6s 2s |
|-------------|-------|-------|-------|-------|-------|
| 1s(\(2S\))2p(\(3P\)) 4P |       |       |       | 3/2-1/2 | 0.0 | -13.61293 | 0.00105 | 0.00039 | 0.00001 | 0.00061 |
|             |       |       |       | 3/2-1/2 | 0.00998 | -0.00115 | 0.0 | 0.0 | 0.00003 |
| 1s(\(2S\))2p(\(3D\)) 2D |       |       |       | 3/2-1/2 | 0.00459 | -0.00270 | 0.0 | 0.0 | 0.00001 |
|             |       |       |       | 5/2-3/2 | 0.00775 | -0.00120 | 0.0 | 0.0 | 0.00001 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00550 | 0.00025 | 0.0 | 0.00001 |
|             |       |       |       | 5/2-3/2 | 0.00455 | 0.00004 | 0.0 | 0.0 | 0.00001 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00746 | -0.00316 | 0.0 | 0.0 | 0.00001 |
|             |       |       |       | 5/2-3/2 | 0.037205 | -0.01394 | -0.00155 | -0.0028 | -0.00632 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00385 | -0.00277 | 0.0 | 0.0 | 0.00001 |
|             |       |       |       | 5/2-3/2 | 0.041280 | -0.01473 | -0.00156 | -0.00343 | -0.00704 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00661 | -0.00456 | 0.0 | 0.0 | 0.0 |
|             |       |       |       | 5/2-3/2 | 0.052906 | -0.01614 | -0.00157 | -0.0019 | -0.00701 |
|             |       |       |       | 3/2-1/2 | 0.00921 | 0.00001 | 0.0 | 0.0 | 0.00002 |
| 1s(\(2S\))2p(\(3S\)) 2S |       |       |       | 1/2 | 54.87079 | -0.01387 | -0.00158 | -0.0028 | -0.00692 |

**Ne (Z = 10), 1 - \(\mu/m\) = 0.00002745, R = 3.005 fm**

| Energy Level | 2s 2s | 2p 2s | 4p 2s | 5s 2s | 6s 2s |
|-------------|-------|-------|-------|-------|-------|
| 1s(\(2S\))2p(\(3P\)) 4P |       |       |       | 3/2-1/2 | 0.0 | -17.57629 | 0.00155 | 0.00048 | 0.00001 | 0.00003 |
|             |       |       |       | 3/2-1/2 | 0.01670 | -0.00170 | 0.0 | 0.0 | 0.00005 |
| 1s(\(2S\))2p(\(3P\)) 2P |       |       |       | 3/2-1/2 | 0.00734 | -0.00384 | 0.0 | 0.0 | 0.00002 |
|             |       |       |       | 5/2-3/2 | 0.01245 | -0.00172 | 0.0 | 0.0 | 0.00002 |

