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Calculations of relativistic, correlation, nuclear and quantum-electrodynamics corrections to the energies and ionization potentials of the ground state of lithium-like ions

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This paper presents all the leading contributions to the relativistic binding energies and ionization potentials of the ground state of lithium-like ions with a nuclear charge in the range $Z = 3 - 20$. Correlation, relativistic and quantum-electrodynamics corrections as well as the contributions due to the finite size of the nucleus (the field shift) and finite mass of the nucleus (the recoil effect) are evaluated. Relativistic calculations are performed by means of the configuration-interaction method in the basis of the Dirac-Fock-Sturm orbitals using the Dirac-Coulomb-Breit Hamiltonian.

Keywords: Li-like ions, ionization potential, relativistic calculations, configuration interaction, electron correlations, Breit interaction, field shift, nuclear recoil effect, QED corrections

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1. Introduction

The lithium (Li) atom and lithium-like ions represent one of the simplest atomic systems whose various characteristics can be calculated with a high degree of accuracy for both the ground and excited states. The joint use of theoretical and experimental data for Li-like ions makes it possible to obtain precise values of magnetic dipole and electric quadrupole moments for various isotopes, to test bound-state quantum electrodynamics, etc. To date, a large number of high-precision nonrelativistic calculations of the ground state $(1s^2 2s)$ have been performed, for example, in the works [1,2] for the lithium atom and [3] for Li-like ions. The works [4–6] present compact interpolation formulas for the non-relativistic energy of Li-like ions as a function of charge Z in the range $Z = 3 - 20$. Relativistic calculations of the binding energies and ionization potentials for the ground state of the Li atom and Li-like ions, taking into account the finite size of the nucleus (the field shift), the finite mass of the nucleus (the nuclear recoil effect), the frequency-dependent Breit interaction, and quantum electrodynamic (QED) corrections, are much more difficult problem. Relativistic calculations of the total binding energy of the Li atom were made in the works [7–9]. The ionization potential for the Li atom was calculated, for example, in the work [10]. The relativistic total energies of Li-like ions were evaluated for the following nuclear charges: $Z = 3 - 10$ [7], $Z = 10 - 92$ [11], $Z =$20, 40, 60, 74, 83, 92 [12]. Relativistic calculations of ionization potentials were performed in the works: in [7] for $Z = 3 - 10$, in [13] for $Z =$ 10, 18, 50, in [12] for $Z = 10 - 100$, in [14] for $Z = 6 = 17$ and in [9] for $Z = 3 - 10$. In addition, high-precision QED calculations of the energies of the $n = 2$ transitions in Li-like ions in a wide range of nuclear charge numbers were performed, for example, in the works [12,15,16].

Despite the fact that a large number of different relativistic calculations of Li-like ions have been undertaken so far, the reliable systematic data on the individual contributions to the total binding energies and ionization potentials for each value of Z in the interval $Z = 3 - 20$ are absent. In the works listed above, these contributions are either not given or obtained for individual values of Z that do not completely cover the interval $Z = 3 - 20$. In this present work, the relativistic calculations of the total binding energies and ionization potentials for $Z = 3 - 20$ are performed. The individual contributions are also calculated, namely nonrelativistic energies in the framework of the Hartree-Fock method, non-relativistic correlation contributions, relativistic corrections, corrections due to the finite size of the nucleus, contributions from the nuclear recoil, QED corrections, contributions associated with the frequency dependence of the Breit interaction. All the listed corrections to the nonrelativistic energy are presented in a convenient form, which makes it possible to get an idea of their absolute magnitude and dependence on the nuclear charge. Similar data in the same range of Z values were obtained by us earlier for He-like ions [17]. In the present work, these data for He-like ions are used to calculate the

ionization potentials for Li-like ions as well as the individual contributions to the corresponding values.

In this work, the calculations are based on the relativistic Dirac-Coulomb-Breit Hamiltonian (DCB-Hamiltonian). To calculate the total binding energy of the ground state of three-electron ions and to separate the individual contributions, the Hartree-Fock (HF), the Dirac-Fock (DF) and the configuration interaction (CI) methods are employed. The CI method is implemented in the basis of the Dirac-Fock-Sturm (DFS) orbitals [18,19] using the concept of restricted active space (RAS) [20]. Nonrelativistic and relativistic calculations are performed using the same one-electron basis and the same configuration space in order to improve the accuracy of separating the individual contributions to the total energy. The division of the ionization potentials into the separate contributions is also presented. We note that all the above corrections to the ground-state ionization potentials were presented earlier in the work [14], however, in a narrower range of Z.

This article is organized as follows. Sect. 2 gives a brief description of the theoretical methods and approaches. The calculation results are presented in detail in Sect. 3. The Hartree atomic units are used ($\hbar = e = m = 1$).

2. Theory. Description of the calculation method

Let us briefly describe the calculation methods. A more detailed presentation can be found in our work [17], where the energies of the $1s^2$ ground state of helium-like ions were calculated.

