

# On the interpolation formula for the bound state energies of atomic systems

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**Abstract** By using results of highly accurate computations of the total energies of a large number of few-electron atoms we construct a few interpolation formulas which can be used to approximate the total energies of bound atomic states. In our procedure the total energies of atomic states  $E$  are represented as a function of the electric charge of atomic nucleus  $Q$  and the total number of bound electrons  $N_e$ . Some general properties of the  $E(Q, N_e)$  function are investigated. The knowledge of the  $E(Q, N_e)$  function allows one to determine the total (and binding) energies of these states in arbitrary atoms and ions with different  $Q$  and  $N_e$ .

**Keywords** Interpolation · Atomic term · Bound state

In this short communication we discuss accurate and relatively simple interpolation formulas which can be used to predict the total energies and other bound state properties in various atoms and ions. Recently, a very substantial progress has been achieved in highly accurate computations of the bound states in few-electron atoms and ions. Based on the results of such calculations we can construct a number of different interpolation formulas for the total and binding energies of atomic few-electron systems, i.e. for atomic systems with different nuclear charges  $Q$  and different number of bounded electrons  $N_e$ . Analogous formulas can be constructed for other bound state properties, including inter-particle delta-functions, various single-, two- and three-particles properties and properties which are determined by the expectation values of some singular operators. In this study we shall not discuss interpolation formulas for arbitrary bound

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state properties. Furthermore, below we restrict ourselves to the consideration of the total energies of the bound states in the non-relativistic atoms and ions. First, note that the overall accuracy of the  $Q^{-1}$  expansions constructed for the ground states in the two-, three- and four-electron atomic systems can be considered as outstanding. In this study we want to make the following step and develop (and later apply) the ‘universal formula’ proposed in [1], which allows one to predict the total energies of arbitrary atomic systems with the known values of  $Q$  and  $N_e$  to very high numerical accuracy and without actual atomic calculations. In other words, we need to construct the universal function  $E(Q, N_e)$  of the two (integer) arguments and investigate its properties.

At the first step of our analysis we need to determine the total energies  $E$  and non-relativistic wave functions as the solutions of the Schrödinger equation [2] for the bound states  $H\Psi = E\Psi$ , where  $E < 0$  and  $H$  is the non-relativistic Hamiltonian of the  $N_e$ -electron ion/atom

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_i^2 - Qe^2 \sum_{i=1}^{N_e} \frac{1}{r_{in}} + e^2 \sum_{j=1}^{N_e-1} \sum_{i=2(i>j)}^{N_e} \frac{1}{r_{ij}} \tag{1}$$

where  $\nabla_i = \left( \frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right)$ ,  $i = 1, 2, \dots, N_e$  and the notation  $n$  stands for the atomic nucleus. In Eq. (1) the notation  $\hbar$  designates for the reduced Planck constant, i.e.  $\hbar = \frac{h}{2\pi}$ , and  $e$  is the elementary electric charge. In this study all masses of the atomic nuclei are assumed to be infinite. In general, it is very convenient to perform all bound state calculations in atomic units where  $\hbar = 1, m_e = 1$  and  $e = 1$ . In these units the velocity of light in vacuum  $c$  numerically coincides with the inverse value of the dimensionless fine structure constant, i.e.  $c = \alpha^{-1}$ , where  $\alpha = \frac{e^2}{\hbar c} \approx 7.2973525698 \times 10^{-3}$ . In atomic units the Hamiltonian, Eq. (1), is written in the form

$$H = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - Q \sum_{i=1}^{N_e} \frac{1}{r_{in}} + \sum_{i=1}^{N_e-1} \sum_{i=2(i>j)}^{N_e} \frac{1}{r_{ij}} \tag{2}$$

As follows from Eq. (2) the Hamiltonian  $H$  is a continuous operator-function of the nuclear charge  $Q$ , or in other words, the nuclear charge  $Q$  is the continuous parameter (or control parameter) of this Hamiltonian. By applying the Poincare theorem one finds that all eigenvalues of the Hamiltonian  $H$ , Eq. (2), and all its eigenfunctions are the continuous functions of  $Q$ . In applications to real atoms the nuclear charge  $Q$  expressed in atomic units is always an integer number. Let us assume that we know the actual atomic wave function  $\Psi$  (or  $|\Psi\rangle$ ). Then we can reduce Eq. (1) by the following equation for the three expectation values

$$E = \langle H \rangle = -\frac{1}{2} N_e \langle \nabla_1^2 \rangle - N_e Q \left\langle \frac{1}{r_{1n}} \right\rangle + \frac{N_e(N_e - 1)}{2} \left\langle \frac{1}{r_{12}} \right\rangle \tag{3}$$

where  $E$  is the total energy of the bound state, while  $\langle \nabla_1^2 \rangle, \left\langle \frac{1}{r_{1n}} \right\rangle = \left\langle r_{1n}^{-1} \right\rangle, \left\langle \frac{1}{r_{12}} \right\rangle = \left\langle r_{12}^{-1} \right\rangle$  are the expectation values of the electron kinetic energy, electron–nucleus (attrac-