**Atkins**
\[
\begin{align*}
1s^2(2S) & \to 2P^o \quad 3P^o \\
& \quad 3/2 - 1/2 \\
1s^2(2S) & \to 2P^o \quad 4P \\
& \quad 3/2 - 1/2 \\
1s^2(2S) & \to 2P^o \quad 2D \\
& \quad 3/2 - 1/2 \\
1s^2(2S) & \to 2P^o \quad 2P \\
& \quad 3/2 - 1/2 \\
1s^2(2S) & \to 2S \\
& \quad 1/2 \\
\textbf{Na (Z = 11), } 1 - \mu/m = 0.00002387, \ R = 2.994 \text{ fm} \\
1s^2(2S) & \to 2S \\
& \quad 1/2 \\
1s^2(2P) & \to 2P^o \\
& \quad 1/2 \\
1s^2(2S) & \to 2P^o \\
& \quad 2S \\
1s^2(2P) & \to 2P^o \\
& \quad 2P \\
\textbf{Mg (Z = 12), } 1 - \mu/m = 0.00002288, \ R = 3.057 \text{ fm} \\
1s^2(2S) & \to 2S \\
& \quad 1/2 \\
1s^2(2P) & \to 2P^o \\
& \quad 1/2 \\
1s^2(2S) & \to 2P^o \\
& \quad 2S \\
1s^2(2P) & \to 2P^o \\
& \quad 2P \\
\textbf{Al (Z = 13), } 1 - \mu/m = 0.00002034, \ R = 3.061 \text{ fm} \\
1s^2(2S) & \to 2S \\
& \quad 1/2 \\
1s^2(2P) & \to 2P^o \\
& \quad 1/2 \\
1s^2(2S) & \to 2P^o \\
& \quad 2S \\
1s^2(2P) & \to 2P^o \\
& \quad 2P \\
\end{align*}
\]
\begin{verbatim}
Si (Z = 14), \(1 - \mu/m = 0.00001961\), \(R = 3.122\) fm
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\(1s(2S)2s2p(3P)\) & 2\(P^o\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.030983 -0.00404 0.0 0.0 0.00099 0.03588 (1) \\
\(3/2-1/2\) & 0.02894 & 0.00019 & 0.0 & 0.00004 & 0.00005 & 0.02922 (9) \\
\(1s(2S)2p^2(3P)\) & 4\(P\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.01856 -0.00586 0.0 & 0.00004 & 0.00007 & 0.0100 (3) \\
\(3/2-1/2\) & 0.03140 & -0.01164 & 0.0 & 0.0 & 0.0 & 0.00008 & 0.01984 (1) \\
\(1s(2S)2s2p(3P)\) & 2\(P^o\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.116 & 0.00000 & 0.0001 & 0.00012 & 0.00199 (1) \\
\(3/2-1/2\) & 0.04040 & 0.00009 & 0.0 & 0.00006 & 0.00006 & 0.04044 (9) \\
\(1s(2S)2p^2(1D)\) & 2\(D\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.01315 & 0.00000 & 0.00000 & 0.00000 & 0.01343 (1) \\
\(3/2-1/2\) & 0.06264 & 0.00000 & 0.00000 & 0.00000 & 0.00000 & 0.06288 (9) \\
\end{tabular}
\end{verbatim}

\begin{verbatim}
P (Z = 15), \(1 - \mu/m = 0.00001772\), \(R = 3.189\) fm
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\(1s(2S)2s2p(3P)\) & 2\(P^o\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.14981 -0.00694 0.0 0.0 0.00001 0.04451 (3) \\
\(3/2-1/2\) & 0.10914 & 0.00579 & 0.0 0.0 0.00003 & 0.10254 (13) \\
\(1s(2S)2s2p(3P)\) & 4\(P\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.07098 & 0.00000 & 0.00001 & 0.00001 & 0.07117 (17) \\
\(3/2-1/2\) & 0.05127 & -0.01370 & 0.0 & 0.00010 & 0.03767 (2) \\
\(1s(2S)2s2p(1D)\) & 2\(D\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.04159 & -0.01459 & 0.0 & 0.00001 & 0.02749 (1) \\
\(3/2-1/2\) & 0.07462 & -0.00633 & 0.0 & 0.00017 & 0.06853 (1) \\
\(1s(2S)2s2p(3P)\) & 2\(P^o\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.05519 & -0.00509 & 0.0 & 0.00008 & 0.05476 (9) \\
\(3/2-1/2\) & 0.04527 & 0.00009 & 0.0 & 0.00011 & 0.04548 (3) \\
\(1s(2S)2p^2(1S)\) & 2\(S\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.06849 & -0.01715 & 0.0 & 0.00013 & 0.05147 (3) \\
\(3/2-1/2\) & 0.03333 & -0.01256 & 0.0 & 0.00008 & 0.00014 & 0.0208 (4) \\
\(1s(2S)2s2p(1D)\) & 2\(D\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.01405 & -0.02400 & 0.0 & 0.00002 & 0.00004 & -0.0099 (6) \\
\(3/2-1/2\) & 0.05199 & -0.00509 & 0.0 & 0.00008 & 0.05476 (9) \\
\end{tabular}
\end{verbatim}

\begin{verbatim}
S (Z = 16), \(1 - \mu/m = 0.00001761\), \(R = 3.261\) fm
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\(1s(2S)2s2p(3P)\) & 2\(P^o\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.014570 -0.00864 0.0 & 0.00011 & 0.01349 (13) \\
\(3/2-1/2\) & 0.02384 & 0.00009 & 0.0 & 0.00005 & 0.00005 & 0.02398 (2) \\
\(1s(2S)2s2p(3P)\) & 4\(P\) & 2\(S\) & 1/2 & 5/2-3/2 & 0.01856 -0.00586 0.0 & 0.00004 & 0.00007 & 0.0100 (3) \\
\(3/2-1/2\) & 0.116704 -0.00441 -0.00237 & 0.00004 & 0.00007 & 0.0100 (3) \\
\end{tabular}
\end{verbatim}

\begin{verbatim}
\end{verbatim}

\end{verbatim}
sis set was increased in different directions (see Ref. [12] for details). The uncertainty of the QED energy shifts was estimated by performing a series of CI calculations with 20-30 different basis sets and 2 SMS, and the QED effects are provided. The theoretical uncertainty comes from two main sources: the Dirac-Coulomb-Breit (DCB) energy and the QED correction. The uncertainty of the DCB energies was estimated by performing a series of CI calculations with 20-30 different basis sets and