The relativistic calculations in this work are performed using the Dirac-Coulomb-Breit Hamiltonian [21–23]

$$\hat{H}_{\mathrm{DCB}} = \Lambda_+ \left[\hat{H}_{\mathrm{D}} + \hat{H}_{\mathrm{C}} + \hat{H}_{\mathrm{B}}\right] \Lambda_+. \tag{1}$$

Here $\hat{H}_{\mathrm{D}} = \sum_i^N \hat{h}_{\mathrm{D}}(i)$ is the sum of the one-electron four-component Dirac Hamiltonians for $N = 3$ electrons,

$$\hat{h}_{\mathrm{D}}(i) = c\left(\boldsymbol{\alpha}_i \cdot \hat{\boldsymbol{p}}_i\right) + c^2(\beta_i - 1) + V_{\mathrm{n}}(r_i), \tag{2}$$

where c is the speed of light, $\hat{\boldsymbol{p}} = -i\boldsymbol{\nabla}$ is the momentum operator, $\boldsymbol{\alpha}$ and β are the Dirac matrices, $V_{\mathrm{n}}(r)$ is the potential of the nucleus. The operators $\hat{H}_{\mathrm{C}}$ and $\hat{H}_{\mathrm{B}}$ in (1) correspond to the Coulomb repulsion operator and the frequency-independent Breit operator in the Coulomb gauge, respectively,

$$\hat{H}_{\mathrm{C}} = \frac{1}{2}\sum_{i\neq j}^{N} \frac{1}{r_{ij}}, \tag{3}$$

$$\hat{H}_{\mathrm{B}} = \frac{1}{2}\sum_{i\neq j}^{N} B_{ij}(0) \equiv \frac{1}{2}\sum_{i\neq j}^{N} \frac{1}{r_{ij}}\Bigg[-\left(\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j\right) - \frac{1}{2}\left(\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i\right)\left(\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j\right) r_{ij}\Bigg], \tag{4}$$

where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. The operator Λ_+ is the product of one-electron projectors on the space of the positive-energy eigenfunctions of some single-particle Hamiltonian, which is chosen to be the Dirac-Fock operator $\hat{h}_{\mathrm{DF}}$ in this work. The correction for the dependence of the Breit operator on the photon frequency in the Coulomb gauge can be written in the form [24,25]

$$\Delta B_{ij}(\omega) = B_{ij}(\omega) - B_{ij}(0), \tag{5}$$

where

$$B_{ij}(\omega) = -\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j \frac{\cos(\omega r_{ij})}{r_{ij}} + \left(\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i\right)\left(\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j\right) \frac{\cos(\omega r_{ij}) - 1}{\omega^2 r_{ij}}. \tag{6}$$

The two-electron matrix elements of the operator $B(\omega)$ are calculated using the formula [26]

$$\langle ab|B(\omega)|cd\rangle = \frac{1}{2}\left[\langle ab|B(\omega_{ac})|cd\rangle + \langle ab|B(\omega_{bd})|cd\rangle\right], \tag{7}$$

where the indices a, b, c, d enumerate the one-electron orbitals and their energies ε, and the frequencies in formula (7) are determined by the expressions $\omega_{ac} = |\varepsilon_a - \varepsilon_c|/c$ and $\omega_{bd} = |\varepsilon_b - \varepsilon_d|/c$.

In this work, the CI method for searching for the many-electron wave function Ψ of the ground state of a lithium-like ion in the DCB approximation is implemented in the basis of the DFS orbitals [18,19,27]. The advantage of choosing this basis is that all the DFS orbitals have approximately the same size as well as the same asymptotics at the infinity. In the calculations performed in this work, all single, double, and partially triple excitations from the ground-state configuration of Li-like ions were taken into account.

In order to take into account the finite size of the nucleus (the field shift), the model of the uniformly charged sphere is used in this work. The sphere radius is related to the root-mean-square (RMS) nucleus radius $\langle R^2\rangle^{1/2}$ by $R_{\mathrm{sph}} = \sqrt{5/3}\,\langle R^2\rangle^{1/2}$. The correction due to the finite size of the nucleus is determined as the difference between the total energies obtained in two calculations: in the first of them, the potential of the uniformly charged sphere is used as the potential of the nucleus $V_{\mathrm{n}}(r)$, in the second one, the potential of the point nucleus is used, $-Z/r$.

The relativistic mass shift operator $\hat{H}_{\mathrm{MS}}$ [18,28–30] is used to take into account the contribution of the nuclear recoil in the first order with respect to the electron-to-nucleus mass ration m/M. The mass shift value is calculated as the average value of this operator using the many-electron wave function Ψ obtained by the CI method.

Finally, the QED corrections in this work are taken into account using the model-QED operator proposed in [31]. The program code for generating the operator can be found in the works [32,33]. The quantum-electrodynamics contribution is defined as the difference between the two

total energies of the ground state of Li-like ions obtained within the CI method. In the first case, a model operator was added to the DCB Hamiltonian and was also used to define the Λ_+ projectors [34]. In the second case, QED operator was not taken into account.