tive) potential energy and electron–electron repulsion, respectively. In derivation of Eq. (3) the fact that all atomic electrons identical particles. As it can be seen from Eq. (3) the total energy  $E$  is a function of the two parameters  $Q$  and  $N_e$  which are both integer. Formally, to determine the exact (or analytical) form of the  $E(Q, N_e)$  function we need to determine three expectation values mentioned in Eq. (3), i.e. the  $\langle \nabla_1^2 \rangle = -\langle \mathbf{p}_1^2 \rangle$ ,  $\langle r_{1n}^{-1} \rangle$  and  $\langle r_{12}^{-1} \rangle$ . In reality, for Coulomb systems one also finds an additional condition which is widely known as the ‘virial theorem’. The virial is written in the form  $2\langle T \rangle = -\langle V \rangle$ , where  $T$  is the operator of kinetic energy, while  $V$  is the operator of the potential energy. The explicit forms of these operators are:

$$T = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 \quad \text{and} \quad V = -Q \sum_{i=1}^{N_e} \frac{1}{r_{in}} + \sum_{i=1}^{N_e-1} \sum_{i=2(i>j)}^{N_e} \frac{1}{r_{ij}} \quad (4)$$

Note that the virial theorem can be written in one of the following forms:  $E = -\langle T \rangle$ ,  $\frac{1}{2}\langle V \rangle = E$ , etc. In general, by applying the virial theorem we can reduce the total number of ‘unknown’ expectation values in the right-hand side of Eq. (3) from three to two. For instance, the expression of the total energy  $E$  in terms of  $\langle \frac{1}{r_{1n}} \rangle$  and  $\langle \frac{1}{r_{12}} \rangle$  expectation values is

$$E = \langle H \rangle = -\frac{1}{2} N_e Q \left\langle \frac{1}{r_{1n}} \right\rangle + \frac{N_e(N_e - 1)}{4} \left\langle \frac{1}{r_{12}} \right\rangle \quad (5)$$

As follows from Eq. (5) to obtain the explicit formula for the  $E(Q, N_e)$  function we need to derive analogous formulas for the  $\langle \frac{1}{r_{en}} \rangle$  and  $\langle \frac{1}{r_{ee}} \rangle$  expectation values. Briefly, this means that these expectation values must be expressed as explicit functions of  $Q$  and  $N_e$ . In reality, it is not possible to derive any closed analytical expression for the  $\langle \frac{1}{r_{en}} \rangle$  and/or  $\langle \frac{1}{r_{ee}} \rangle$  expectation values written as a function of  $Q$  and  $N_e$ . An obvious exclusion is the Thomas–Fermi method.<sup>1</sup> By using other methods which are more accurate than Thomas–Fermi method it is impossible to derive the closed analytical formulas for the  $\langle \frac{1}{r_{en}} \rangle$  and  $\langle \frac{1}{r_{ee}} \rangle$  expectation values. This means that it is impossible to obtain any closed analytical formula for the  $E(Q, N_e)$  function. However, the ‘atomic function’  $E(Q, N_e)$  can be approximated to very good accuracy by using results of highly accurate numerical calculations for a large number of a few-electron atoms/ions. Formally, if the total number of bounded electrons  $N_e$  is fixed, then we are dealing with the so-called  $Q^{-1}$  expansions for the total energies of a number of atoms/ions with different  $Q$ . For two-electron atoms and ions such series are well known since the middle of 1930s and first papers by Hylleraas for two-electron ions (see e.g., [3–5] and references therein). Analogous series for three- and four-electron atomic systems

<sup>1</sup> This problem has a unique solution for the Thomas–Fermi method, where one finds that  $T = -\frac{3}{7}U_{en}$  and  $U_{ee} = -\frac{1}{7}U_{en}$ . This means that the total energy is  $E = \frac{3}{7}U_{en}$ , where  $T$ ,  $U_{en}$ ,  $U_{ee}$  are the expectation values of the (electron) kinetic energy, electron–nucleus attraction and electron–electron repulsion, respectively.

were not used in applications, since they provided a very modest overall accuracy which was not sufficient for accurate evaluations.

At this moment the situation with accurate numerical calculations of the three- and four-electron atoms and ions has changed. Currently, we have a large number of highly accurate results for the two-electron ions and quite a few different sets of accurate numerical results obtained for three- and four-electron atoms and ions (see e.g., [6, 7] and references therein). These results allow us to construct some accurate  $Q^{-1}$  expansions which also describe the total energies of the three- and four-electron atomic systems. Based on these formulas for the  $Q^{-1}$  expansions for two-, three- and four-electron atoms and ions we can try to guess the explicit formulas for an universal function  $E(Q, N_e)$ , where  $N_e$  is the total number of bounded electrons. This problem has a fundamental value for whole atomic physics. Indeed, if we know the  $E(Q, N_e)$  function, then we can predict the total energy of an arbitrary atom/ion with the given  $Q$  and  $N_e$  to high accuracy which is sufficient for many actual problems known from stellar astrophysics, physics of high-temperature plasmas, etc. In reality, accurate predictions of the total and binding energies of atoms/ions with different  $Q$  and  $N_e$  was an ultimate goal for many generations of atomic physicists. In this study we show that currently we are very close to fulfill this goal.

