Bound state spectra and properties of the doublet states in three-electron atomic systems

Alexei M. Frolov

Department of Applied Mathematics
University of Western Ontario, London, Ontario N6H 5B7, Canada

María Belén Ruiz

Department of Theoretical Chemistry,
Friedrich-Alexander-University Erlangen-Nürnberg,
Egerlandstraße 3, D-91058, Erlangen, Germany

David M. Wardlaw

Department of Chemistry, Memorial University of Newfoundland,
St.John’s, Newfoundland and Labrador, A1C 5S7, Canada

(Dated: April 1, 2014)

Abstract

The bound state spectra of the doublet states in three-electron atomic systems are investigated. By using different variational expansions we determine various bound state properties in these systems. Such properties include electron-nucleus and electron-electron delta-functions and cusp values. The general structure of the bound state spectra in several three-electron atomic systems (Li, Be+, C3+ and F6+) is investigated with the use of the Hylleraas-Configuration Interaction and the Configuration Interaction wave functions. The advantage of our Configuration Interaction based procedure follows from the fact that it provides high numerical accuracy for all rotationally excited states, including all bound states with \( L \geq 3 \).
I. INTRODUCTION

In this study we investigate the bound doublet states in the three-electron atoms and ions by using a few different variational expansions written in the relative coordinates, or interparticle distances $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$, where $\mathbf{r}_i$ $(i = 1, 2, 3)$ are the Cartesian coordinates of the three electrons, while $\mathbf{r}_4$ are the Cartesian coordinates of the positively charged nucleus. Another our goal is to determine the bound state properties of some of these bound (doublet) states and discuss problems arising during this procedure. By calculating these properties we want to correct mistakes which have been made in earlier papers and continue to propagate in the modern scientific literature.

As is well known in the lowest-order approximation upon the fine structure constant $\alpha = \frac{e^2}{\hbar c}$ an arbitrary three-electron atom/ion is described by the non-relativistic Schrödinger equation $H \Psi = E \Psi$, where $E < 0$ and the bound state wave function $\Psi$ has the unit norm. The non-relativistic Hamiltonian $H$ of the three-electron atom/ion is (see, e.g., [1])

$$H = -\frac{\hbar^2}{2m_e} \left[ \nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \frac{m_e}{M} \nabla_4^2 \right] - \frac{Qe^2}{r_{14}} - \frac{Qe^2}{r_{24}} - \frac{Qe^2}{r_{34}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}$$

(1)

where $\hbar = \frac{h}{2\pi}$ is the reduced Planck constant, $m_e$ is the electron mass and $e$ is the electric charge of an electron. In this equation and everywhere below in this study the subscripts 1, 2, 3 designate the three electrons $e^-$, while the subscript 4 denotes the heavy nucleus with mass $M$ ($M \gg m_e$) and positive electric (nuclear) charge $Qe$. The notations $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$ stand for the six interparticle distances (= relative coordinates) defined above. In Eq.(1) and everywhere below in this work we shall assume that $(ij) = (ji) = (12), (13), (14), (23), (24), (34)$. Below only atomic units $\hbar = 1, |e| = 1, m_e = 1$ are employed. In these units the explicit form of the Hamiltonian $H$, Eq.(1), is simplified.

For last fifty years (since the paper [2] was published) the problem of highly accurate calculations of the bound states in three-electron atomic systems has attracted a significant attention. A very nice review of the three-electron atomic problem can be found in [3] which also contains all references prior to 1969. A great theoretical interest in three-electron atomic systems can be explained by a number of facts known for such systems. First, three-electron atomic systems are very convenient objects for the study of the overall and relative contributions of the electron-electron correlations. It follows from the fact that the potential energy in the Hamiltonian, Eq.(1), is represented by two sums each of which contains equal
number of terms: electron-nucleus attractions and electron-electron repulsions. Therefore, by varying only one parameter \( Q \) in Eq. (1) we can study electron-electron correlations in such systems and relations between electron-electron and electron-nucleus correlations. Second, all three-electron atoms and ions are well known subjects in atomic physics. On the other hand, the overall accuracy of bound state computations achieved for three-electron atoms and ions is still substantially lower than analogous accuracy known for two-electron atomic systems. Therefore, the development of new, rapidly converging variational expansions and effective, fast computational methods is of paramount importance for the future of highly accurate calculations of three-electron atoms and ions. Third, despite a rapidly increasing stream of computational publications on three-electron atomic systems some fundamental aspects of such systems have not been discussed yet. For instance, the quality of the wave function constructed for an arbitrary Coulomb few- and many-body system can be tested by comparing the computed and expected cusp values, or cusps, for short. However, it appears that neither the electron-nucleus, nor electron-electron cusps were ever determined for three-electron atoms and ions. Another well known problem is related to an incorrect definition of some electron-nucleus and electron-electron properties accepted in quite a few earlier works performed for three-electron atoms and ions. Furthermore, it was found that the expectation values of some bound state properties computed with the use of different variational expansions deviate from each other. In a few cases such deviations are relatively large and may lead to contradictions with the known experimental results.

In our analysis below we re-consider all these problems by performing highly accurate calculations of some bound states in three-electron atomic systems. This work has the following structure. In the next Section we discuss the semi-exponential variational expansion in relative coordinates \(^4\). This very compact and accurate variational expansion was introduced in \(^4\). In this study this expansion is applied to determine various bound state properties in the ground \(^2S^\text{−}\) state(s) of the three-electron Li-atom and Be\(^+\) and B\(^{2+}\) ions. The computed expectation values include electron-nucleus and electron-electron delta-functions and cusp-values. In Section III we consider a number of bound (doublet) \(^2S^\text{−}\) states in different three-electron atoms and ions by using another variational expansion of the wave functions. Here all wave functions are approximated by expansions in six-dimensional gaussoids \(^5\). Note that analytical formulas for all matrix elements which arise in variational calculations of arbitrary \( A \)−body system in the basis of multi-dimensional gaussoids, where \( A \geq 2 \) is an
arbitrary integer, have been derived in the mid-1970’s (see \[5\] and earlier references therein). Subsequently this variational expansion was successfully applied for bound state computations in many hundreds of nuclear, atomic and molecular systems. In Section III we use this variational expansion to determine the total energies and other bound state properties of some excited states in the Li-atom. The results obtained in Section III can also be used to correct a few mistakes and misprints made in earlier studies of three-electron atomic systems. In Section IV by using the Hylleraas-Configuration Interaction (Hy-CI) and Configuration Ineraction (CI) variational expansions of the wave functions we investigate the general structure of the bound state spectra (or optical spectra, for short) of three-electron (or Li-like) atoms and ions. Section IV also contains a brief discussion of the ‘scaling’ procedure which can be used to study the electron-electron correlations in three-electron atomic systems. Concluding remarks can be found in the last Section.