3. Calculation results and discussion

In this work, variational calculations of the ground-state energy of lithium-like ions are performed in the range of nuclear charge $Z = 3 - 20$ both in nonrelativistic and relativistic approximations. In the latter case, the value of the speed of light $c = 137.035\,999\,139$ [35] is used. In all the calculations, a one-electron basis set is used, which includes the DFS orbitals up to the values of the orbital quantum number $l_{\max} = 5$ and the principal quantum number $n_{\max} = 30$. The study of the convergence of the obtained results with respect to the size of the basis set revealed that this basis is optimal for obtaining the energies with the accuracy required for the purposes of the present work. In addition, the results have been extrapolated to $l_{\max} \to \infty$, the discussion of the corresponding procedure can be found in [36].

Table 1 presents the results of the nonrelativistic calculations of the total binding energies of Li-like ions for the point-nucleus model. The second column of the table shows the energy $E_{\rm HF}$ obtained in the Hartree-Fock approximation. The third column shows the value of the nonrelativistic correlation correction, $\Delta^{\rm nr}_{\rm corr} = E^{\rm nr} - E_{\rm HF}$, which was calculated as the difference between the energies obtained by the CI method ($E^{\rm nr}$) and the HF method ($E_{\rm HF}$). The values of the total nonrelativistic energies $E^{\rm nr}$ obtained in this work are collected in the fourth column. For comparison, the fifth column gives the nonrelativistic total energies of Li-like ions from [3], which have been rounded to five significant digits after the decimal point in atomic units. The nonrelativistic values of the ground-state energy of Li-like ions obtained in this work demonstrate good agreement with the results of the high-precision calculations. This comparison allows us to estimate the absolute error of our calculations based on the nonrelativistic Schrödinger Hamiltonian as a value of the order of 0.000 01 a.u.

Table 2 presents various corrections to the nonrelativistic energy $E^{\rm nr}$ of the ground state, which were obtained using the DCB Hamiltonian. The second column of Table 2 gives the values of root-mean-square nuclear radii in the Fermi units [37]. The third column shows the relativistic correction $\Delta_{\rm DF}$ to the Hartree-Fock energy $E_{\rm HF}$. It is calculated as the difference between the energies obtained by the relativistic DF method and the nonrelativistic HF method, $\Delta_{\rm DF} = E_{\rm DF} - E_{\rm HF}$. The fourth column shows the relativistic correction $\Delta^{\rm rel\text{-}nr}_{\rm corr}$ to the correlation energy $\Delta^{\rm nr}_{\rm corr}$ from Table 1. Here, by the relativistic correlation energy we mean the difference between the energy $E^{\rm rel}_{\rm DC}$ calculated by the CI method using the Dirac-Coulomb Hamiltonian (that is, the Hamiltonian (1) without the operator $\hat{H}_B$), and the Dirac-Fock energy $E_{\rm DF}$, $\Delta^{\rm rel}_{\rm corr} = E^{\rm rel}_{\rm DC} - E_{\rm DF}$. Therefore, the relativistic correction to the correlation energy is $\Delta^{\rm rel\text{-}nr}_{\rm corr} = \Delta^{\rm rel}_{\rm corr} - \Delta^{\rm nr}_{\rm corr}$. This correction can also be expressed in the form $\Delta^{\rm rel\text{-}nr}_{\rm corr} = (E^{\rm rel}_{\rm DC} - E^{\rm nr}) - \Delta_{\rm DF}$. The next column shows the value of the Breit correction $\Delta_{\rm Breit}$, defined as the difference between the two energies calculated by the CI method with and without the Breit interaction (4), i.e., $\Delta_{\rm Breit} = E^{\rm rel}_{\rm DCB} - E^{\rm rel}_{\rm DC}$. All the corrections listed above, $\Delta_{\rm DF}$, $\Delta^{\rm rel\text{-}nr}_{\rm corr}$ and $\Delta_{\rm Breit}$, are calculated for the point-nucleus model, [p.n.]. The sixth column in Table 2 shows the total relativistic correction to the nonrelativistic energy $E^{\rm nr}$[p.n.] of the ground state of Li-like ions for the point nucleus, $\Delta^{\rm rel}_{\rm DCB}$[p.n.] $= E^{\rm rel}_{\rm DCB}$[p.n.] $-$ E$^{\rm nr}$[p.n.]. This correction is the sum of the contributions $\Delta_{\rm DF}$, $\Delta^{\rm rel\text{-}nr}_{\rm corr}$ and $\Delta_{\rm Breit}$. The penultimate column shows the value of the field shift $\Delta_{\rm FNS}$. This contribution is defined as the difference between the energies calculated by the relativistic CI method with and without the allowance for the finite size of the nucleus. Therefore, $\Delta_{\rm FNS} = E^{\rm rel}_{\rm DCB}$[f.n.] $- E^{\rm rel}_{\rm DCB}$[p.n.]. Finally, the last column in Table 2 gives the total correction $\Delta^{\rm rel}_{\rm DCB}$[f.n.] to the nonrelativistic energy $E^{\rm nr}$[p.n.] taking into account the effect associated with the finite size of the nucleus. This correction is equal to $\Delta^{\rm rel}_{\rm DCB}$[f.n.] $= E^{\rm rel}_{\rm DCB}$[f.n.] $- E^{\rm nr}$[p.n.], or else it can be expressed as $\Delta^{\rm rel}_{\rm DCB}$[f.n.] $= \Delta^{\rm rel}_{\rm DCB}$[p.n.] $+ \Delta_{\rm FNS}$.