Accurate non-relativistic energies  $E$  of a large number of the ground states in the two-, three- and four-electron atoms/ions can be found in Table 1. All total energies are given in Table 1 in atomic units. The total energies of the two-electron (or helium-like) atoms and ions from Table 1 have been determined to very high accuracy with the use of our computational procedure which allows one to perform calculations with 3500 exponential basis functions in the wave functions. All basis functions are written in the relative coordinates  $r_{32}$ ,  $r_{31}$  and  $r_{21}$ . For three-electron (or lithium-like) ions (and Li atom) such energies have been taken from [6], while for four-electron atoms/ions they were chosen from [7]. The overall accuracy of the ground state energies in three- and four-electron atomic systems is still significantly lower than the analogous accuracy for two-electron atoms and ions (see Table 1). Note also that the  $\text{Li}^-$  ion, i.e. atomic system with  $Q = 3$  and  $N_e = 4$ , is bound, i.e. its ground  $2^1S$ -state is stable, but our current variational results for this system (e.g.,  $E = -7.5007185$  a.u.) are not highly accurate. This is the reason why we exclude this ion from Table 1. By using the total energies of all atoms/ions mentioned in Table 1 (with the same value of  $N_e$ ) one can determine some numerical coefficients in the  $Q^{-1}$  expansion

$$E(Q) = a_2 Q^2 + a_1 Q + a_0 + b_1 Q^{-1} + b_2 Q^{-2} + b_3 Q^{-3} + \dots \quad (6)$$

where  $a_2, a_1, a_0$  are the coefficients of the regular part of the Laurent expansion (or series), while  $b_1, b_2, \dots$  are the coefficients of the principal part of the Laurent series  $E(Q)$ , Eq. (6). Note that the  $Q^{-1}$ -expansion (or  $Q^{-1}$ -series), Eq. (6), is a typical ‘asymptotic expansion’. Briefly, this means that after some  $n \geq n_{max}$  all coefficients  $b_n$  in Eq. (6) rapidly increase with  $n$ . Contributions of the corresponding terms also rapidly increase with  $n$  and the total sum computed with the use of Eq. (6), which includes such ‘growing terms’, has nothing to do with the original problem. Briefly, this means that in such cases the  $Q^{-1}$  expansion cannot be used to approximate the actual total energies. To avoid this problem we need to restrict the total number of terms

**Table 1** The total non-relativistic energies  $E$  of the different atoms/ions in their ground states in atomic units

$Q$	$N_e = 2$	$N_e = 3$	$N_e = 4$
1	-0.5277510165443771965925	-	-
2	-2.90372437703411959831115924519440	-	-
3	-7.27991341266930596491875	-7.4780603236503	-
4	-13.65556623842358670208051	-14.3247631764654	-14.667356407951
5	-22.03097158024278154165469	-23.424605720957	-24.348884381902
6	-32.40624660189853031055685	-34.775511275626	-36.534852285202
7	-44.781445148772704645183	-48.376898319137	-51.222712616143
8	-59.156595122757925558542	-64.228542082701	-68.411541657589
9	-75.531712363959491104856	-82.330338097298	-88.100927676354
10	-93.906806515037549421417	-102.682231482398	-110.290661070069
11	-114.28188377607272189582	-125.2841907536473	-134.980624604257
12	-136.65694831264692990427	-150.1361966044594	-162.170747906692
13	-161.03200302605835987252	-177.238236559961	-191.860986338262
14	-187.40704999866292631487	-206.5903022122780	-224.051310298012
15	-215.78209076353716023462	-238.1923876941461	-258.741699427160
16	-246.15712647425473932009	-272.0444887900725	-295.932139288646
17	-278.53215801540009570337	-308.1466023952556	-335.622619375075
18	-312.90718607661114879880	-346.4987261736714	-377.813131866050
19	-349.28221120345316700447	-387.1008583345610	-422.503670826658
20	-387.65723383315855621790	-429.9529974827626	-469.694231675265
21	-428.03225432023469116264	-	-519.384810821074
22	-470.40727295513838395930	-	-571.575405411671
23	-514.78228997811177388135	-	-626.266013153662
24	-561.15730558958127234352	-	-683.456632182920
25	-609.53231995807574620568	-	-743.147260969064
26	-659.90733322632780520901	-	-805.337898245040
27	-712.28234551602655145614	-	-870.028542951686
28	-766.65735693155709991040	-	-937.219194199135
30	-	-	-1079.100513407098
36	-	-	-1564.744568198454

All nuclear masses are infinite.  $Q$  is the nuclear electric charge and  $N_e$  is the total number of bounded electrons

in Eq. (6). For instance, if we use  $N = 18$  values of the total energies  $E(Q)$  (computed for eighteen different values of  $Q$ ), then the total number of terms in Eq. (6) can be 8, or 10, but not 16, or 18. An universal criterion can be formulated in the following form: overall contribution to the total sum, Eq. (6), from the last term must be smaller (and even much smaller) than analogous contribution from the pre-last term.