II. SEMI-EXPONENTIAL VARIATIONAL EXPANSION

A semi-exponential variational expansion for three-electron wave functions was developed a few years ago \[4\] in order to modify the traditional Hylleraas variational expansion which has been used for three-electron atomic systems since Larsson’s work \[2\]. Recently it became clear that the Hylleraas variational expansion of the three-electron wave functions has a very slow convergence rate. Our main idea in \[4\] was to increase the total number of varied, non-linear parameters in each basis function included from the variational expansion. Finally, we developed a very effective variational expansion for three-electron atoms and ions which can now be used to construct very compact and accurate wave functions for arbitrary three-electron atom and/or ion. For simplicity, below we consider only the doublet $2^2S(L = 0)$—states in the three-electron Li atom and similar Be$^+$ and B$^{2+}$ ions. By using our semi-exponential variational expansion we determine bound state properties of these three-electron atomic systems. It should be mentioned that some of these properties have never been determined in earlier studies.

The variational wave function of the doublet $S(L = 0)$—states of the three-electron atom/ion is written in the form

$$
\Psi_{L=0} = \psi_{L=0}(A; \{r_{ij}\})(\alpha\beta\alpha - \beta\alpha\alpha) + \phi_{L=0}(B; \{r_{ij}\})(2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha) \quad (2)
$$
where $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ are the two independent spatial parts (also called the radial parts, or radial functions) of the total wave function. Each of these two radial functions is, in fact, a radial factor (for states with $L = 0$) in front of the corresponding three-electron spin functions $\chi_1 = \alpha \beta \alpha - \beta \alpha \alpha$ and $\chi_2 = 2\alpha \alpha \beta - \beta \alpha \alpha - \alpha \beta \alpha$. Here the notations $\alpha$ and $\beta$ are the one-electron spin-up and spin-down functions, respectively (their definition can be found, e.g., in [6]). The notations $A$ and $B$ in Eq.(2) mean that the two sets of non-linear parameters associated with radial functions $\psi$ and $\phi$ can be optimized independently. In the general case, each of the radial basis functions explicitly depends upon all six interparticle (relative) coordinates $r_{12}, r_{13}, r_{23}, r_{14}, r_{24}, r_{34}$. It is clear that in actual bound state calculations only one spin function, e.g., the $\chi_1$ function, can be used. Note also that when the corresponding radial function has been constructed, then one can use an artifice called the ‘doubling’ of the wave function (see, e.g., [7]). This trick is based on the use of the same set of non-linear parameters in the two radial functions in Eq.(2). Obviously, this is not an optimal choice of the non-linear parameters in the wave function, but in many cases this simple handling leads to a substantial improvement of the answer.

The semi-exponential variational expansion of the radial function $\psi_{L=0}(A; \{r_{ij}\})$ from Eq.(2) is written in the form

$$\psi_{L=0}(A; \{r_{ij}\}) = \sum_{k=1}^{N} C_k r_{23}^{n_1(k)} r_{13}^{n_2(k)} r_{12}^{n_3(k)} r_{14}^{m_1(k)} r_{24}^{m_2(k)} r_{34}^{m_3(k)} \exp(-\alpha_k r_{14} - \beta_k r_{24} - \gamma_k r_{34})$$

(3)

where $\alpha_k, \beta_k, \gamma_k$ ($k = 1, 2, \ldots, N$) are the varied non-linear parameters. The presence of the varied non-linear parameters in Eq.(3) is the main and very important difference with the traditional Hylleraas variational expansion (see, e.g., [2]). In the last case in Eq.(3) we have $\alpha_1 = \ldots = \alpha_N, \beta_1 = \ldots = \beta_N$ and $\gamma_1 = \ldots = \gamma_N$. Note that all matrix elements of the Hamiltonian, Eq.(1), and overlap matrix needed in computations with the use of the semi-exponential basis, Eq.(3), contain the same three-electron integrals which arise for the usual Hylleraas expansion (for more detail, see discussion in [4]). In other words, numerical calculation of all matrix elements with semi-exponential functions is not a more difficult task than for the traditional Hylleraas radial functions. This also simplifies numerical computations of the bound state properties (i.e. expectation values) in the semi-exponential basis set. In particular, our algorithms used in calculations of all required matrix elements is based on the old Perkins formula for three-electron integrals [8] in relative coordinates. The explicit symmetrization of the wave function upon all permutations of identical particles
(electron) is discussed in detail in our earlier works (see, e.g., [4] and references therein). Note also that all calculations in this work have been performed with the use of standard quadruple precision accuracy (30 decimal digits per computer word). In our calculations we have used variational wave functions for the Li atom, Be$^+$ and B$^{3+}$ ions with 60 terms. To construct these wave functions we follow the procedure described in detail in [4].

As mentioned above in this study we consider the doublet $2^2S(L=0)$-states in the three-electron Li atom and in analogous Be$^+$ and B$^{2+}$ ions. The corresponding expectation values (or properties) can be found in Table I (in atomic units $\hbar = 1$, $e = 1$, $m_e = 1$). For most of the properties mentioned in Table I their meaning is clear from the notation used. Therefore, here we can restrict ourselves to a few following remarks. All electron-nucleus properties are designated below with the use of a general index $eN$ (electron-nucleus), while the notation $ee$ stands for electron-electron properties. For instance, the notations $\langle r_{eN} \rangle$ and $\langle r_{ee} \rangle$ mean the electron-nucleus and electron-electron distances, respectively. The total energies obtained with these 60-term wave functions are: $E = -7.47805$ 86794 4751 a.u. (Li atom), $E = -14.32475$ 2251 4351 a.u. (Be$^+$ ion) and $E = -23.42457$ 46190 439 a.u. (B$^{2+}$ ion), respectively.

The expectation values of the electron-nucleus and electron-electron delta-functions, i.e. $\langle \delta_{eN} \rangle$ and $\langle \delta_{ee} \rangle$ are of great interest in various applications. Therefore, it is important to be sure that these values have been determined correctly. For atomic and molecular systems with the Coulomb interaction between each pair of particles there is a very effective test which can be used to estimate the actual accuracy of the expectation values of all two-particle delta-functions $\langle \delta_r \rangle$. This test is based on accurate numerical evaluation of the electron-nucleus and electron-electron cusp values. In general, the cusp value between two point particles $a$ and $b$ with electrical charges $q_a$ and $q_b$ and masses $m_a$ and $m_b$ (in atomic units) is:

$$\nu_{ab} = \frac{q_a q_b m_a m_b}{m_a + m_b}$$

This is the expected (or ‘classical’) numerical value of the cusp between the electrically charged particles $a$ and $b$. In general, the cusp is defined by the equation (see, e.g., [9])

$$\nu_{ab} = \frac{\langle \delta(r_{ab}) \frac{\partial}{\partial r_{ab}} \rangle}{\langle \delta(r_{ab}) \rangle}.$$  \hspace{1cm} (5)

Numerical coincidence of the $\nu_{ab}$ and $\nu_{ab}$ values is a good test for the overall quality of the wave functions constructed for different atomic and molecular systems.
It should be mentioned that the ‘classical’ definition of the cusp (or cusp-condition) given by Eq.(5) can be generalized to quantum mechanics in a number of different ways. To explain this let us introduce the following cusp-operator

\[ \hat{\nu}_{ab} = \frac{1}{\langle \delta(r_{ab}) \rangle} \delta(r_{ab}) \frac{\partial}{\partial r_{ab}} \] (6)

For the expectation values one finds \( \nu_{ab} = \langle \Psi | \hat{\nu}_{ab} | \Psi \rangle \). Formally, we can consider the quantity \( \langle \Psi_i | \hat{\nu}_{ab} | \Psi_j \rangle \), where \( \Psi_i \) and \( \Psi_j \) are the two different wave functions from the bound state spectrum. The last expression, however, is not symmetric upon the \( i \leftrightarrow j \) substitution. Such a symmetry can be restored with the following redefinition of the cusp operator, Eq.(6):

\[ \hat{\nu}_{ab} = \frac{1}{2\langle \delta(r_{ab}) \rangle} \left[ \left( \frac{\partial}{\partial r_{ab}} \right) \delta(r_{ab}) + \delta(r_{ab}) \left( \frac{\partial}{\partial r_{ab}} \right) \right] \] (7)

where the differential operator with the index ‘→’ acts on its right, while analogous operator with the index ‘←’ acts on its left. The definition of the cusp operator based on Eq.(7) has a number of advantages in applications. In particular, it allows one to obtain more accurate values of the electron-nucleus and electron-electron cusps with the use of relatively short wave functions. In this study to determine the numerical values of all cusps mentioned in this Section we used the cusp operators written in the form of Eq.(7).