The values of the relativistic binding energy $E^{\rm rel}_{\rm DCB}$[f.n.], obtained by the CI method using the DCB Hamiltonian,

Table 1. Nonrelativistic energy of the ground state of lithium-like ions with the nuclear charge $Z = 3 - 20$, the point-nucleus model is used. $E_{\rm HF}$ is the Hartree-Fock energy, $\Delta^{\rm nr}_{\rm corr}$ is the correlation energy, $E^{\rm nr} = E_{\rm HF} + \Delta^{\rm nr}_{\rm corr}$ is the total energy obtained by the nonrelativistic configuration interaction method. All values are given in atomic units

Z	$E_{\rm HF}$	$\Delta^{\rm nr}_{\rm corr}$	$E^{\rm nr}$	
			this study	[3]
3	−7.43273	−0.04533	−7.47806	−7.47806
4	−14.27740	−0.04736	−14.32476	−14.32476
5	−23.37599	−0.04861	−23.42460	−23.42461
6	−34.72606	−0.04945	−34.77551	−34.77551
7	−48.32685	−0.05004	−48.37689	−48.37690
8	−64.17805	−0.05049	−64.22854	−64.22854
9	−82.27949	−0.05084	−82.33033	−82.33034
10	−102.63111	−0.05112	−102.68223	−102.68223
11	−125.23284	−0.05135	−125.28419	−125.28419
12	−150.08466	−0.05153	−150.13619	−150.13620
13	−177.18654	−0.05170	−177.23823	−177.23824
14	−206.53846	−0.05183	−206.59030	−206.59030
15	−238.14043	−0.05195	−238.19238	−238.19239
16	−271.99243	−0.05206	−272.04448	−272.04449
17	−308.09445	−0.05215	−308.14660	−308.14660
18	−346.44649	−0.05223	−346.49872	−346.49873
19	−387.04855	−0.05230	−387.10085	−387.10086
20	−429.90062	−0.05237	−429.95299	−429.95300

Note. The data from the work [3] are rounded to five significant digits after the decimal point.

Table 2. Corrections to the nonrelativistic energy $E^{\rm nr}$ of the ground state of lithium-like ions with the nuclear charge $Z = 3 - 20$. RMS is the root-mean-square radius of the nucleus expressed in fermi [37]. $\Delta_{\rm DF}$ is the relativistic correction to the Hartree-Fock energy $E_{\rm HF}$, $\Delta_{\rm corr}^{\rm rel\text{-}nr}$ is the relativistic correction to the correlation energy $\Delta_{\rm corr}^{\rm nr}$ (without contribution from the Breit interaction), $\Delta_{\rm Breit}$ is the contribution from the Breit interaction, $\Delta_{\rm DCB}^{\rm rel}[\text{p.n.}] = \Delta_{\rm DF} + \Delta_{\rm corr}^{\rm rel\text{-}nr} + \Delta_{\rm Breit}$. Corrections $\Delta_{\rm DF}$, $\Delta_{\rm corr}^{\rm rel\text{-}nr}$ and $\Delta_{\rm Breit}$ are calculated for the point nucleus. $\Delta_{\rm FNS}$ is the correction due to the finite nuclear size, $\Delta_{\rm DCB}^{\rm rel}[\text{f.n.}] = \Delta_{\rm DCB}^{\rm rel}[\text{p.n.}] + \Delta_{\rm FNS}$. All values of the corrections are given in atomic units