Table III presents the total theoretical energies as well as individual theoretical contributions. For each level the Dirac-Coulomb energy and corrections to it due to the Breit interaction, the normal mass shift (NMS), the specific mass shift (SMS), and the QED effects are provided. The theoretical uncertainty comes from two main sources: the Dirac-Coulomb-Breit (DCB) energy and the QED correction. The uncertainty of the DCB energies was estimated by performing a series of CI calculations with 20-30 different basis sets and by analysing consecutive increments of the results as the basis set was increased in different directions (see Ref. [12] for details). The uncertainty of the QED energy shifts was estimated on the basis of the analysis presented in Sec. III. For single energy levels, we assume the uncertainty of the QED correction to be 1%. For the energy differences, we take the smallest of the two values, 4% of the QED correction to the energy difference and the two QED uncertainties for the two states added quadratically.

For the fine-structure intervals, the QED correction and its uncertainty largely cancel in the difference, so our theoretical values are more accurate for these intervals than for the center-of-gravity energies. The remaining theoretical uncertainty is dominated by the estimated error of the DCB energies, obtained by adding quadratically the uncertainties for the two levels.

Our final theoretical results for the wavelengths of the 22 strongest 1s2l′/→1s2l transitions are summarized in Table IV The transitions are labelled from "a" to "v", following the widely used notations by Gabriel [29].

| Key | Transition | Z = 6 | Z = 7 | Z = 8 | Z = 9 | Z = 10 | Z = 11 |
|-----|------------|-------|-------|-------|-------|--------|--------|
| a   | 1s(2s)2p(2P) 2P1/2 → 1s2p2P3/2 | 41.36411 (27) 29.46580 (15) 22.04950 (10) 17.11070 (77) 13.661412 (60) 11.169775 (52) |
| b   | 1s(2s)2p(2P) 2P3/2 → 1s2p2P3/2 | 41.36230 (26) 29.46357 (15) 22.04692 (10) 17.114208 (75) 13.668325 (60) 11.166499 (51) |
| c   | 1s(2s)2p(2P) 2P1/2 → 1s2p2P3/2 | 41.36661 (25) 29.46851 (15) 22.05234 (10) 17.120020 (76) 13.674489 (60) 11.172962 (52) |
We now turn to analyzing the obtained results. We start with comparing our predictions with benchmark theoretical and experimental results available for the ground and first excited states of Li-like ions. Rigorous QED calculations to all orders in the nuclear binding strength parameter $Z_0$ were performed in Refs. [9, 26, 30], yielding the presently best theoretical results for the $1s^22s, 1s^22p_{1/2},$ and $1s^22p_{3/2}$ states of Li-like ions with $Z \geq 10$. The ionization potential of the $1s^22s$ state was not presented explicitly but can be extracted. The corresponding comparison is presented in Table VII. Excellent agreement with the results of the rigorous QED calculations confirms that we were able to keep the electron-correlation and QED effects in our calculations well under control.

Table VII presents a comparison of our predictions for the $2p_{1/2}$-$2s$ transition energies with the best theoretical and experimental data. There are remarkably many experimental results with accuracy significantly better than that of our predictions, most of them produced decades ago and summarized in Ref. [32]. The rigorous QED calculations [7] provide results only for $Z = 10$ and 15 in the region of $Z$ relevant for the present work. Because of this, we also compare our values against the MBPT results of Ref. [34] supplemented by the QED correction evaluated separately in Ref. [35]. Although these results do not have estimations of uncertainties, they reproduce the experimental data remarkably well. We observe
agreement within the estimated error bars for all cases listed in the table.