III. BASIS OF SIX-DIMENSIONAL GAUSSOIDS

For three-electron atoms and ions there is another variational expansion which can be effective to perform accurate computations of low-lying bound states, e.g., the low-lying bound \( S(L = 0) \)– and \( P(L = 1) \)–states. The high efficiency of such an expansion for bound state computations is based on very simple and numerically stable formulas for all matrix elements needed in computations of the total energies of these states. This variational expansion was developed in the mid-1970 by Kolesnikov and his group (see, e.g., [5] and references therein). In general, this expansion is also represented in the form of Eq.(2), but only radial functions are represented as linear combinations of the six-dimensional gaussoids, e.g., for \( \psi_{L=0}(A; \{r_{ij}\}) \) we have

\[ \psi_{L=0}(A; \{r_{ij}\}) = \sum_{k=1}^{N} C_k exp(-\alpha_{12}^{(k)} r_{12}^2 - \alpha_{13}^{(k)} r_{13}^2 - \alpha_{23}^{(k)} r_{23}^2 - \alpha_{14}^{(k)} r_{14}^2 - \alpha_{24}^{(k)} r_{24}^2 - \alpha_{34}^{(k)} r_{34}^2) \] (8)
where \( C_k \) are the linear coefficients (or linear variational parameters), and \( \alpha^{(k)}_{ij} r_{ij}^2 \) are the varied non-linear parameters. It is clear that for Coulomb systems each of the basis functions in Eq.(8) does not provide the correct long-range asymptotic between particles. Indeed, for the \( i \) and \( j \) particles the leading term in the asymptotics of the actual atomic wave function must be represented in the form \( r_{ij}^6 \exp(-\beta r_{ij}) \). Additional terms for Coulomb (or atomic) systems may include different powers of \( \log r_{ij}, \log |\log r_{ij}| \) and other similar factors. This follows from the general theory of bound states in the few-body Coulomb systems (see, e.g., [10] and references therein). It is clear that such terms cannot be derived from the approximate wave function Eq.(8). Based on this conclusion we can predict a number of different bound state properties with the use of variational expansion, Eq.(8). In reality, the variational expansion, Eq.(8), can be used for approximate evaluations of the bound state properties in atomic systems. Moreover, the spatial distribution of particles predicted from the wave function, Eq.(8), is always more diffuse than follows from similar calculations with the use of so-called ‘realistic’ variational expansions, e.g., Hylleraas expansion and/or exponential Hylleraas. Briefly, this means that in actual computations one will always obtain larger expectation values for all positive powers of interparticle distances \( r_{ij} \) than can be found with the use of ‘realistic’ variational expansions. For negative powers of interparticle distances \( r_{ij} \), e.g., for the \( \langle r_{ij}^{-1} \rangle \) and \( \langle r_{kl}^{-2} \rangle \) expectation values, the situation is opposite.

Formally, this means that the expectation values determined with the use of multi-dimensional gaussoids can be used as a one-sided approximation to the actual bound state properties of atomic systems. The procedure works in the following way. By using relatively large numbers of multi-dimensional gaussoids with carefully optimized non-linear parameters \( \alpha^{(k)}_{ij} \) in Eq.(8) we can obtain accurate numerical values of the total energies. Then we continue optimization of the non-linear parameters \( \alpha^{(k)}_{ij} \) in Eq.(8). The total energies continue to converge to their limiting values. However, the expectation values of many bound state properties rapidly improve during such an additional optimization. The principal question here is to evaluate the convergence rate of the variational expansion, Eq.(8). In our calculations we have found that the actual convergence rate for the total energies is relatively fast and already for \( N = 700 – 1000 \) in Eq.(8) we obtain results which can be considered as accurate, or even highly accurate.

The total energies of the ground \( 2S(L = 0) \)– and some excited \( n^2S(L = 0) \)–states \((n \geq 3)\) in some three-electron atoms and ions can be found in Table II (in atomic units).
Table III contains the bound state properties determined with the use of our best variational wave functions. In such calculations we have used only 700 basis functions (six-dimensional gausoids) with carefully optimized non-linear parameters. It should be mentioned here that highly accurate wave functions can be constructed with the use of 2000 (or more) basis functions (six-dimensional gausoids) with carefully optimized non-linear parameters. The explicit construction of such accurate wave functions with 2000 terms (or more) does not require excessive computational resources, but in calculations performed for this study we restrict ourselves to bound state wave functions with \( N = 700 \) terms only. There are two reasons for this. First, we compare our bound state properties with analogous properties computed in earlier papers (see, e.g., [11] and references therein) where the total number of basis functions used was \( \approx 500 - 800 \), which is comparable to 700. Second, many differences between accurate bound state properties obtained with \( N = 700 \) basis functions in Eq.(8) and highly accurate values determined with \( N = 2000 \) basis functions in Eq.(8) are of interest for some special purposes only. The overall accuracy of our computed bound state properties is sufficient to predict the results of various experiments performed for three-electron atomic systems. Moreover, our results obtained for the three-electron atomic systems presented in Tables I and III can be used as a basis for more accurate calculations of bound state properties in the future.

To conclude this Section we note that there is another fundamental question about accurate calculations of bound state properties. In general, the physical meaning of each property is clear only for those few-body systems where any group of particles do not form any closed shells, or cluster structures. Otherwise, the meaning of the computed properties rapidly became unclear when the total number of identical particles increases. For instance, for highly excited \( ^2S(L = 0) \)–states in the Li atom (see Tables II and III) one of the three electrons is moving as almost free particle. In old atomic physics such a motion was considered as the pre-dissociation. This means that the electron-nucleus distance for that electron is extremely large in comparison to the analogous distances determined for two other electrons which occupy the closed \( 1^2s \)–shell. To calculate the expectation value \( \langle r_{eN} \rangle \) we need to sum up all three electron-nucleus distances (two relatively short and one very large \( r_{eN} \) distances) and divide the arising sum by three. Finally, we obtain the expectation value \( \langle r_{eN} \rangle \) which, in fact, gives us no useful information. It is similar to the mean patient temperature measured over the 'whole hospital'. The same is true for other bound state
properties, including all electron-nucleus and electron-electron properties. Formally, in such cases we need to assume that some originally identical particles becomes ‘less-identical’, or even ‘non-identical’ for highly excited states. If such an assumption has been made, then the expectation values of different properties provide us with useful information which has a direct physical sense. However, at this moment we do not have reliable recipes for calculations of such values, since \textit{a priori} the ‘power of non-identity’ for the outer most electron is no clear, e.g., in the $4^2S^-, 5^2S^-$ and $6^2S^-$ state (see Tables II and III). The power of ‘non-identity’ increases with the excitation, i.e. with the principal quantum number $n$.

