General structure of the bound state spectrum of the 
four-electron Be atom

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(Dated: November 18, 2013)

Abstract

A large number of bound singlet states in the four-electron Be-atom are determined to high numerical accuracy. These states include the bound singlet $S$-, $P$-, $D$-, $F$-, $G$-, $H$- and $I$-states. Based on our computational results we analyze the singlet series of the bound state spectrum of the Be atom. Analogous study of the triplet states have been performed in our earlier study (A.M. Frolov and M.B. Ruiz, ArXiv: 1310.2657v2 (2013)). Our computational data allowed us to draw the first spectral diagram of the bound state spectrum of the Be atom which contains the two optically separated series: singlet states and triplet states.
I. INTRODUCTION

The electronic structure of the beryllium atom is of great interest in various problems arising in different areas of modern science, including stellar astrophysics, physics of the hot laboratory and stellar plasmas, applied nuclear physics, etc. Beryllium and some of its compounds (BeO, Be₂C) are extensively used in nuclear industry mainly as very effective (almost ideal) moderators of neutrons of all energies. Nevertheless, currently there are many gaps in our understanding of the optical spectrum of the Be-atom. In particular, the total energies of all rotationally excited (bound) states with \( L \geq 4 \) have never been evaluated accurately. Another interesting problem is to describe the transitions from the spectra of low-lying bound states in the Be atom to the weakly-bound (or Rydberg) states.

Recently, we have studied the general structure of the bound state spectrum of the triplet states in the four-electron Be atom \([1]\). For the first time we have performed accurate calculations of a large number of low-lying (bound) \( S-, P-, D-, F-, G-, H- \) and \( I- \)states, i.e. bound states with \( L \leq 6 \). Our computational results obtained in \([1]\) allowed us to draw a spectral diagram of the triplet states of the Be atom. It appears that our theoretical/computational spectral diagram agrees very well with the known experimental data (see, e.g., \([2]\) and references therein). Note that any of the \( G(L = 5)-, H(L = 6)- \) and \( I(L = 7)- \) states are not even mentioned in \([2]\).

Since \([3]\) the bound states in the four-electron Be-atom and Be-like ions were considered by many authors with the use of various methods specifically designed for the four-electron atomic systems. In reality, however, such calculations were restricted to the ground \( 2^1 S \)-state and a very few excited state only. In particular, to determine the ground state energy for the Be-atom different groups applied the Configuration Interaction method with Slater orbitals (CI) \([4, 5]\), the Hylleraas method (Hy) \([6, 7]\), the Hylleraas-Configuration Interaction method (Hy-CI) \([3, 8]\) and variational expansion in multi-dimensional gaussoids \([9]\) (also called the Exponential Correlated Gaussian method (or ECG method) \([10, 11]\)). A few selected bound singlet \( S-, P- \) and \( D- \) states were calculated by the Monte Carlo methods \([14]\) and by the ECG method \([10–13]\). In contrast with the singlet states, the triplet states in the Be atom were investigated only in a very few earlier studies \([14–16]\) (see also \([1]\) and references therein).

To complete our analysis of the bound state spectrum of the Be-atom \([1]\) we need to consider the singlet series of bound states in this system. In this study we determine the
total energies of the bound singlet $S$, $P$, $D$, $F$, $G$, $H$- and $I$-states. We have found that our method allows one to obtain the total energies of these states to high numerical accuracy, which is significantly better (for highly excited states) than accuracy which Hartree-Fock based methods can provide. It is important to note, since currently we have no reliable experimental information about rotationally excited states with $L \geq 4$ in the Be atom. Therefore, our main goal of this study is to determine the bound state spectrum of low-lying singlet states in the four-electron Be-atom, including rotationally excited states with $L = 4, 5, 6$ and $7$. The results of our study have been represented in the form of the spectral diagram for the singlet bound states in the Be-atom. For convenience of the reader and to complete our analysis we also present analogous spectral diagram for the bound triplet states in the Be atom [1].