Z	RMS	$\Delta_{\rm DF}$	$\Delta_{\rm corr}^{\rm rel\text{-}nr}$	$\Delta_{\rm Breit}$	$\Delta_{\rm DCB}^{\rm rel}$[p.n.]	$\Delta_{\rm FNS}$	$\Delta_{\rm DCB}^{\rm rel}$[f.n.]
3	2.4440	−0.00081	0.00000	0.00017	−0.00063	0.00000	−0.00063
4	2.5190	−0.00282	0.00001	0.00050	−0.00231	0.00000	−0.00231
5	2.4060	−0.00734	0.00002	0.00111	−0.00622	0.00000	−0.00621
6	2.4702	−0.01590	0.00003	0.00209	−0.01379	0.00000	−0.01379
7	2.5582	−0.03042	0.00004	0.00353	−0.02686	0.00001	−0.02685
8	2.6991	−0.05317	0.00005	0.00551	−0.04762	0.00001	−0.04760
9	2.8976	−0.08682	0.00006	0.00813	−0.07863	0.00003	−0.07861
10	3.0055	−0.13440	0.00007	0.01148	−0.12286	0.00004	−0.12282
11	2.9936	−0.19934	0.00008	0.01564	−0.18363	0.00007	−0.18356
12	3.0570	−0.28544	0.00009	0.02070	−0.26465	0.00010	−0.26455
13	3.0610	−0.39688	0.00010	0.02676	−0.37002	0.00014	−0.36989
14	3.1224	−0.53825	0.00011	0.03390	−0.50424	0.00019	−0.50406
15	3.1889	−0.71453	0.00012	0.04222	−0.67219	0.00027	−0.67192
16	3.2611	−0.93108	0.00013	0.05180	−0.87914	0.00037	−0.87878
17	3.3654	−1.19368	0.00014	0.06274	−1.13080	0.00051	−1.13029
18	3.4274	−1.50851	0.00015	0.07513	−1.43324	0.00067	−1.43256
19	3.4349	−1.88218	0.00015	0.08906	−1.79297	0.00085	−1.79211
20	3.4776	−2.32169	0.00016	0.10462	−2.21691	0.00109	−2.21582

Table 3. Ground state binding energy of lithium-like ions with the nuclear charge $Z = 3 - 20$, A is the mass number. $E^{\rm nr}$[p.n.] is the non-relativistic energy calculated by the configuration interaction method for the point-nucleus model; $\Delta_{\rm DCB}^{\rm rel}$[f.n.] is the relativistic correction which takes into account the contribution of the Breit interaction and the field shift; $E_{\rm DCB}^{\rm rel}[\text{f.n.}] = E^{\rm nr}[\text{p.n.}] + \Delta_{\rm DCB}^{\rm rel}[\text{f.n.}]$ is the total relativistic energy calculated by the configuration interaction method using the Dirac-Coulomb-Breit Hamiltonian and the uniformly-charged-sphere model for the nuclear density; Δ_ω is correction due to the frequency dependence of the Breit interaction; $\Delta_{\rm MS}$ is the nuclear-recoil correction; $\Delta_{\rm QED}$ is the correction due to the QED effects; $E_{\rm tot} = E_{\rm DCB}^{\rm rel} + \Delta_\omega + \Delta_{\rm MS} + \Delta_{\rm QED}$ is the total binding energy of the ground state, taking into account all the above listed corrections. All values are given in atomic units

Z	A	$E^{\rm nr}$[p.n.]	$\Delta_{\rm DCB}^{\rm rel}$[f.n.]	$E_{\rm DCB}^{\rm rel}$[f.n.]	Δ_ω	$\Delta_{\rm MS}$	$\Delta_{\rm QED}$	$E_{\rm tot}$	$E_{\rm tot}$
3	7	−7.47806	−0.00063	−7.47869	0.00000	0.00061	0.00012	−7.47797	
4	9	−14.32476	−0.00231	−14.32707	0.00000	0.00090	0.00035	−14.32582	
5	11	−23.42460	−0.00621	−23.43082	0.00000	0.00120	0.00083	−23.42879	
6	12	−34.77551	−0.01379	−34.78929	0.00000	0.00163	0.00164	−34.78604	
7	14	−48.37689	−0.02685	−48.40375	0.00000	0.00193	0.00290	−48.39892	
8	16	−64.22854	−0.04760	−64.27614	−0.00001	0.00224	0.00472	−64.26918	
9	19	−82.33033	−0.07861	−82.40894	−0.00001	0.00241	0.00725	−82.39929	
10	20	−102.68223	−0.12282	−102.80504	−0.00001	0.00286	0.01060	−102.79160	−102.79472[b]
11	23	−125.28419	−0.18356	−125.46775	−0.00002	0.00303	0.01492	−125.44982	
12	24	−150.13619	−0.26455	−150.40074	−0.00003	0.00347	0.02034	−150.37696	
13	27	−177.23823	−0.36989	−177.60812	−0.00004	0.00364	0.02701	−177.57751	
14	28	−206.59030	−0.50405	−207.09434	−0.00005	0.00409	0.03506	−207.05524	
15	31	−238.19238	−0.67192	−238.86430	−0.00006	0.00426	0.04466	−238.81544	−238.81573[a]
									−238.82049[b]
16	32	−272.04448	−0.87878	−272.92326	−0.00008	0.00471	0.05596	−272.86267	−272.86285[a]
17	35	−308.14660	−1.13029	−309.27689	−0.00010	0.00487	0.06909	−309.20302	−309.20310[a]
18	40	−346.49872	−1.43256	−347.93128	−0.00012	0.00479	0.08423	−347.84238	−347.84235[a]
19	39	−387.10085	−1.79211	−388.89297	−0.00014	0.00549	0.10152	−388.78610	−388.78596[a]
20	40	−429.95299	−2.21582	−432.16881	−0.00017	0.00594	0.12111	−432.04192	−432.04166[a]
									−432.04940[b]

Note. [a] Indelicato, Desclaux [40]. [b] Chen *et al.* [11].