**IV. ON GENERAL STRUCTURE OF THE BOUND STATE SPECTRA**

The general structure of the bound state spectra in three-electron atoms and ions was considered in our earlier paper [12]. In this paper by using the energy values obtained in [12] for the Li atom and the Be$^+$ ion we have drawn the spectral diagrams of these species. For this study we slightly improved numerical values of the total energies and draw the spectral diagrams for the doublet series of the Li atom and the Be$^+$ ion (see Figs. 1 and 2). In particular, the spectra of the Li atom is identical to the experimental spectra given in the classical book [13]. In this work we would like to continue our theoretical analysis of the bound state spectra in three-electron atoms and ions. The analysis of the bound state spectra in similar atomic systems is based on the use of fast-convergent variational expansions which provide high numerical accuracy not only for the ground and some low-lying rotationally excited states, but for all excited states in few-electron atom(s) and ions. This expansion is the Hylleraas-configuration interaction (Hy-CI) wave function, proposed by Sims and Hagstrom [14, 15], which we have used to determine the $S-, P-, D-$ states of the C$^{3+}$ and F$^{6+}$ ions and the Configuration Interaction (CI) wave function with Slater orbitals and $LS$ configurations for the states of higher symmetry $F, G, H, I$ and $K$. Note that the Hy-CI is general for any symmetry. At the moment in our computer program the kinetic energy integrals are restricted to $l = 3$, work is in progress to generalize our code for $l \geq 3$. Nevertheless, the CI wave function leads to very good results for states with quantum number $L \geq 3$. The Hy-CI and CI wave functions can be summarized in the following...
expression:

\[ \Psi = \sum_{p=1}^{N} C_p \Phi_p, \quad \Phi_p = \hat{O} (\hat{L}^2) \hat{A} \psi_p \chi \]  

\( N \) is the number of configurations \( \Phi_p \), and \( C_p \) a variational coefficient. All configurations are symmetry-adapted (this is expressed in the last equation with the operator \( \hat{O}(\hat{L}^2) \)). The operator \( \hat{A} \) is the antisymmetrization operator and \( \chi \) is the spin eigenfunction:

\[ \chi = [(\alpha \beta - \beta \alpha) \alpha] . \]  

The Hartree products are multiplied by up to one interelectronic coordinate \( r_{ij} \)

\[ \psi_p = r_{ij}^\nu \prod_{k=1}^{n} \phi_k(r_k, \theta_k, \varphi_k), \]  

where the choice \( \nu = 0 \) corresponds to the CI wave function, while for \( \nu = 1 \) we have the Hy-CI wave function. To calculate the bound (doublet) states in the \( \mathrm{C}^{3+} \) and \( \mathrm{F}^{6+} \) ions we have optimized the exponents of the wave function expansions for the \( \mathrm{Li} \) and \( \mathrm{Be}^+ \) atoms of Ref. [12] for the nuclear charges \( Z = 6 \) and \( Z = 9 \). In the Hy-CI calculations we have employed \( \approx 1000 \) configurations, while in the CI calculations between \( 1000 \) and \( 1500 \) configurations. The construction of the configurations is described in [12], as so as further details of the calculations. The obtained energies are listed in Table IV. For these ions, the literature is very scarce. Here we have tried to improve our earlier results for the bound states of the \( \mathrm{Li} \) atom and \( \mathrm{Be}^+ \) ion. However, for most of these states we could not obtain any noticeable/substantial improvement. With the data of Table IV we have drawn the spectral diagrams of these ions, see Figs. 3 and 4. We have scaled these diagrams taking for every one the ground state energy level as lowest point and the limit of ionization as highest point, and calculating the position of the states with respect to this interval. Therefore we can compare the relative position or contraction of the energy levels of every specie with respect to its ground state. Our theoretical distribution of energy levels agrees completely with the experimental results [16]. In addition we have determined in this work atomic levels which experimental values have not been yet reported, like states with \( L \geq 4 \) in \( \mathrm{Li} \) atom, \( L \geq 6 \) of \( \mathrm{Be}^+ \) ion, \( L = 7 \) of \( \mathrm{C}^{3+} \) and \( L \geq 4 \) of \( \mathrm{F}^{6+} \) ion.

As is well known from basics of atomic spectroscopy (see, e.g., [17]) all three-electron atoms and ions are observed in the two series of states: (a) doublet states with \( S_e = \frac{1}{2} \), and (b) quartet states with \( S_e = \frac{3}{2} \), where \( S_e \) designates the total electron spin. The quartet
states in these atomic systems are non-stable, i.e. they decay for relatively short times. Thus, the only bound states which are observed in actual spectroscopy of three-electron atomic systems are the doublet states. Therefore, below in this Section we restrict ourselves to the consideration of the doublet (bound) states only. As mentioned in the Introduction the atomic Hamiltonian, Eq. (1), contains equal numbers of electron-nucleus and electron-electron terms. Indeed, in Eq. (1) one finds three terms which describe electron-nucleus attraction and three other terms which describe electron-electron repulsion. The first four terms in Eq. (1) represent the kinetic energy of the four particles (three electrons and one nucleus). This means that by varying the electric charge of the central nucleus $Q$ we can study the role of electron-electron correlations in three-electron atomic systems. It is clear that by increasing $Q$ we can reduce the overall role of electron-electron repulsions in three-electron ions. There are three electron-nucleus terms and three electron-electron terms in the potential energy of the Hamiltonian, Eq. (1). This means that by varying $Q$ we change relations between each electron-nucleus and electron-electron terms. On the other hand, an analogous relation between the total sum of the three electron-nucleus terms and the total sum of the three electron-electron terms changes in the same proportion.

The electronic structure of the ground (bound) doublet $2^2S$—state of the three-electron Li atom is $1s^22s^1$, while all excited states have a similar structure where the two electrons occupy the $1s^2$-electron shell (its excitation energy is extremely large), while the third electron can occupy any free electron orbital in the atom. Formally, we can say that the third electron is located in one of the $n\ell$-shells, where $\ell \geq 0$, $n = k + \ell + 1$ and $k \geq 0$ (all these numbers are integer). Possible excitations of the Li atom always mean the excitation of the third electron, which sometimes is considered as an ‘optical’ electron. Any excitation of the central electron $1^2s$-shell leads to the complete dissociation of the whole atom. In the lowest-order approximation we can say that the optical spectrum of the Li-atom is similar to the well known spectrum of the hydrogen atom. However, the actual similarities in optical spectra can be found only for highly excited bound states in the Li atom which are often called the Rydberg states.