First ten coefficients of the  $Q^{-1}$  expansion, Eq. (6), determined from the results of highly accurate numerical calculations of few-electron atoms and ions mentioned in Table 1 can be found in Table 2. These coefficients can be used in applications

**Table 2** Coefficients  $a_2^{(N_e)}$ ,  $a_1^{(N_e)}$ ,  $a_0^{(N_e)}$  and  $b_1^{(N_e)}$ ,  $b_2^{(N_e)}$ ,  $\dots$ ,  $b_7^{(N_e)}$  in the ten-term expansion of the  $E(Q, N_e)$ -function [see Eq. (12)]

coefficients	$N_e = 2$	$N_e = 3$	$N_e = 4$
$a_2^{(N_e)}$	-1.0000000000	-1.1249999945	-1.2499999978
$a_1^{(N_e)}$	0.6249999961	1.0228047058	1.5592739061
$a_0^{(N_e)}$	-0.1576662873	-0.4081459572	-0.8771019520
$b_1^{(N_e)}$	0.0086962674	-0.0170061678	-0.0429178704
$b_2^{(N_e)}$	-0.0008567981	-0.0341594959	-0.1694257553
$b_3^{(N_e)}$	-0.0012640360	-0.1084597316	-0.3362058744
$b_4^{(N_e)}$	0.0003957668	0.2941494433	0.6932000874
$b_5^{(N_e)}$	-0.0030653579	-1.4458330710	-5.7572871897
$b_6^{(N_e)}$	0.0037323637	2.9184336113	14.3319856750
$b_7^{(N_e)}$	-0.0027229312	-3.3508481226	-22.3281869042

of the  $Q^{-1}$  expansion, Eq. (6), to other two-, three- and four-electron atoms and ions. The overall accuracy of the  $Q^{-1}$  expansion, Eq. (6), for the total energies of the ground states in these atoms and ions is outstanding and can be evaluated as  $1 \times 10^{-9} - 5 \times 10^{-12}$  a.u. of the total energies. In general, the  $Q^{-1}$  expansion, Eq. (6), can be used in applications to different iso-electron atomic systems. However, due to numerous problems in accurate computations of the three-, four- and many-electron atoms and ions the most successful applications of the  $Q^{-1}$  expansion are still restricted to the two-electron (or helium-like) atoms and ions. It should be mentioned that similar  $Q^{-1}$  expansions can be used for other bound state properties, e.g., to predict interparticle distances, expectation values of some delta-functions, etc. As mentioned above in this study we restrict ourselves to the total energies only and (brief discussion of the interpolation formulas for other bound state properties can be found e.g., in [1]).

Based on the results from Tables 1 and 2 we can make the new step which must lead to better understanding of the structure of bound state spectra in atoms and ions. Instead of dealing with many different  $E(Q)$  functions constructed for each series of iso-electron atomic systems, i.e. atoms/ions with the same  $N_e$ , we introduce a ‘universal function’  $E(Q, N_e)$  which depends upon two integer numbers:  $Q$  (nuclear electric charge) and  $N_e$  (total number of bound electrons). If  $N_e$  is fixed, e.g.,  $N_e = 2$ , then the corresponding function  $E(Q, N_e = 2) = E(Q, 2)$  must coincide with the function  $E(Q)$  known for the two-electron atomic systems. There are few possible approaches which can be used to determine the universal  $E(Q, N_e)$  function. In this study we apply the so-called direct approach which is based on the results presented in Table 2. In fact, we shall assume below that coefficients presented in all columns of Table 2 correspond to one ‘universal’ function  $E(Q, N_e)$ . Numerical differences in these coefficients can only be related with the variations in  $N_e$ . For instance, consider the first coefficients  $a_2$  from Table 2. The exact value of these coefficients are  $-1$ ,  $-\frac{9}{8}$  and  $-\frac{5}{4}$  for  $N_e = 2, 3$ , and  $4$ , respectively. Therefore, the following general formula can be written in the form

$$a_2 = -\left(\frac{8 + N_e - 2}{8}\right) = -\left(\frac{6 + N_e}{8}\right) \quad (7)$$

where  $N_e$  is the total number of bounded electrons in the atom/ion. As follows from Table 2 the analogous expression for the second coefficient can be written in the following form