Table 4. Ionization potentials for the ground state of lithium-like ions with the nuclear charge $Z = 3 - 20$ (excluding the QED contributions and the nuclear recoil corrections). $IP^{nr} = IP_{HF} + \delta^{nr}_{corr}$ is the ionization potential for the point nucleus obtained within the framework of the nonrelativistic configuration interaction method, where IP_{HF} is the ionization potential in the Hartree-Fock approximation; δ^{nr}_{corr} is the nonrelativistic correlation contribution; δ_{DF} is the relativistic correction to the ionization potential in the Hartree-Fock approximation, IP_{HF}; $\delta^{rel\text{-}nr}_{corr}$ is the relativistic correction to the correlation contribution δ^{nr}_{corr} (disregarding the Breit interaction); δ_{Breit} is the contribution of the Breit interaction. The corrections δ_{DF}, $\delta^{rel\text{-}nr}_{corr}$ and δ_{Breit} are calculated for the point-nucleus model, δ_{FNS} is the correction due to the finite nuclear size, $IP^{rel}_{DCB} = IP^{nr} + \delta_{DF} + \delta^{rel\text{-}nr}_{corr} + \delta_{Breit} + \delta_{FNS}$ is the relativistic ionization potential for the extended nucleus, obtained on the basis of the Dirac-Coulomb-Breit Hamiltonian. All values are given in atomic units

Z	IP^{nr}	δ_{DF}	$\delta^{rel\text{-}nr}_{corr}$	δ_{Breit}	δ_{FNS}	IP^{rel}_{DCB}	IP^{rel}_{DCB}
3	0.19815	0.00002	−0.00001	−0.00001	0.00000	0.19815	0.19809[b]
4	0.66919	0.00012	−0.00001	−0.00003	0.00000	0.66928	0.66923[b]
5	1.39363	0.00043	−0.00001	−0.00007	0.00000	1.39399	1.39396[b]
6	2.36926	0.00111	0.00000	−0.00013	0.00000	2.37024	2.37026[a]
							2.37022[b]
7	3.59545	0.00238	0.00000	−0.00023	0.00000	3.59760	3.59763[a]
							3.59760[b]
8	5.07194	0.00452	0.00000	−0.00037	0.00000	5.07609	5.07612[a]
							5.07610[b]
9	6.79862	0.00784	0.00000	−0.00057	0.00000	6.80590	6.80594[a]
							6.80591[b]
10	8.77542	0.01272	0.00000	−0.00082	0.00000	8.78732	8.78737[a]
							8.78733[b]
11	11.00230	0.01957	0.00000	−0.00114	0.00000	11.02074	11.02081[a]
							11.02076[b]
12	13.47924	0.02888	0.00000	−0.00153	−0.00001	13.50659	13.50668[a]
13	16.20623	0.04116	0.00001	−0.00201	−0.00001	16.24538	16.24549[a]
							16.24541[b]
14	19.18325	0.05701	0.00001	−0.00258	−0.00001	19.23767	19.23780[a]
15	22.41029	0.07704	0.00001	−0.00325	−0.00001	22.48408	22.48423[a]
							22.48410[b]
16	25.88736	0.10195	0.00001	−0.00402	−0.00002	25.98528	25.98545[a]
17	29.61444	0.13247	0.00002	−0.00491	−0.00003	29.74199	29.74219[a]
							29.74201[b]
18	33.59154	0.16941	0.00002	−0.00593	−0.00003	33.75500	
19	37.81864	0.21361	0.00002	−0.00708	−0.00004	38.02516	
20	42.29576	0.26598	0.00003	−0.00836	−0.00006	42.55335	42.55334[b]

Note. [a] Yerokhin *et al.* [14]. [b] Johnson *et al.* [43]. The data from the work [43] are given taking into account the frequency dependence of the Breit interaction.

are presented in the fifth column of Table 3. This energy can be expressed as the sum of the nonrelativistic energy E^{nr}[p.n.] and the total relativistic correction from Table 2, i.e., E^{rel}_{DCB}[f.n.] = E^{nr}[p.n.] + Δ^{rel}_{DCB}[f.n.]. For convenience, in the third and fourth columns of Table 3, the nonrelativistic energies E^{nr}[p.n.] and the corrections Δ^{rel}_{DCB}[f.n.] are shown once again. In addition, it is also necessary to take into account the frequency-dependence of the Breit interaction in the Coulomb gauge (Δ_ω), the nuclear recoil effect (Δ_{MS}), and the QED correction (Δ_{QED}). The values of the corresponding contributions are presented in the sixth, seventh, and eighth columns of Table 3, respectively. The isotope for each ion is listed in the second column. The isotope masses needed to calculate the mass shift Δ_{MS} are taken from the compilation [38] in accordance with [39]. The penultimate column of Table 3 shows the total relativistic energies, $E_{tot} = E^{rel}_{DCB}$[f.n.] + Δ_ω + Δ_{MS} + Δ_{QED}. The dominant uncertainty for the obtained energy values is determined by the approximation used to calculate the QED contributions, and, in particular, by the unaccounted higher-order radiative corrections. The last column of Table 3 shows the total energies of the ground state of Li-like ions taken from the papers [11,40]. Our values for E_{tot} demonstrate good agreement with the results of the previous calculations.