As follows from the general theory of atomic spectra the total energies of weakly-bound Rydberg states in any neutral atom must be represented by a formula which is similar to the well known formula for the hydrogen-like atoms. Let us discuss such a formula in detail. First, note that the dissociation threshold for the neutral Li-atom corresponds to the
formation of the two-electron Li$^+$ ion in its ground $1^1S$-state (singlet). The non-relativistic energy of this state is $E_{\infty \text{Li}^+} \approx -7.279913 412669 305964 91895(15)$ a.u. \[18\]. This dissociation threshold corresponds to the following ionization process for the neutral Li atom

$$\text{Li} = \text{Li}^+(1^1S) + e^- \quad (12)$$

where the symbol Li$^+(1^1S)$ means that the final two-electron Li$^+$ ion is in its ground (singlet) $1^1S$-state. Now, we can write the following expression for the total energies of the weakly-bound states, i.e. for the states which are close to the dissociation threshold of the Li atom (in atomic units):

$$E(\text{Li}; nL) = E(\text{Li}^+; 1^1S) - \frac{m_e e^4}{2\hbar^2} \frac{1 - \epsilon_\ell}{(n + \Delta_\ell)^2} = -7.279913412669305 \ldots - \frac{1 - \epsilon_\ell}{2(n + \Delta_\ell)^2} \quad (13)$$

where $L = \ell$ (in this case), $n$ is the principal quantum number of the $nL$ state ($L$ is the angular quantum number) of the Li atom, while $\epsilon_\ell$ and $\Delta_\ell$ are the Rydberg corrections ($\Delta_\ell$ is also called the ‘quantum defect’) which explicitly depends upon $\ell$ (angular momentum of the outer most electron) and the total electron spin of this atomic state. It can be shown that both Rydberg corrections rapidly vanish when $\ell$ increases (for given $n$ and $L$). Moreover, these two corrections also decrease when the principal quantum number $n$ grows. The formula, Eq.(13), can be used to approximate the total energies of weakly-bound Rydberg states in the Li atom. In reality, by using a few accurate (or highly accurate) results from numerical calculations of some excited (bound) states in the Li atom one finds the approximate values for the $\epsilon_\ell$ and $\Delta_\ell$ constants in Eq.(13). Analogous formulas can be derived to describe the total energies of the excited bound states in three-electron ions, e.g., in the Be$^+$, C$^{3+}$ and F$^{6+}$ ions. However, after neon the validity of the non-relativistic approximation for three-electron ions rapidly diminishes as the parameter $Q$ in Eq.(11) continue to grow. In the lowest-order approximation the leading relativistic corrections can directly be introduced into Eq.(13), but in this paper we do not discuss this problem. Note only that the numerical values of the quantum defect $\Delta_\ell$ are uniformly related to the short-range (or non-Coulomb) component of the phase shifts of elastic scattering of single-electron scattering by the two-electron positively charged ions [19]. This directly follows from the unitarity of the $S$–matrix (see, e.g., [20], [21]).

By using our computational results for the large number of bound states in the three-electron Li atom and in analogous Be$^+$, C$^{3+}$ and F$^{6+}$ ions (see Table IV) we were able to
draw the energy levels of all computed doublet (bound) states in these atomic systems as functions of angular momentum $L$ of these states (see, Figs. 1 - 4). Note that the total energies of all states shown on these Figures are lower than the corresponding threshold energies of these systems: $E_{\infty \text{Li}^+} \approx -7.279913\,412669\,305964\,91895(15)$ a.u., $E_{\infty \text{Be}^{2+}} \approx -13.65556\,623842\,358670\,208085(55)$ a.u., $E_{\infty \text{C}^{3+}} \approx -32.40624\,660189\,853031\,055785(45)$ a.u. and $E_{\infty \text{F}^{7+}} \approx -75.53171\,236395\,949115(3)$ a.u. In old books on atomic spectroscopy such pictures (or diagrams) were called ‘spectral diagrams’. Spectral diagrams can be very useful tools to study various effects related with the electron density distribution in different bound $LS$-states of the atomic systems which contain the same number of electrons. In general, such spectral diagrams can be drawn for the neutral atoms as well as for various positively charged ions, e.g., for the Be atom and $\text{B}^{2+}$, $\text{N}^{4+}$ and other similar three-electron ions. The bound state spectra of the negatively charged ions, e.g., the $\text{Li}^-$ ion) contain only a very few bound states (usually one bound state [22]) and the corresponding spectral diagrams are very simple and not informative.

Let us discuss the spectral diagrams of the three-electron atomic systems shown on Figs. 1 - 4. As follows from these pictures the increase of the nuclear charge $Q$ in these systems leads to the ‘hydrogenization’ of the optical spectrum along the line: $\text{Li} \rightarrow \text{Be}^+ \rightarrow \text{C}^{3+} \rightarrow \text{F}^{6+}$. The energy levels are re-grouping (when $Q$ increases) into clusters which contain the energy levels with the same principal quantum number $n$. In other words, the differences between energies of levels with the same principal quantum number $n$ become much smaller than analogous differences between two energy levels with different principal quantum numbers $n$ and $n'$. As one can see from our pictures such a clusterization rule is applied even to the energy levels with $n = 2$ and $n = 3$. Based on this observation we can predict that in the limit $Q \rightarrow \infty$ the bound state spectrum of three-electron ions looks like the bound state spectrum (or optical spectrum, for short) of a typical hydrogen-like ion in which, however, the ground state (or $1^2S$-state) is missing. Briefly, we can say that the ‘optical’ spectrum of the doublet bound states in three-electron ions converges (at $Q \rightarrow \infty$) to the doublet spectrum of a hydrogen-like atomic system, where the ground $1^2S$-state is missing. This explains why the traditional classification scheme used for bound state spectra in atomic spectroscopy is correct. For all atoms from the second row the ground state(s) must have the fundamental quantum number $n = 2$ (not $n = 1$, or $n = 3$). It is clear that changes in the optical spectra of the three-electron atomic systems: $\text{Li}$, $\text{Be}^+$, $\text{C}^{3+}$ and $\text{F}^{6+}$ are
directly related with the $Q$–dependent balance between the electron-nucleus attractions and electron-electron repulsions. Another observation when comparing the spectral diagrams of the three-electron systems is the larger relative stabilization or contraction of the $2^2P$ level when growing the nuclear charge, while other low-lying levels are only slightly contracted. There are many other observations which follow from Figs. 1 - 4, which shall stimulate future research.

Similarity between spectra of bound doublet $^2S$–states in different three-electron atomic systems can be seen from comparison of Figs.1 - 4 with each other. However, if we compare the same spectra reduced to the unit scale, then the observed agreement improves drastically. The procedure of reduction can be described as follows. First, for each three-electron atomic system with the nuclear charge $Q$ one needs to know the corresponding threshold energy $E_{tr}$. Usually, such an energy coincides with the total energy of the ground $1^1S$–state of the two-electron ion which is formed from the incident three-electron atomic system after single-electron ionization. Second, the total energy of the ground $2^2S$–state $E_{gr}$ must be determined (i.e. measured and/or calculated) to the maximal numerical accuracy. The total energies of other bound doublet states are recalculated with the use of the formula: 
$$\tilde{E}_n = \frac{E_n - E_{tr}}{E_{gr} - E_{tr}}.$$ 
Finally, we have the new ‘energy’ spectrum $\tilde{E}_n$. All eigenvalues from this spectrum are bounded between 0 and 1. Furthermore, there is only one limiting point for the spectrum of bound states $\tilde{E}_n$ and it coincides with 0 (or $E_{tr}$ in the original units). Briefly, we can say that all bound states $\tilde{E}_n$ can converge only to this ‘limiting’ point. Since the threshold state is an actual state of any three-electron atomic system then the wave functions of bound states do not form a complete system of functions (for more detail, see, e.g., [22]). The energy spectra $\tilde{E}_n$ of different three-electron atoms and ions (doublet states) once reduced to the same energy scale can be compared with each other directly.