$$a_1 = \frac{5}{8} + a_1^{(1)}(N_e - 2) + a_1^{(2)}(N_e - 2)^2 \quad (8)$$

where  $a_1^{(1)}$  and  $a_1^{(2)}$  are the two unknown coefficients which are determined with the use of numerical values for this coefficient from the second and third columns of Table 2. The formula, Eq. (8), can be re-written into a slightly different form

$$a_1^{(N_e)} = \frac{5}{8} + \left[a_1^{(3)} - \frac{5}{8}\right](N_e - 2) + \left[a_1^{(4)} - 2a_1^{(3)} + \frac{5}{8}\right] \frac{(N_e - 2)(N_e - 3)}{2} \quad (9)$$

where  $a_1^{(3)}$  and  $a_1^{(4)}$  are the coefficients from Table 1 for the three- and four-electron atomic system, respectively. The unknown value of the  $a_1$  coefficient for atomic system with  $N_e$ -electrons is designated in the left-hand side of Eq. (9) as  $a_1^{(N_e)}$ . The formula, Eq. (9), can be generalized to more complex cases, e.g.,

$$a_0^{(N_e)} = a_0^{(2)} + \left[a_0^{(3)} - a_0^{(2)}\right](N_e - 2) + \left[a_0^{(4)} - 2a_0^{(3)} + a_0^{(2)}\right] \frac{(N_e - 2)(N_e - 3)}{2} \quad (10)$$

where  $a_0^{(N_e)}$  is the  $a_0$  coefficient from Eq. (6) defined for atomic systems with  $N_e$  bound electrons. Analogously, for  $b_k$  coefficients from Eq. (6) one finds

$$b_k^{(N_e)} = b_k^{(2)} + \left[b_k^{(3)} - b_k^{(2)}\right](N_e - 2) + \left[b_k^{(4)} - 2b_k^{(3)} + b_k^{(2)}\right] \frac{(N_e - 2)(N_e - 3)}{2} \quad (11)$$

where notation  $a_k^{(N_e)}$  stands for the  $b_k$  coefficients ( $k = 1, 2, 3, \dots$ ) from Eq. (6) defined for atomic systems with  $N_e$  bound electrons, where  $N_e = 2, 3, 4, \dots$ . This expression is, in fact, the Taylor–Maclaurin expansion for the  $b_k^{(N_e)}$  coefficients upon the total number of bound electrons  $N_e$ . Note that the formulas Eqs. (7)–(11) for the coefficient  $a_2 - a_0$  and  $b_k$  ( $k = 1, 2, \dots$ ) are essentially exact upon  $N_e$  for all two-, three- and four-atoms/ions presented in Table 1. This means that the total energies of these ions are reproduced with the same accuracy which is provided by their  $Q^{-1}$  expansion.

As follows from Eq. (7) the coefficient  $a_2$  is the ratio of two small integer numbers, and numerator of this fraction is a linear function of  $N_e$ . This follows from the fact that the main contribution to the total energy of any atom/ion comes from the  $N_e Q^2$ -term which represents the leading term in the electron-nucleus attraction. In atomic units this term equals to an integer, or semi-integer number (for an arbitrary atom/ion). The coefficient  $a_1$  for two-electron atomic systems is also a simple fraction, e.g.,  $\frac{5}{8}$  for the ground states. The same conclusion is true for other bound states, e.g., for the  $2^3S$ -triplet states, in the two-electron atoms/ions [8].

In general, the analysis of the  $E(Q, N_e)$  function(s) is very similar to operations with the Weizäcker mass formula in nuclear physics. Such a similarity follows from the fact that in both cases we are dealing with the finite Fermi systems [9]. Note that atoms and ions were considered as the finite Fermi systems in atomic physics since first papers published in earlier 1960s [10, 11] (see also [12] and references therein). More recent references can be found, e.g., in [13]. This general theory allows one to obtain the asymptotic form of the  $E(Q, N_e)$  function at very large  $Q$  and  $N_e$  [12]. A few other advantages of that theory include the correct theoretical expressions for the  $a_0$  and  $a_1$  coefficients [see Eqs. (7)–(8)] which either coincide with ours (see Table 2), or very close to them. The coefficients  $a_2, b_1, b_2, \dots$  predicted in the general theory are known only approximately, even in the case of the ground (bound) atomic states. For excited atomic states the accuracy of predictions of this theory is substantially lower. In many cases applications of the general theory to the excited atomic states [12] lead to very inaccurate predictions of ionization potentials and other properties. Such a situation with excited states lead to a conclusion that applications of the general theory to the ground states in atomic systems only. However, in this case we have to face the following crucial question: *why do we need to perform dozens of highly accurate, atomic computations for construction of the accurate interpolation formula for the total energies, if in modern atomic physics highly accurate computations of any ground state in arbitrary atom/ion are significantly faster?* It is clear that if we cannot generalize our interpolation formulas to the excited atomic states, then chances of the ‘general theory’ [10–12] to survive in the future are very low.