Table VII compares our theoretical results for the fine-structure splitting intervals of the $1s^2 2p^2 3P$, $1s2s2p^3 4P$, and $1s2p^2 4P^e$ states with the available experimental data. We observe that for the $1s^2 2p^2 3P$ state, the fine structure has been measured up to an accuracy significantly higher than that of our theoretical predictions. The agreement between theory and experiment is very good for $Z ≤ 13$, but for $Z = 14$-17 we observe deviations on the level of 2-3 $σ$. For the $1s2s2p^3 4P^o$ and $1s2p^2 4P^e$ fine structure, our theory is more accurate than experiment.

In Table VIII we compare our theoretical results with the experimental data on the multiplet separation center-of-gravity energies of the core-excited $P$ levels. In this case, theory and experiment are on a similar level of accuracy. The agreement is very good for $Z ≤ 10$ and deteriorates somewhat for $Z = 12$ and 13.

Finally, in Table IX we present a comparison of theoretical and experimental results for the center-of-gravity energies of different levels relative to the ground state. In this case the accuracy of our theory is significantly higher than that of the experimental data. The agreement is good in the case of carbon. For higher-$Z$ ions, however, we observe numerous devi-

### Table VI: Comparison of theory and experiment for the $2p_{1/2} - 2s$ transition energy, in a.u.

| $Z$ | This work | Other theory | Experiment |
|-----|-----------|--------------|------------|
| 6   | 0.29380 (5) | 0.293811 (5) | a          |
| 7   | 0.36660 (6) | 0.366616 (5) | a          |
| 8   | 0.43909 (6) | 0.4391117 (5)| a          |
| 9   | 0.51147 (6) | 0.511501 (a) |            |
| 10  | 0.58385 (7) | 0.5838901 (a)|            |
| 11  | 0.65637 (9) | 0.656401 (a) |            |
| 12  | 0.72903 (9) | 0.729071 (a) |            |
| 13  | 0.80189 (12)| 0.801971 (a) |            |
| 14  | 0.87502 (13)| 0.875091 (a) |            |
| 15  | 0.94847 (14)| 0.948495 (a) |            |
| 16  | 1.02224 (16)| 1.022323 (a) | a          |
| 17  | 1.09640 (19)| 1.096538 (a) | a          |

- a Ref. [32].
- b Ref. [32].
- c MBPT results from Ref. [34] and QED results from Ref. [35].
- d Ref. [7].
TABLE VIII: Comparison of theory and experiment for the center-of-gravity multiplet separation wavelengths, in Å.

| Z   | This work | Experiment | Ref. |
|-----|-----------|------------|------|
| 6   | 1344.41 (21) | 1344.2 (3) | 36   |
| 7   | 1110.94 (15) | 1111.1 (1) | 36   |
| 8   | 945.87 (11) | 946.8 (1)  | 36   |
| 9   | 822.54 (9)  | 822.47 (8) | 38   |
| 10  | 726.62 (8)  | 726.51 (5) | 39   |
| 12  | 586.24 (8)  | 586.04 (5) | 41   |
| 13  | 533.03 (7)  | 532.83 (9) | 43   |

1s2s2p (1p⁰)⁰2p⁰ - 1s2s2p (3p⁰)⁰2p⁰

| Z   | This work | Experiment | Ref. |
|-----|-----------|------------|------|
| 6   | 3592.6 (6) | 3582.4 (4) | 44   |

Using specially balanced basis sets, we were able to improve the convergence of our results and enhance the numerical accuracy of the calculated energy levels by up to two orders of magnitude compared to that for the standard basis. The uncertainty of the Dirac-Coulomb-Breit energies was evaluated by analysing the convergence of the results with respect to the number of partial waves included and the size of the one-electron basis.

The relativistic energies were supplemented with the QED energy shifts. To this end, the model QED operator approach as implemented by the QEDMOD package was used. In order to cover the range of the nuclear charge numbers Z aimed at in the present work, we extended the QEDMOD package (originally limited to Z ≤ 10) to the lower values of Z. The uncertainty estimation of the QED energy shifts was based on the comparison with results of rigorous QED calculations available for the ground and first excited states of Li-like ions.

The main result of the present work is the tabulation of theoretical energy levels and transition wavelengths for the 1s²2l and 1s2l2l' states of ions along the lithium isoelectronic sequence from carbon to chlorine. All our theoretical predictions are supplied with uncertainties that include estimations of effects omitted in the theoretical treatment. For the 1s²2l states, our results agree well with the benchmark theoretical and experimental results available in the literature. For the core-excited 1s2l2l' energy levels, our theory is an order of magnitude more accurate than the measurements performed.