II. HAMILTONIAN AND BOUND STATE WAVE FUNCTIONS IN CI-METHOD

The computational goal of this study is to determine the accurate numerical solutions of the five-body (or four-electron) Schrödinger equation $H \Psi = E \Psi$, where the Hamiltonian written in Hylleraas coordinates for a CI wave function is written in the form (see, e.g., [17])

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^{n} \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^{n} \frac{Z}{r_i} + \sum_{i<j}^{n} \frac{1}{r_{ij}}$$

$$- \frac{1}{2} \sum_{i=1}^{n} \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^{n} \frac{1}{r_i^2} \sin^2 \theta_i \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^{n} \cot \theta_i \frac{\partial}{\partial \theta_i},$$  \hspace{1cm} (1)

Note that when the Hamiltonian in Hylleraas coordinates is applied to the CI wave function (the CI wave function does not include explicitly $r_{ij}$ coordinates) some terms of [17] vanish. In addition, the operator of kinetic energy is represented as a sum of a few terms each of which has its own radial and angular parts. The operator $\hat{H}$ is diagonal in the basis of the spherical harmonics which are used below as angular parts of the orbital functions. Note also that the operator of angular momentum can easily be extracted from Eq.(1):

$$\sum_{i=1}^{n} \frac{1}{r_i^2} \hat{l}_i^2 = -\frac{1}{2} \sum_{i=1}^{n} \frac{1}{r_i^2} \frac{\partial}{\partial r_i} - \frac{1}{2} \sum_{i=1}^{n} \frac{1}{r_i^2} \sin^2 \theta_i \frac{\partial}{\partial \varphi_i} - \frac{1}{2} \sum_{i=1}^{n} \cot \theta_i \frac{\partial}{\partial \theta_i},$$  \hspace{1cm} (2)

For the orbital basis functions $\phi_i$ (or orbitals, for short) we can write

$$L_i^2 \phi_i = l_i (l_i + 1) \phi_i,$$  \hspace{1cm} (3)
with \( l_i \) the angular quantum number of the orbital \( \phi_i \). The Hamiltonian is reduced to the form

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^{n} \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^{n} \frac{Z}{r_i} + \sum_{i<j}^{n} \frac{1}{r_{ij}} + \sum_{i=1}^{n} \frac{1}{2} l_i (l_i + 1)
\] (4)

Now, from the variational principle one obtains the following eigenvalue problem:

\[
(H - ES)C = 0,
\] (5)

where the matrix elements of the Hamiltonian matrix \( H \) and overlap matrix \( S \) are:

\[
H_{kl} = \int \Phi_k \hat{H} \Phi_l d\tau, \quad S_{kl} = \int \Phi_k \Phi_l d\tau.
\] (6)

The integrals occurring in the CI calculations of an \( n \)-electron atom are of one- and two-electron integrals. The two-electron integrals are of the type [18]

\[
\langle \phi(r_1) \phi(r_2) \frac{1}{r_{12}} \phi(r_1) \phi(r_2) \rangle
\] (7)

and they are expressed as sums of the auxiliary two-electron integrals \( V(m, n; \alpha, \beta) \), defined as:

\[
V(m, n; \alpha, \beta) = \int_0^\infty r_1^m e^{-\alpha r_1} dr_1 \int_0^\infty r_2^n e^{-\beta r_2} dr_2 .
\] (8)

The auxiliary integrals \( V(m, n; \alpha, \beta) \) for positive indices \( m, n \) consist on a sum of \( A(n, \alpha) \) auxiliary integrals [19, Eq. (5)]:

\[
V(m, n; \alpha, \beta) = \sum_{n' = 0}^{n} \binom{n}{n'} A(n', \alpha) A(m + n - n', \alpha + \beta), \quad m, n \geq 0
\] (9)

This formula, developed by Frolov and Smith, is very useful because it is numerically stable and provides very fast convergence. For negative \( n \) and positive \( m \) (but \( m + n \geq -1 \) always) the formula for the Sims and Hagstrom sum [20, Eq. (33)] must be computed. In quantum mechanical calculations of two-electron systems this formula is employed to calculate the \( V \)-auxiliary integrals with the lowest index \( n = -1 \):

\[
V(m, n; \alpha, \beta) = \sum_{q=1}^{\infty} \frac{\alpha^{q-1} m!}{(m + q)!} A(m + n + q; \alpha + \beta), \quad m + n \geq -1, \quad m > 0, \quad n < 0
\] (10)
where the $A(n, \alpha)$ auxiliary integrals are:

$$A(n, \alpha) = \frac{n!}{\alpha^{n+1}}$$  \hspace{1cm} (11)

Let us briefly discuss the explicit construction of the trial wave functions which are used to approximate the exact wave functions of bound states in the four-electron Be atom. In this work we shall use the CI wave functions constructed from Slater orbitals and $LS$ eigenfunctions. These wave functions are represented in the form

$$\Psi = \sum_{p=1}^{N} C_p \Phi_p, \quad \Phi_p = \hat{O}(\hat{L}^2) \hat{A} \phi_p \chi$$ \hspace{1cm} (12)

i.e. it is a linear combination of $N$ symmetry adapted configurations $\Phi_p$, where the coefficients $C_p$ are determined variationally by solving the eigenvalue problem which follows from the Schrödinger equation.