V. CONCLUSION

We have considered bound state spectra and properties of the doublet states in three-electron atomic systems. In this study we applied three different variational expansions for the bound state wave functions: (a) semi-exponential expansion in the relative coordinates, (b) expansion written in six-dimensional gaussoids, and (c) Hy-CI expansion for the low-lying $S$, $P$, and $D$–states of C$^{3+}$ and F$^{6+}$ ions, and (d) CI expansion for the $L \geq 3$ states.
Very compact wave functions constructed with the use of the semi-exponential expansion in the relative coordinates allow one to determine a large number of bound state properties, including the expectation values of electron-nucleus and electron-electron delta-functions and cusp values. The observed coincidence of the computed cusp values with the predicted cusps (for Coulomb systems) is sufficient to recognize our trial wave functions accurate for numerical computations of all bound state properties. Variational expansion in six-dimensional gaussoids is used to perform fast and accurate calculations of some excited states in three-electron atomic systems (atoms and ions). Results of such calculations include not only the total energies, but also a large number of other bound state properties. Moreover, numerical results of our calculations presented in Tables I and III allows us to correct a few mistakes/misprints made in earlier works in definition of these properties and/or in their numerical values. Our variational Hy-CI and CI wave function expansions are used to determine the total energies of various ‘rotationally’ and ‘vibrationally’ excited states in three-electron atoms and ions. In our calculations we consider a large number of the $S(L = 0)-, P(L = 1)-, D(L = 2)-, F(L = 3)-, G(L = 4)-, H(L = 5)-, I(L = 6)-, \text{and } K(L = 7)-$states. Accurate results for highly excited rotational states have been determined in this study for the first time. The coincidence of our theoretically predicted spectrum (or computational spectrum) with the known optical spectrum of the three-electron Li atom is absolute [13], [16] since we correctly predicted the actual order of different energy levels (or bound states) in this spectrum and evaluated the energy distances between different levels (to very good numerical accuracy).

Our main goal in this study was to consider the bound state spectra and properties of the doublet states in three-electron atomic systems: Li atom, Be$^+$, C$^9+$ and F$^+$ ions. The general structure of the bound state spectra in these three-electron atomic systems has been determined from the results of accurate numerical computations performed with the use of the Hy-CI and CI variational expansions. By varying the nuclear electric charge $Q$ we investigated changes in the bound state spectra of such systems. The overall and partial contributions of the electron-electron correlations in the total energies of bound (doublet) states have been evaluated to high numerical accuracy. Formally, it is the first theoretical study in which a large number of bound states in a few three-electron atoms/ions are determined in highly accurate computations. In contrast with many modern studies we considered not one, or two bound states in three-electron atoms/ions, but essentially a whole
bound state spectrum for each of the systems mentioned in this study. At the post Hatree-Fock level of accuracy for the doublet (bound) states in three-electron atoms and ions this was made for the first time. In the future, we are planning to study some other aspects of physics of three-electron atomic systems.

[1] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics. Non-Relativistic Theory*, (3rd ed., Oxford, England, Pergamon Press (1977)).
[2] S. Larsson, Phys. Rev. **169**, 49 (1968).
[3] R. McWeeny and B.T. Satcliffe, *Methods of Molecular Quantum Mechanics*, (New York: Academic Press, 1969), Chp. 7.
[4] A.M. Frolov, Phys. Lett. A **374**, 2361 (2010).
[5] N.N. Kolesnikov and V.I. Tarasov, Yad. Phys. **35**, 609 (1982) [Sov. Phys. Nucl. Phys. **35**, 354 (1982)].
[6] P.A.M. Dirac, *The Principles of Quantum Mechanics* (4th ed., Oxford at the Clarendon Press, Oxford, (1958)).
[7] A.M. Frolov, Europ. Phys. J. D **61**, 571 (2011).
[8] J.F. Perkins, J. Chem. Phys. **48**, 1985 (1968).
[9] D.P. Chong and D.M. Schrader, Mol. Phys. **16**, 137 (1969).
[10] V.A. Fock, Izv. Acad. Nauk USSR (Ser. Fiz.) **18**, 161 (1954).
[11] F.W. King, Phys. Rev. **40**, 1735 (1989).
[12] M.B. Ruiz, J.T. Margraf, and A.M. Frolov, Phys. Rev. A, **88**, 012505 (2013).
[13] *Handbook. Tables of Physical Quantities* (Ed. I.K. Kikoin, Moscow, Atomizdat, (1974)), p.654 (in Russian).
[14] J.S. Sims and S.A. Hagstrom, J. Chem. Phys. **55**, 4699 (1971).
[15] J.S. Sims and S.A. Hagstrom, Phys. Rev. A **4**, 908 (1971).
[16] A. Kramida, Yu. Ralchenko, J. Reader and NIST ASD Team (2013). NIST Atomic Spectra Database (ver. 5.1), [Online]. Available: [http://physics.nist.gov/asd](http://physics.nist.gov/asd) [2014, March 17]. National Institute of Standards and Technology, Gaithersburg, MD.
[17] I.I. Sobelman, *Theory of Atomic Spectra*, (Alpha Science International Ltd., 2006), Chp. 2.
[18] A.M. Frolov and D.M. Wardlaw, *On the isotopic shifts in light two-electron ions,*
[19] P.G. Burke and C.J. Joachain, *Theory of Electron-Atom Collisions: Part One: Potential Scattering*, (New York: Plenum Press, 1995).

[20] P.L. Kapur and R.L. Peierls, Proc. Roy. Soc. (London) A *166*, 277 (1938).

[21] A.I. Baz, Ya.B. Zeldovich and A.M. Perelomov, *Scattering, Reactions and Decays in the Non-Relativistic Quantum Mechanics*, (2nd ed., Moscow: Science, 1973). (in Russian).

[22] A.M. Frolov, Phys. Rev. A *59*, 4270 (1999).
FIG. 1 – Energy levels for the duplet states of the lithium atom. The threshold energy -7.279913 412669 . . . a.u. coincides with the total energy of the ground 1^1S state of the two-electron Li^+ ion.
FIG. 2 – Energy levels for the duplet states of the Be$^+$ ion. The threshold energy -13.65566 623842 a.u. coincides with the total energy of the ground $1^1S$ state of the two-electron Be$^{2+}$ ion.
FIG. 3 – Energy levels for the duplet states of the C\(^{3+}\) ion. The threshold energy \(-32.40624 \pm 660189\) a.u. coincides with the total energy of the ground \(1^1S\) state of the two-electron C\(^{4+}\) ion.
| E(F^{7+}) | \(^2S\) | \(^2P\) | \(^2D\) | \(^2F\) | \(^2G\) | \(^2H\) | \(^2I\) | \(^2K\) |
|-----------|--------|--------|--------|--------|--------|--------|--------|--------|
| \(n\)    | \(6s\) | \(6p\) | \(6d\) | \(6f\) | \(6g\) | \(6h\) | \(7i\) | \(8k\) |
| \(7\)    |        |        |        |        |        |        |        |        |
| \(6\)    |        |        |        |        |        |        |        |        |
| \(5\)    |        |        |        |        |        |        |        |        |
| \(4\)    |        |        |        |        |        |        |        |        |
| \(3\)    |        |        |        |        |        |        |        |        |
| \(2\)    |        |        |        |        |        |        |        |        |