In addition, the calculations of the ionization potentials (IP) for the ground state of lithium-like ions were performed. The ionization potential can be obtained as the difference between the binding energies of the $1s^2$ state of the He-like ion and the $1s^22s$ state of the corresponding Li-like ion. The energies of He-like ions, as well as the individual contributions to them, are taken from our previous work [17].

In Table 4, the second column shows the values of the nonrelativistic ionization potentials for the ground state of lithium-like ions, IP^{nr}[p.n.] = $E^{nr}_{1s^2}$[p.n.] − E^{nr}[p.n.],

Table 5. Ionization potentials for the ground state of lithium-like ions with the nuclear charge $Z = 3 - 20$. IP^{rel}_{DCB} is the relativistic ionization potential for the extended nucleus obtained from the DCB Hamiltonian; δ_ω is the correction due to the frequency-dependence of the Breit interaction, δ_{MS} is the nuclear recoil correction, δ_{QED} is the correction due to the quantum-electrodynamics effects; $IP_{tot} = IP^{rel}_{DCB} + \delta_\omega + \delta_{MS} + \delta_{QED}$ is the total ground-state ionization potential. All values are given in atomic units

Z	IP^{rel}_{DCB}	δ_ω	δ_{MS}	δ_{QED}	IP_{tot}	IP_{tot}
3	0.19815	0.00000	−0.00002	0.00000	0.19813	0.19816[b]
						0.19814[c]
						0.19805[d]
4	0.66928	0.00000	−0.00004	−0.00001	0.66923	0.66929[b]
5	1.39399	0.00000	−0.00007	−0.00002	1.39389	1.39399[b]
						1.39386[d]
6	2.37024	0.00000	−0.00011	−0.00005	2.37007	2.37010(05)[a]
						2.37022[b]
7	3.59760	0.00000	−0.00014	−0.00010	3.59735	3.59738(05)[a]
						3.59755[b]
8	5.07609	−0.00001	−0.00018	−0.00019	5.07572	5.07577(05)[a]
						5.07599(01)[b]
9	6.80590	−0.00001	−0.00020	−0.00030	6.80538	6.80544(06)[a]
						6.80572(01)[b]
10	8.78732	−0.00002	−0.00025	−0.00046	8.78659	8.78666(06)[a]
						8.78703(02)[b]
						8.78700[d]
						8.78657[e]
11	11.02074	−0.00002	−0.00027	−0.00068	11.01977	11.01987(08)[a]
						11.01975[e]
12	13.50659	−0.00003	−0.00031	−0.00095	13.50529	13.50542(09)[a]
						13.50530[e]
13	16.24538	−0.00004	−0.00034	−0.00130	16.24371	16.24386(10)[a]
						16.24373[e]
14	19.23767	−0.00005	−0.00038	−0.00172	19.23552	19.23569(11)[a]
						19.23555[e]
15	22.48408	−0.00007	−0.00040	−0.00224	22.48137	22.48159(12)[a]
						22.48144[e]
16	25.98528	−0.00009	−0.00045	−0.00285	25.98189	25.98215(15)[a]
						25.98197[e]
17	29.74199	−0.00010	−0.00047	−0.00358	29.73784	29.73815(15)[a]
						29.73794[e]
18	33.75500	−0.00013	−0.00047	−0.00443	33.74998	33.75011[e]
19	38.02516	−0.00015	−0.00054	−0.00540	38.01907	38.01921[e]
20	42.55335	−0.00018	−0.00059	−0.00652	42.54606	42.54621[e]

Note. [a] Yerokhin *et al.* [14]. [b] Chung [7]. [c] King *et al.* [41]. [d] Ishikawa, Koc [42]. [e] Sapirstein, Cheng [12].

obtained for the point-nucleus model taking into account the correlation effects. In the subsequent columns of Table 4, from the third to the sixth, the relativistic correction in the Dirac-Fock approximation, $\delta_{DF} = \Delta_{DF,1s^2} - \Delta_{DF}$, the relativistic correction to the correlation contribution, $\delta^{rel\text{-}nr}_{corr} = \Delta^{rel\text{-}nr}_{corr,1s^2} - \Delta^{rel\text{-}nr}_{corr}$, the Breit interaction contribution, $\delta_{Breit} = \Delta_{Breit,1s^2} - \Delta_{Breit}$, and the correction due to the finite size of the nucleus (the field shift), $\delta_{FNS} = \Delta_{FNS,1s^2} - \Delta_{FNS}$, are shown respectively. The seventh column of Table 4 shows the total values of the ionization potentials IP^{rel}_{DCB} obtained by the CI method using the DCB Hamiltonian, which can also be expressed as: $IP^{rel}_{DCB} = IP^{nr} + \delta_{DF} + \delta^{rel}_{corr} + \delta_{Breit} + \delta_{FNS}$. The last column of the table gives the values of the ionization potentials obtained in the papers [14] and [43]. As can be seen from Table 4, the values of the ionization potentials IP^{rel}_{DCB} calculated by us are in good agreement with the systematic data from [14]. The relative difference remains at the level of 0.001%.