Our approach based on the use of highly accurate computational data for different atoms/ions allows one to reconstruct the  $E(Q, N_e)$  function can be applied, in principle to any atomic state, including excited states. As is well known from atomic spectroscopy, the bound state spectrum of any multi-electron atom/ion is represented as a set of different terms, where each term has its unique quantum numbers of angular momentum  $L$  and total electron spin  $S$ . For our analysis this means that the function  $E(Q, N_e)$  (total energy) defined above must be labeled by the two indexes  $L$  and  $S$ , which are good (= conserving) quantum numbers for an isolated atom/ion with  $N_e$  bound electrons. These two quantum numbers are the labels of the corresponding atomic term. The bound state spectrum of any atom is represented as a combination of different  $LS$ -terms. An ultimate goal is to approximate the total (non-relativistic) energies of all bound states from all possible terms which can be found in real atoms and ions. In the ‘general theory’ [10, 11] this problem is extremely complex, since often the atomic  $LS$ -term does not exist in atoms/ions with fewer electrons. Formally, this means that we need to construct the  $Q^{-1}$  expansions for each different atomic  $LS$ -term.

In part, such a strategy already works for the ground atomic states. Indeed, the ground states in different atoms correspond to the different terms, e.g., the ground state in the B-atom (five bound electrons) is the  $2^1P$ -state, analogous state in the carbon atom is the  $2^2P$ -state. It is clear that by including future highly results for atoms/ions with larger number of electrons we can reach the ground states of the Fe atom ( $^5D_4$ -term), Co atom ( $^4D_{\frac{9}{2}}$ -term), etc. However, if it is possible to connect all ground atomic states by one interpolation formula, then we can do the same for



the excited atomic states too. Let us describe our current vision of this two-stage procedure. At the first stage the approach is based on the formulas, Eqs. (7), (9), (10) and (11) allows one to determine other unknown coefficients  $a_0, a_1, a_2, b_1, b_2, \dots$ . The arising formulas are simple and convenient in applications to atoms and ions. The known coefficients  $a_0, a_1, a_2, b_1, b_2, \dots$  are used in the ‘usual’  $Q^{-1}$ -expansion

$$E(Q, N_e) = a_2(N_e)Q^2 + a_1(N_e)Q + a_0(N_e) + b_1(N_e)Q^{-1} + b_1(N_e)Q^{-1} + b_2(N_e)Q^{-2} + b_3(N_e)Q^{-3} + \dots \quad (12)$$

where now all coefficients are the functions of the total number of bound electrons  $N_e$ . In this study all coefficients in Eq. (12) are constructed as polynomial functions of  $N_e$ . The  $Q^{-1}$ -expansion, Eq. (12), provides high numerical accuracy for the total energies of all two-, three- and four-electron atomic systems presented in Table 1. Very likely, that the analytical expression for each of the  $b_i(N_e)$  coefficients ( $i = 1, 2, \dots$ ) in Eq. (12) is more complicated than a simple polynomial in  $N_e$ . It is clear that such an expansion must also include the negative powers of  $N_e$ . In reality, we can investigate the  $E(Q, N_e)$  function in detail when we can obtain highly accurate results for five- and six-electron atoms and ions. When highly accurate computations of the five- and six-electron atoms will be completed, then we can substantially improve our current knowledge of the  $E(Q, N_e)$  function(s). Moreover, we can derive some compact and accurate formulas for numerical approximations of these functions for different bound atomic states. This is an answer to an old question about possibility to find an analytical formula for the total non-relativistic energies of bound states in atomic system which contains  $N_e$  bound electrons moving in the field of infinitely heavy nucleus with the electric charge  $Qe$ . In this study to approximate the  $E(Q, N_e)$  function we have restricted to the ten-term formula for the  $Q^{-1}$  expansion, Eq. (6). In part, such a restriction is related with relatively low accuracy of the computational energies obtained for the three- and four-electron atoms/ions.

At the second stage of the procedure we need to find relations between coefficients of these series, define these coefficients as the functions of  $N_e$ , etc. As mentioned above some bound  $LS$ -state (or  $LS$ -term) may not exist for atoms/ions with fewer electrons. Therefore, we need to solve the problem of genealogical relation between terms (or bound states) in atoms/ions with different number(s) of bound electrons  $N_e$ . To explain this problem let us assume that we have determined known function  $E_{LS}(Q, N_e)$  (total energy) for atoms/ions with the same number bound electrons  $N_e$  ( $Q$  is varied). Now, suppose that the total number of bound electrons increases by one, i.e.  $N_e \rightarrow N_e + 1$ . Now, we have the new term  $L'S'$  and the new function  $E_{L'S'}(Q, N_e + 1)$  (total energy). We need to predict possible numerical values of  $L'$  and  $S'$  quantum numbers. As it follows from the fundamental principles of atomic theory for the new spin quantum number we have  $S' = S \pm \frac{1}{2}$ , if  $S \neq 0$ , and  $S' = S + \frac{1}{2}$ , if  $S = 0$ . To predict the new value of  $L'$  we have to know the angular momentum  $\ell$  of the additional electron. If we know this value, then one finds that all possible  $L'$  values are located between the two following limits  $|L - \ell|$  (lower limit) and  $L + \ell$  (upper limit), i.e.  $|L - \ell| \leq L' \leq L + \ell$ . If these conditions for the  $L'$  and  $S'$  are obeyed, then the total energies  $E_{LS}(Q, N_e)$  and  $E_{L'S'}(Q, N_e + 1)$  can be used in one series.