**FIG. 4** – Energy levels for the duplet states of the F\(^{6+}\) ion. The threshold energy -75.53171 236395 a.u. coincides with the total energy of the ground \(^1S\) state of the two-electron F\(^{7+}\) ion.
TABLE I – The expectation values of a number of electron-nuclear (en) and electron-electron (ee) properties of the ground $^2S$ states of the $\infty$Li atom and in the $\infty$Be$^+$ and $\infty$B$^{2+}$ ions (in atomic units). The notations $\langle V \rangle$ and $\langle T \rangle$ stand for the expectation values of the potential and kinetic energy, respectively.

| atom/ion | state | $\langle r_{eN}^{-1} \rangle$ | $\langle r_{eN} \rangle$ | $\langle r_{eN}^2 \rangle$ | $\langle r_{eN}^3 \rangle$ | $\langle r_{eN}^4 \rangle$ |
|----------|-------|-----------------|-------------|-----------------|-----------------|-----------------|
| Li       | $^2S$  | 1.906 035 791   | 1.663 195 075 | 6.118 405 34    | 30.869 167      | 183.374 94      |
| Be$^+$   | $^2S$  | 2.657 954 038   | 1.033 837 514 | 2.169 559 41    | 6.230 124 0     | 21.078 833      |
| B$^{2+}$ | $^2S$  | 3.408 499 326   | 0.760 963 580 | 1.132 751 15    | 2.301 051 6     | 5.509 837 4     |
| Li       | $^2S$  | 0.732 736 059   | 2.889 506 202 | 12.283 005 19   | 64.032 401 8    | 385.287 08      |
| Be$^+$   | $^2S$  | 1.082 004 350   | 1.755 762 092 | 4.358 489 915   | 13.143 659 0    | 45.476 089      |
| B$^{2+}$ | $^2S$  | 1.426 153 105   | 1.278 851 329 | 2.275 177 620   | 4.895 786 45    | 12.056 833      |

The expected value of the electron-nucleus cusp $\nu_{eN}$ for these atomic systems are -3.0, -4.0 and -5.0, respectively. The expected value of the electron-electron cusp equals 0.5 for all systems.

TABLE II – The total energies $E$ of some bound $^2S(L = 0)$ states of three-electron atomic systems (in atomic units).

| atom (state)       | $E$     | ion (state)       | $E$     |
|-------------------|---------|-------------------|---------|
| Li($^2S$-state)    | -7.478 059 305 6 | Be$^+$ ($^2S$-state) | -14.324 762 475 |
| Li($^3S$-state)    | -7.354 092 191 5 | B$^{2+}$ ($^2S$-state) | -23.424 605 665 |
| Li($^4S$-state)    | -7.318 322 871 7 | C$^{3+}$ ($^2S$-state) | -34.775 510 611 |
| Li($^5S$-state)    | -7.303 035 987 5 | N$^{4+}$ ($^2S$-state) | -48.376 895 687 |
| Li($^6S$-state)    | -7.294 185 650 9 | O$^{5+}$ ($^2S$-state) | -64.228 536 798 |
TABLE III – The expectation values of a number of electron-nuclear \((eN)\) and electron-electron \((ee)\) properties of some \(n^3S\)–states of the \(\infty\) Li atom (in atomic units).

| atom/ion | state | \(\langle r_{eN}^{-2} \rangle\) | \(\langle r_{eN}^{-1} \rangle\) | \(\langle r_{eN} \rangle\) | \(\langle r_{eN}^2 \rangle\) | \(\langle r_{eN}^3 \rangle\) | \(\langle r_{eN}^4 \rangle\) |
|----------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Li       | \(2^2S\) | 10.080 299 4    | 1.906 039 847  | 1.663 109 090  | 6.117 134 5    | 30.851 654  | 183.123 19 |
| Li       | \(3^2S\) | 9.981 917 49    | 1.837 285 201  | 3.761 794 359  | 39.355 058  | 494.128 87 | 6754.515 6 |
| Li       | \(4^2S\) | 9.964 058 61    | 1.816 645 372  | 6.770 167 230  | 137.786 12    | 3162.403 2  | 76536.723 |
| Li       | \(5^2S\) | 9.958 617 52    | 1.807 857 735  | 10.679 326 23  | 355.933 01    | 13021.648 | 497002.44 |
| Li       | \(6^2S\) | 9.953 624 06    | 1.806 881 865  | 13.496 976 48  | 605.601 45    | 30273.607  | 1593843.5 |
| Be\(^+\) | \(2^2S\) | 18.998 590 7    | 2.657 962 909  | 1.033 794 541  | 2.169 283 9    | 6.228 668 9  | 21.071 369 |
| B\(^{2+}\) | \(2^2S\) | 30.753 953 0    | 3.408 508 316  | 0.760 947 608  | 1.132 687 8    | 2.300 818 2  | 5.508 807 8 |
| C\(^{3+}\) | \(2^2S\) | 45.344 321 5    | 4.158 733 330  | 0.604 265 262  | 0.699 597 9    | 1.103 076 8  | 2.050 509 3 |

| atom/ion | state | \(\langle r_{ee}^{-2} \rangle\) | \(\langle r_{ee}^{-1} \rangle\) | \(\langle r_{ee} \rangle\) | \(\langle r_{ee}^2 \rangle\) | \(\langle r_{ee}^3 \rangle\) | \(\langle r_{ee}^4 \rangle\) |
|----------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Li       | \(2^2S\) | 1.460 400 61    | 0.732 741 804  | 2.889 335 105  | 12.280 459 71  | 63.997 183 3  | 384.779 568 |
| Li       | \(3^2S\) | 1.384 494 71    | 0.609 106 619  | 7.062 134 612  | 78.736 745 89  | 994.292 830  | 13628.009 3 |
| Li       | \(4^2S\) | 1.370 301 61    | 0.570 107 087  | 13.071 985 49  | 275.591 830 6  | 6336.194 77  | 153487.273 |
| Li       | \(5^2S\) | 1.366 225 95    | 0.552 955 112  | 20.887 497 96  | 711.881 351 3  | 26061.569 8  | 995065.738 |
| Li       | \(6^2S\) | 1.365 134 34    | 0.549 884 122  | 26.522 667 32  | 1211.220 091  | 60570.560 6  | 3189490.25 |
| Be\(^+\) | \(2^2S\) | 2.965 647 83    | 1.082 010 050  | 1.755 675 812  | 4.357 934 64  | 13.140 698 4  | 45.460 678 |
| B\(^{2+}\) | \(2^2S\) | 5.003 263 19    | 1.426 139 241  | 1.278 829 658  | 2.275 086 36  | 4.895 414 30 | 12.054 916 |
| C\(^{3+}\) | \(2^2S\) | 7.573 737 72    | 1.768 726 769  | 1.009 280 654  | 1.404 716 97  | 2.358 787 32 | 4.526 486 7 |