In this work, the symmetry adapted configurations are constructed 'a priori' so that they are eigenfunctions of the angular momentum operator $\hat{L}^2$. Another possibility would be the posterior projection of the configurations over the proper spatial space, as indicated in Eq. (12) by the projection operator $\hat{O}(\hat{L}^2)$, where $\hat{A}$ is the antisymmetrization operator and $\chi$ is the spin eigenfunction for $S = 0$ and $M_S = 0$.

$$\chi = [(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)]$$ \hspace{1cm} (13)

As discussed in the case of the Li atom in Ref. [21] and calculations of the Be atom [8] it is sufficient to consider only one spin-function (formally, a linear combination of all possible spin eigenfunctions would be necessary). Indeed, the Slater determinants produced by the antisymmetrization of further spin functions would be repeated when considering the spin eigenfunction Eq. (13). The spatial part of the basis functions consists of Hartree products of Slater orbitals:

$$\phi_p = \prod_{k=1}^{n} \phi_k(r_k, \theta_k, \varphi_k),$$ \hspace{1cm} (14)

The basis functions $\phi_p$, are products of $s$-, $p$-, $d$-, $f$-, $g$-, $h$-, and $i$-Slater orbitals, defined as

$$\phi(r) = r^{n-1} e^{-ar} Y_l^m(\theta, \varphi)$$ \hspace{1cm} (15)

where $Y_l^m(\theta, \varphi)$ are the spherical harmonics [22].
We have written a four-electron CI computer program for four-electron atomic systems in Fortran 90. Numerical calculations have been conducted with the use of double precision arithmetic. This program has been thoroughly checked by comparing results of our numerical calculations with the results by Sims and Hagstrom for the Be atom \cite{3, 8}. In these calculations we have observed a complete agreement.

The ground state configuration of the Be atom is \textit{ssss} (i.e. $s(1)s(2)s(3)s(4)$). The further considered configurations for S-symmetry states ($L=0$) are, ordered by decreasing energetic contribution, \textit{sspp}, \textit{spps}, \textit{ppss}, \textit{pppp}, \textit{ssdd}, \textit{sdss}, \textit{ddss}, \textit{sppd}, \textit{dpps}, \ldots, \textit{ffdd}. The energetically important configurations for $L = 1, \ldots, 6$ are listed in Table I. The quantum number $M_L = 0$ was chosen, because for this case a smaller number of Slater determinants is required. We performed a systematical selection of the CI configurations according to their energy contribution. This was done by performing calculations on blocks constructed for all possible configurations. The eigenvalue equation was diagonalized upon each addition of a configuration. In this manner, the contribution of every single configuration and of each block of a given type to the total energy was evaluated. Configurations with an overall energy contribution below $1 \cdot 10^{-8}$ a.u. were not considered.

The procedure of selection of the configurations is similar to the one described in our previous works, Refs. \cite{1, 21}. In this work we construct the full-CI (FCI) wave function for every symmetry and basis set including the types of configurations which contribute more to the total energy of the lowest state of every symmetry. The contribution of a configuration is larger, the smaller the sum of the $l$ quantum numbers of the employed orbitals $l_1 + l_2 + l_3 + l_4$ is; i.e. the contribution of the configuration \textit{sssp} > \textit{sppp} for a $P$-state. In cases such as the $P$ states \textit{sspd} and \textit{ppsp}, where the sum of $l_i$ is equal, the two inner electrons in \textit{ppsp} form a $S$-configuration. The resulting four-electron configuration is $({^1}S)sp$ (a $P$-configuration), and contributes more than the \textit{sspd} one. This is especially important in the case of $F$-, $G$-, $H$-, and $I$-states. Among the many possibilities to construct configurations of these symmetries, the energetically most important configurations were proven to be those with an inner $S$-shell and a single occupied orbital with the symmetry of the state under consideration, i.e. $({^1}S)sf$, $({^1}S)sg$, $({^1}S)sh$, and $({^1}S)si$. The inner shell is described with a sum of configurations $({^1}S) = ss + pp + dd + ff + gg + hh + ii$. In the CI calculations of $S$-, $P$-, and $D$ states we employed $s$-, $p$-, $d$-, and $f$-orbitals (see Table I). In the CI calculations of the $F$-, $G$-, $H$-, and $I$-states we have used in addition $g$-, $h$-, and $i$-orbitals as shown in Table I.
More types of configurations than the ones discussed here can be constructed for a given \( L \) quantum number. For instance, configurations like \( pssp \) could be considered, if the exponents \( \alpha_1 \neq \alpha_2 \). However, we have kept the orbital exponents in the K-shell and in the L-shell equal, respectively.