As follows from the results of our study the function  $E(Q, N_e)$  can be constructed for all bound states in multi-electron atomic systems, if (and only if) their terms are directly connected by the ‘selection’ rule mentioned above. For instance, in this study we discuss the total energies of two-, three- and four-electron atoms/ions which have their ground  $1^1S$ -,  $2^2S$ - and  $2^1S$ -states, respectively. These bound states have different multiplicities, i.e. they are singlets and doublets states. Suppose we want to include in our analysis five-electron atoms/ions (B-like ions) for which the ground state is the  $2^2P$ -state. The ‘selection rules’ mentioned above works in this case. Therefore, we can construct the  $E(Q, N_e)$  function for the  $1^1S$ -,  $2^2S$ -,  $2^1S$ - and  $2^2P$ -states in the two-, three-, four- and five-electron atoms/ions, respectively. However, if we want to evaluate, e.g., the total energies of the  $3^4D$ -states in the five-electron ions, then we have to use a slightly different consequence of bound states the two-, three- and four-electron atoms/ions, respectively. A natural choice in this case is to consider the bound  $1^1S$ -,  $2^2S$ - and  $2^3P$ -states in the two-, three- and four-electron atoms/ions, respectively. The total energies determined for the bound  $3^4D$ -states in the five-electron atoms/ions perfectly complete the data (total energies) computed for the bound  $1^1S$ -,  $2^2S$ - and  $2^3P$ -states in the two-, three- and four-electron atoms/ions. On the other hand, it is clear that our total energies from the third column of Table 1 (total energies of the  $2^1S$ -states in the four-electron atoms/ions) are useless in this case. In other words, these energies cannot be used to predict the total energies of the bound  $3^4D$ -states in five-electron atoms/ions. Formally, this means that to construct highly accurate interpolation formula for the total energies of the bound  $3^4D$ -states in the five-electron atoms and ions one needs to perform a number of separate, highly accurate computations of the bound  $2^3P$ -states in the four-electron atomic systems. In general, the total energies of any bound state in multi-electron atomic system can be predicted to relatively high accuracy, if we know a number of total energies of bound states in atomic systems with fewer electrons. Such bound states in atomic systems with fewer electrons correspond to the different  $LS$ -terms. However, all these bound states (or terms) must be related to each other by the selection rules mentioned above. An additional problem follows from the fact that some of the atomic terms can be connected by using different atomic terms in the systems with fewer bounded electrons. It is clear that the procedure must be self-correlated. This means that we must have some additional relations between the  $E_{LS}(Q, N_e)$  and  $E_{L'S'}(Q, N'_e)$  functions constructed for different atomic terms and for atoms/ions which contain different number(s) of bound electrons. This interesting question cannot be answered at the current level of theoretical and computational development.

## Appendix

The formulas Eqs. (7), (9), (10) and (11) for the coefficients  $a_2, a_1, a_0$  and  $b_1, b_2, \dots$  from the main text can be re-written in a number of different forms which are often more convenient in applications. In this Appendix we present the explicit formulas for the coefficients  $a_2, a_1, a_0$  and  $b_1, b_2, \dots$  for five- and six-electron atomic systems (i.e. atoms and ions). In all these cases the formula for the  $a_2$  coefficient coincides with

Eq. (7) (here we do not want to repeat it). The formulas for other coefficients from Eq. (12) take the following forms. For  $N_e = 5$  one finds:

$$a_1^{(N_e=5)} = \frac{5}{8} + \left[ a_1^{(3)} - \frac{5}{8} \right] (N_e - 2) + \left[ a_1^{(4)} - 2a_1^{(3)} + \frac{5}{8} \right] \frac{(N_e - 2)(N_e - 3)}{2} \\ + \left[ a_1^{(5)} - 3a_1^{(4)} + 3a_1^{(3)} - \frac{5}{8} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)}{6} \quad (13)$$

$$a_0^{(N_e=5)} = a_0^{(2)} + \left[ a_0^{(3)} - a_0^{(2)} \right] (N_e - 2) + \left[ a_0^{(4)} - 2a_0^{(3)} + a_0^{(2)} \right] \frac{(N_e - 2)(N_e - 3)}{2} \\ + \left[ a_2^{(5)} - 3a_2^{(4)} + 3a_2^{(3)} - a_2^{(2)} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)}{6} \quad (14)$$

and

$$b_k^{(N_e=5)} = b_k^{(2)} + \left[ b_k^{(3)} - b_k^{(2)} \right] (N_e - 2) + \left[ b_k^{(4)} - 2b_k^{(3)} + b_k^{(2)} \right] \frac{(N_e - 2)(N_e - 3)}{2} \\ + \left[ b_k^{(5)} - 3b_k^{(4)} + 3b_k^{(3)} - b_k^{(2)} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)}{6} \quad (15)$$

where  $N_e = 5$  in the right-hand sides of these equations.