Conclusion

We performed extensive relativistic calculations of the energy levels and the fine-structure splitting of the n = 2 valence and core-excited states of Li-like ions. The Dirac-Coulomb-Breit energies were obtained by the configuration-interaction method adapted for treatment of autoionizing core-excited states. By using specially balanced basis sets, we were able to improve the convergence of our results and enhance the numerical accuracy of the calculated energy levels by up to two orders of magnitude compared to that for the standard basis. The uncertainty of the Dirac-Coulomb-Breit energies was evaluated by analysing the convergence of the results with respect to the number of partial waves included and the size of the one-electron basis.

The relativistic energies were supplemented with the QED energy shifts. To this end, the model QED operator approach as implemented by the QEDMOD package was used. In order to cover the range of the nuclear charge numbers Z aimed at in the present work, we extended the QEDMOD package (originally limited to Z ≤ 10) to the lower values of Z. The uncertainty estimation of the QED energy shifts was based on the comparison with results of rigorous QED calculations available for the ground and first excited states of Li-like ions.

The main result of the present work is the tabulation of theoretical energy levels and transition wavelengths for the 1s²2l and 1s2l2l' states of ions along the lithium isoelectronic sequence from carbon to chlorine. All our theoretical predictions are supplied with uncertainties that include estimations of effects omitted in the theoretical treatment. For the 1s²2l states, our results agree well with the benchmark theoretical and experimental results available in the literature. For the core-excited 1s2l2l' energy levels, our theory is an order of magnitude more accurate than the measurements performed.

TABLE IX: Comparison of theory and experiment for the center-of-gravity level energies, relative to the ground (1s)² 2s state, in eV.

| Z   | State          | This work | Experiment | Ref. |
|-----|----------------|-----------|------------|------|
| 6   | 1s2s²2S        | 291.59 (8) | 291.59 (10) | 35^a |
| 1s2s2p (3p⁰)²2p⁰ | 299.966 (1)| 299.98 (3)  | 44   |
| 1s2s2p (1p⁰)²2p⁰ | 303.418 (5)| 303.44 (3)  | 44   |
| 1s2p²2D        | 306.489 (4) | 306.54 (5)  | 45^a |
| 1s2p²2S        | 312.62 (1)  | 312.67 (5)  | 45^a |
| 7   | 1s2s2p (3p⁰)²2p⁰/2 | 421.284 (2)| 421.52 (5)  | 48   |
| 1s2s2p (1p⁰)²2p⁰ | 421.276 (2)| 421.47 (3)  | 49   |
| 1s2p²2D        | 429.215 (5) | 429.07 (13)| 46^a |
| 1s2p²2S        | 436.675 (10)| 436.61 (10)| 46^a |
| 8   | 1s2s²2S        | 550.699 (8)| 550.79 (8)  | 46^a |
| 1s2s2p (3p⁰)²2p⁰ | 563.064 (2)| 562.93 (8)  | 46^a |
| 1s2s2p (1p⁰)²2p⁰ | 567.720 (5)| 567.50 (15)| 46^a |
| 1s2p²2D        | 572.421 (5) | 572.43 (8)  | 46^a |
| 1s2p²2S        | 581.21 (1)  | 581.04 (8)  | 46^a |
| 10  | 1s2s²2S       | 891.72 (1) | 891.52 (10)| 52   |
| 1s2s2p (3p⁰)⁰4p⁰ | 896.098 (4)| 895.98 (4)  | 52   |
| 1s2s2p (3p⁰)²4p⁰ | 908.152 (4)| 907.90 (9)  | 52   |
| 1s2p²3P⁰⁰        | 913.161 (3)| 913.05 (4)  | 52   |
| 1s2s2p (3p⁰)³2p⁰ | 914.007 (5)| 913.91 (20)| 52   |
| 1s2p²2D        | 920.39 (1)  | 920.38 (6)  | 52   |
| 1s2p²2S        | 931.82 (1)  | 932.19 (27)| 52   |

^a the statistical uncertainty as given in Table IV of Ref. [45] is added quadratically to the energy scale uncertainty of 0.05 eV mentioned in the text.

^a using the ionization energy of the ground state of the corresponding ion from Table III.

so far, which opens possibilities for using theoretical predictions for calibrating experimental X-ray and electron spectra.

Acknowledgement

V.A.Y. acknowledges support by the Ministry of Education and Science of the Russian Federation Grant No. 3.5397.2017/6.7.