Finally, Table 5 shows the contributions to the ionization potentials associated with the frequency dependence of the Breit interaction, $\delta_\omega = \Delta_{\omega,1s^2} - \Delta_\omega$, the nuclear recoil effect, $\delta_{MS} = \Delta_{MS,1s^2} - \Delta_{MS}$, and the QED corrections, $\delta_{QED} = \Delta_{QED,1s^2} - \Delta_{QED}$. For convenience, the second column once again gives the values of the ionization potentials IP^{rel}_{DCB}, which were obtained by the relativistic CI method using the DCB Hamiltonian and taking into account the finite size of the nucleus. The final values of the

Table 6. Contributions of the Breit interaction to the binding energy, Δ_{Breit}, and ionization potential, δ_{Breit}, of the ground state of lithium-like ions. Values are given in atomic units

Z	Δ_{Breit}		δ_{Breit}	
	this work	other works	this work	[14]
3	0.00017	0.00016[b]	−0.00001	–
4	0.00050	–	−0.00003	–
5	0.00111	0.00110[b]	−0.00007	–
6	0.00209	–	−0.00013	−0.00011
7	0.00353	–	−0.00023	−0.00020
8	0.00551	–	−0.00037	−0.00034
9	0.00813	–	−0.00057	−0.00053
10	0.01148	0.01146[a] 0.01150[b]	−0.00082	−0.00078
11	0.01564	–	−0.00114	−0.00107
12	0.02070	–	−0.00153	−0.00145
13	0.02676	–	−0.00201	−0.00191
14	0.03390	–	−0.00258	−0.00247
15	0.04222	0.04219[a] 0.04252[c]	−0.00325	−0.00312
16	0.05180	–	−0.00402	−0.00387
17	0.06274	–	−0.00491	−0.00474
18	0.07513	–	−0.00593	–
19	0.08906	–	−0.00708	–
20	0.10462	0.10459[a]	−0.00836	–

Note. [a] Chen *et al.* [11]. [b] Ishikawa, Koc [42]. [c] Indelicato, Declaux [40].

ionization potentials, $\text{IP}_{\text{tot}} = \text{IP}^{\text{rel}}_{\text{DCB}} + \delta_\omega + \delta_{\text{MS}} + \delta_{\text{QED}}$, are presented in the sixth column. The seventh column contains the values taken from the works [7,14,41,42]. Of the greatest interest is the comparison between the data obtained by us and the results of the systematic calculations performed in the work [14]. As can be seen, the values IP_{tot} are in good agreement. There is, however, a slight discrepancy due to the contribution of the Breit interaction δ_{Breit}. Table 6 allows us to compare the calculated contributions to the binding energies and ionization potentials from the Breit interaction with the corresponding data from the works [11,14,40,42]. The values of δ_{Breit} for the ionization potentials from the paper [14] show a slightly greater discrepancy with our results than the similar Δ_{Breit} contributions for the binding energies from the papers [11,40,42]. As for the total binding energies E_{tot}, the main source of the uncertainty for the ionization potentials IP_{tot} obtained in this paper is the approximate method of accounting for the QED contributions.

4. Conclusion

In this paper, the systematic calculations of the binding energies and ionization potentials of the ground state of Li-like ions with the nuclear charge in the range $Z = 3 - 20$ are performed. In addition to the total values, the individual contributions from the various effects are also presented. Namely, the nonrelativistic energies in the Hartree-Fock approximation, the nonrelativistic correlation contributions, the relativistic corrections in the Dirac-Fock approximation, the relativistic corrections to the nonrelativistic correlation contributions, the Breit interaction contributions with the frequency dependence taken into account, the quantum-electrodynamics corrections, the corrections related to the finite size and the finite mass of the nucleus are evaluated. The presentation form of the results makes it possible to use both the total values of the binding energies and ionization potentials and the contributions due to the individual effects.

The values of the binding energies and ionization potentials, calculated in this work on the basis of the Dirac-Coulomb-Breit Hamiltonian, as well as the final values, obtained taking into account the nuclear recoil and QED effects and the frequency dependence of the Breit interaction, are compared with the data of the previous relativistic calculations. Good agreement is found.

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Conflict of interest

The authors declare that they have no conflict of interest.

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