| atom/ion | state | \(\langle \frac{\langle p_r^2 \rangle}{n} \rangle\) | \(\langle \frac{\langle p_r^2 \rangle}{n^2} \rangle\) | \(\langle \delta_{eN} \rangle\) | \(\langle \delta_{ee} \rangle\) | \(\langle \delta_{eeN} \rangle\) |
|----------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Li       | \(2^2S\) | 2.492 691 382   | 7.779 910 372 5 | 4.606 012 64   | 0.181 680  | 0.0  | 0.0 |
| Li       | \(3^2S\) | 2.451 385 231   | 7.646 135 483 5 | 4.561 675 57   | 0.179 148 | 0.0  | 0.0 |
| Li       | \(4^2S\) | 2.440 390 622   | 7.611 055 084 9 | 4.539 860 86   | 0.178 983 | 0.0  | 0.0 |
| Li       | \(5^2S\) | 2.436 280 805   | 7.595 599 533 0 | 4.509 057 69   | 0.178 294 | 0.0  | 0.0 |
| Li       | \(6^2S\) | 2.434 539 590   | 7.594 103 936 3 | 4.505 469 21   | 0.178 076 | 0.0  | 0.0 |
| Be\(^+\) | \(2^2S\) | 4.774 920 765 8 | 14.777 678 267 | 11.675 327 7   | 0.527 407 | 0.0  | 0.0 |
| B\(^{2+}\) | \(2^2S\) | 7.808 200 762 4 | 24.030 675 323 | 23.762 894 4   | 1.159 956 | 0.0  | 0.0 |
| C\(^{3+}\) | \(2^2S\) | 11.591 836 343  | 35.535 669 731 | 42.250 351 4   | 2.166 298 | 0.0  | 0.0 |
TABLE IV – Calculated Hy-Cl / Cl energies of the ground S-state and low-lying S-, P-, D-, F-, G-, H-, I-, and K-excited states of the C$^{3+}$ and F$^{6+}$ ions.

| State | Energy (Li)$^a$ | Energy (Be$^+$)$^b$ | Energy (C$^{3+}$)$^c$ | Energy (F$^{6+}$)$^d$ |
|-------|----------------|-----------------|-----------------|-----------------|
| 2S    | -7.478 058 969 | -14.324 761 678 | -34.775 407 123 | -82.330 336 543 |
| 3S    | -7.354 093 706 | -13.922 784 968 | -33.396 193 013 | -78.441 024 591 |
| 4S    | -7.318 517 759 | -13.798 706 849 | -32.947 562 660 | -77.139 946 952 |
| 5S    | -7.303 512 964 | -13.744 580 355 | -32.746 301 042 | -76.542 595 063 |
| 6S    | -7.295 739 603 | -13.716 223 859 | -32.640 301 515 | -76.234 472 428 |
| 7S    | -7.291 231 582 | -13.699 298 491 | -32.576 281 553 | -76.044 227 651 |
| 8S    | -7.288 391 657 | -13.687 953 747 | -32.534 060 652 | -75.918 626 871 |
| 2P    | -7.410 149 407 | -14.179 327 999 | -34.482 061 251 | -81.820 872 700 |
| 3P    | -7.337 113 114 | -13.885 115 345 | -33.317 932 151 | -78.300 897 021 |
| 4P    | -7.311 811 529 | -13.783 574 124 | -32.915 327 522 | -77.083 158 097 |
| 5P    | -7.300 137 068 | -13.736 854 458 | -32.730 766 119 | -76.521 194 900 |
| 6P    | -7.293 967 122 | -13.711 935 268 | -32.631 098 568 | -76.217 166 129 |
| 7P    | -7.289 814 402 | -13.696 356 527 | -32.570 511 575 | -76.033 783 122 |
| 8P    | -7.288 391 657 | -13.687 953 747 | -32.534 060 652 | -75.918 626 871 |
| 3D    | -7.335 512 623 | -13.878 041 021 | -33.296 030 365 | -75.834 760 570 |
| 4D    | -7.311 211 047 | -13.780 663 883 | -32.906 635 904 | -77.063 937 284 |
| 5D    | -7.299 889 424 | -13.735 539 056 | -32.725 486 398 | -76.512 140 941 |
| 6D    | -7.293 697 654 | -13.710 204 495 | -32.575 805 332 | -76.211 610 266 |
| 7D    | -7.289 806 792 | -13.695 586 302 | -32.430 255 083 | -76.011 876 013 |
| 8D    | -7.286 877   | -13.510 107    | -32.530 098    | -75.913 270    |
| 2F    | -7.310 610   | -13.779 946    | -32.905 543    | -77.062 191    |
| 5F    | -7.299 340   | -13.734 924    | -32.725 519    | -76.510 913    |
| 6F    | -7.293 211   | -13.710 457    | -32.627 715    | -76.211 439    |
| 7F    | -7.289 401   | -13.695 579    | -32.568 601    | -76.030 711    |
| 8F    | -7.286 877   | -13.510 107    | -32.530 098    | -75.913 270    |
Continuation Table IV Calculated Hy-Cl / CI energies of the ground S-state and low-lying S-, P-, D-, F-, G-, H-, I-, and K-excited states of the C$^{3+}$ and F$^{6+}$ ions.

| State | Energy (Li)\textsuperscript{a} \textsuperscript{[12]} | Energy (Be\textsuperscript{+})\textsuperscript{b} \textsuperscript{[12]} | Energy (C$^{3+}$)\textsuperscript{c} | Energy (F$^{6+}$)\textsuperscript{d} |
|-------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 5\textsuperscript{2}G | -7.299 430 | -13.734 968 | -32.725 629 | -76.511 030 |
| 6\textsuperscript{2}G | -7.293 317 | -13.710 575 | -32.616 005 | -76.045 060 |
| 7\textsuperscript{2}G | -7.289 605 | -13.695 662 | -32.568 689 | -75.925 387 |
| 8\textsuperscript{2}G | -7.287 191 | -13.686 138 | -32.530 498 | -75.913 584 |
| 6\textsuperscript{2}H | -7.293 320 | -13.710 578 | -32.627 852 | -76.211 587 |
| 7\textsuperscript{2}H | -7.289 625 | -13.695 828 | -32.568 882 | -76.031 019 |
| 8\textsuperscript{2}H | -7.287 164 | -13.678 867 | -32.530 528 | -75.913 734 |
| 7\textsuperscript{2}I | -7.289 635 | -13.695 844 | -32.568 900 | -76.031 036 |
| 8\textsuperscript{2}I | -7.287 159 | -13.686 179 | -32.529 952 | -75.913 730 |
| 8\textsuperscript{2}K | -7.287 006 | -13.686 277 | -32.530 633 | -75.913 847 |

\textsuperscript{a}The ionization limit of Li$^{+}$ ion is -7.27991 34126 69305 96491 810(15) a.u.
\textsuperscript{b}The ionization limit of Be$^{2+}$ ion is -13.65556 62384 23586 70207 810(15) a.u.
\textsuperscript{c}The ionization limit of C$^{4+}$ ion is -32.40624 660189 853031 055785(45) a.u.
\textsuperscript{d}The ionization limit of F$^{7+}$ ion is -75.53171 236395 949115(3) a.u.