Analogous formulas for the  $N_e = 6$  are

$$a_1^{(N_e=6)} = \frac{5}{8} + \left[ a_1^{(3)} - \frac{5}{8} \right] (N_e - 2) + \left[ a_1^{(4)} - 2a_1^{(3)} + \frac{5}{8} \right] \frac{(N_e - 2)(N_e - 3)}{2} \\ + \left[ a_1^{(5)} - 3a_1^{(4)} + 3a_1^{(3)} - \frac{5}{8} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)}{6} \\ + \left[ a_1^{(6)} - 4a_1^{(5)} + 6a_1^{(4)} - 4a_1^{(3)} + \frac{5}{8} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)(N_e - 5)}{24} \quad (16)$$

$$a_0^{(N_e=6)} = a_0^{(2)} + \left[ a_0^{(3)} - a_0^{(2)} \right] (N_e - 2) + \left[ a_0^{(4)} - 2a_0^{(3)} + a_0^{(2)} \right] \frac{(N_e - 2)(N_e - 3)}{2} \\ + \left[ a_2^{(5)} - 3a_2^{(4)} + 3a_2^{(3)} - a_2^{(2)} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)}{6} \\ + \left[ a_2^{(6)} - 4a_2^{(5)} + 6a_2^{(4)} - 4a_2^{(3)} + a_2^{(2)} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)(N_e - 5)}{24} \quad (17)$$

and

$$b_k^{(N_e=6)} = b_k^{(2)} + \left[ b_k^{(3)} - b_k^{(2)} \right] (N_e - 2) + \left[ b_k^{(4)} - 2b_k^{(3)} + b_k^{(2)} \right] \frac{(N_e - 2)(N_e - 3)}{2} \\ + \left[ b_k^{(5)} - 3b_k^{(4)} + 3b_k^{(3)} - b_k^{(2)} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)}{6} \\ + \left[ b_k^{(6)} - 4b_k^{(5)} + 6b_k^{(4)} - 4b_k^{(3)} + b_k^{(2)} \right] \frac{(N_e - 2)(N_e - 3)(N_e - 4)(N_e - 5)}{24} \quad (18)$$

where in the right-hand sides of these equations we must put  $N_e = 6$ . Generalization of these formulas to the cases when  $N_e \geq 7$  is straightforward and relatively simple.

As follows from these formulas the addition of one electron, i.e.  $N_e - 1 \rightarrow N_e$ , affects only the last term in each of these formulas, while all previous terms contains coefficients known for atomic systems with  $N_e - 1$  electrons. This allows one to consider different atomic  $LS$ -terms for the bound states with different  $N_e$  (it is assumed that the ‘selection rules’ mentioned in the main text are obeyed for these  $LS$ -terms).

## References

1. A.M. Frolov, D.M. Wardlaw, *Europ. Phys. J. D* **50**, 9 (2008)
2. C. Froese Fisher, T. Brage, P. Jönsson, *Computational Atomic Structure* (IOP, Bristol, 1997)
3. H.A. Bethe, E.E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, (Springer, Berlin, 1957), §33
4. I.I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer, Berlin, 1979)
5. S.T. Epstein, *The Variation Method in Quantum Chemistry* (Academic Press, New York 1974), Chpt. IV, § 29
6. Z.C. Yan, M. Tambasco, G.W.F. Drake, *Phys. Rev. A* **57**, 1652 (1998)
7. J.S. Sims, A.S. Hagstrom, *J. Chem. Phys.* **140**, 224312 (2014)
8. A.M. Frolov, *J. Phys. B* **38**, 3233 (2005)
9. A.B. Migdal, *Theory of the Finite Fermi System and Properties of Atomic Nuclei*, 2nd edn. (Science, Moscow, 1983). **(in Russian)**
10. J. Linderberg, H. Shull, *J. Mol. Spectr.* **5**, 1 (1960)
11. C.W. Scherr, J.N. Silverman, F.A. Matsen, *Phys. Rev.* **127**, 830 (1962)
12. N.H. March, W.H. Young, S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (General Publishing Company, Toronto, 1967), Chpts. 1–7
13. S.J. Chakravorty, E.R. Davidson, *J. Phys. Chem.* **100**, 6167 (1996)