Note that there are more possible 'degenerate L-eigenfunction' solutions with a larger number of Slater determinants. Specifically, these are degenerate with respect to the quantum numbers \( L \) and \( M \), but with possible different energy contribution, i.e. non-degenerate with respect to the energy \[4\]. Although the inclusion of various degenerate configurations has been shown to improve the energy of the state, such a contribution is very small. This is important for very accurate CI calculations, as reported e.g. by Bunge \[4\]. In our work, we have concentrated on the energetically most important CI configurations.

Another important aspect in CI and Hy-CI calculations is the symmetry adaptation of the configurations. As mentioned above, the configurations are constructed 'a priori' to be eigenfunctions of the angular momentum operator \( \hat{L}^2 \). The configurations of Table I are constructed as sums of Slater determinants. The determinants are pairwise symmetric (i.e. \( ssp_1p_{-1} \) and \( ssp_{-1}p_1 \) in the \( sspp \) configuration) and lead to the same values of the electronic integrals. Therefore, it is possible and desirable to consider only one of the determinants and to deduce the result from the other.

In other words, the solution of the eigenvalue problem obtained when using reduced \( 1 \times 1 \) matrix elements (where the integrals are added, configuration \( sp_1p_{-1} + sp_{-1}p_1 \)) or when using explicit \( 2 \times 2 \) matrix elements of the Slater determinants is the same. The symmetry adaptation is computationally favorable, since the number of Slater determinants in the input is smaller and the repeated computation of equal integrals is avoided. The explicit sums of symmetry adapted configurations in the three-electron case are listed in \[21\].

In this work we start with the full-CI wave function (FCI) constructed with configurations of the type of the ground configuration of a given state (see first configuration of every symmetry in Table I) and we use the large basis set \( n = 8 \). The notation \( n = 4 \) stands for the basis set \([4s3p2d1f]\). The first step consists in an optimization of the orbital exponents for this truncated wave function. The optimization is carried out via a parabolic procedure, explained in Ref. \[21\]. The orbital exponents are optimized for each atomic state of the Be atom. A set of two exponents is used (one for the \( K \)-shell and the other for the electrons in the \( L \)-shell), and kept equal for all configurations. This technique accelerates computa-
tions, while still producing sufficiently accurate wave functions to determine the bound state properties. During calculations we have used the following virial factor

$$\chi = -\frac{\langle V \rangle}{\langle T \rangle}$$

as a criterion to check the quality of the wave function and guide the numerical optimization of the exponents in the trial wave functions.

Using the appropriate exponents for every state we filtered the configurations of the first configuration block of the FCI wave function calculating the total energy $E_i$ everytime that a single configuration was added, and comparing it to the total energy without this configuration $E_{i-1}$. If the difference of the energy was smaller than the energy criterion $|E_{i-1} - E_i| > 1 \cdot 10^{-8}$a.u, the new configuration was discarded. In this manner, all configurations were checked, leading to a relatively compact CI wave function.

The next step consists to add a new block of configurations (FCI) of the following type given in Table I. As the wave function would be very large, a new selection of the newly added configurations is carried out. The resulting compact wave function is optimized again, and the procedure is repeated everytime that a new block of configurations is added. In this work we employ the basis set $n = 8$. Using this method we obtain rapidly a good energy value and the addition of configurations with higher $l_i$ quantum numbers contributes to the convergence to the non-relativistic energy value. The final wave function is a compact wave function containing one to two thousands of configurations which is millihartree accurate for the lowest states of every symmetry. This technique is a result of a balance between selection and optimization procedures.

By using the CI method we have calculated the bound $S^-$, $P^-$, $D^-$, $F^-$, $G^-$, $H^-$ and $I^-$ states in the Be atom. In particular, we have determined the energies of the four (lowest) S-states, three P-states, three D-states, two F-states, two G-states, one H-state and one I-state. The total energies of the F-, G-, H- and I-states in the Be atom are reported here for the first time. They have not been determined in earlier studies neither computationally, nor experimentally. Our results are summarized in Table II. The overall accuracy of our calculations for the lowest states of every symmetry can be evaluated as $\approx \pm 1 \cdot 10^{-3}$ a.u. Higher excited states are in general less accurate. This is due to the exponent restrictions of the method used here. Nevertheless, i.e. for the $5^1S$ state we have obtained the best energy to date.
III. GENERAL STRUCTURE OF THE BOUND STATE SPECTRA

As mentioned above the bound state spectrum of the Be atom contains two series of bound states: singlet series and triplet series. In the lowest order (dipole) approximation these two series are independent of each other, i.e. any dipole transition between the two states from different spectral series is strictly prohibited. In reality, transitions between singlet and triplet states of the Be-atom are always possible due to non-elastic collisions of these atoms with electrons, ions and other atoms. It is clear that the probabilities of such collisional transitions substantially depend upon the spatial densities of electrons, Be-atoms, etc. In very good vacuum (≈ 10^{-12} atm) and at relatively large temperatures one can easily see the two different optical series (singlet and triplet) in the gaseous mixture of the ^9Be atoms.

The electronic structure of the ground singlet state of the Be atom is 1s^22s^2, 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 is always located at the 2s-shell. The fourth electron can occupy any free electron orbital in the atom. The occupation numbers of this (fourth) electron determine the actual state (or configuration) of the Be-atom. The pair of the third and fourth electron can be either in the singlet state, or in the triplet state (as the whole Be-atom). It follows from here that the bound state-spectrum of the Be-atom must be similar to the bound state spectra of the two-electron He-atom. Indeed, such a similarity can be observed (the two series of bound states, the ground state is the singlet S-state, etc). However, the actual order of different bound states is different for the He- and Be-atoms. For instance, the lowest state in the triplet series is 2^3S-state in the helium atom and 2^3P-state in the beryllium atom. For the excited bound states in the He- and Be-atoms one finds more differences than similarities, while for singlet states close to the ground state similarities with between the spectra of these two elements can easily be seen.

Since the three-electron core of the Be-atom has the 1s^22s electron configuration, then the dissociation threshold for the neutral Be-atom corresponds to the formation of the three-electron Be^+ ion in its grouns 2^2S-state (doublet). The non-relativistic energy of this state is \( E_{\infty \text{Be}^+} \approx -14.324 \text{ 763 176 465 4 a.u.} \) \[23\]. This dissociation threshold corresponds to the
following ionization process of the Be atom

$$\text{Be} = \text{Be}^+ (2^2S) + e^-$$ (17)

where the symbol \( \text{Be}^+ (2^2S) \) means that the final three-electron \( \text{Be}^+ \) ion is in its ground \( 2^2S \)-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 Be-atom (in atomic units):

$$E(\text{Be}; nL) = E(\text{Be}^+; 2^2S) - \frac{m_e e^4}{2\hbar^2} \frac{1}{(n + \Delta \ell)^2} = -14.3247631764654 - \frac{1}{2(n + \Delta \ell)^2}$$ (18)

where \( L = \ell \) (in this case), \( n \) is the principal quantum number of the \( nL \) state (\( L \) is the angular quantum number) of the Be-atom and \( \Delta \ell \) is the Rydberg correction 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 the Rydberg correction rapidly vanishes when \( \ell \) increases (for given \( n \) and \( L \)). Moreover, the \( \Delta \ell \) correction also decreases when the principal quantum number \( n \) grows. The formula, Eq.(18), can be used to approximate the total energies of weakly bound, Rydberg states in the Be-atom. However, by following the original ideas of Heisenberg and Bethe (see, e.g., 25 and references therein) we can write a significantly more accurate formula which can be used to approximate the same Rydberg states to very good numerical accuracy. This formula is written in the form

$$E(\text{Be}; nL) = E(\text{Be}^+; 2^2S) - \frac{m_e e^4}{2\hbar^2} \frac{1 - \epsilon_L}{(n + \Delta \ell + (-1)^S \Delta A)^2} \approx -14.3247631764654 - \frac{1 - \epsilon_L}{2(n + \Delta \ell + (-1)^S \Delta A)^2}$$ (19)

where \( S \) is the total electron spin, while \( \epsilon_L, \Delta \ell \) and \( \Delta A \) are the three parameters which must be varied in actual cases to obtain better numerical approximations. All these parameters are rapidly decrease when \( \ell \) (and \( L \)) grows. In reality, to apply the formula, Eq.(19), one needs to know the accurate values of the total energies of at least three bound states in each spectral series, i.e. the total energies of three singlet and three triplet bound states with \( n \geq 5 \).

Based on Eq.(19) one can predict that the total energies of the singlet and triplet highly excited states (with the same \( n \)) equal to each other to a good accuracy (almost coincide). In general, such a coincidence of energy levels becomes almost exact when \( n \) grows. It is a well known property of the Rydberg states and it can be observed in any atomic system.
which has energy spectrum consisting of a few different spectral series. Formally, based on
the formula, Eq. (19), we can classify all bound states in the Be atom as the Rydberg states,
pre-Rydberg and non-Rydberg states. Each group of these states has its unique electron
density distribution.

In general, it is very difficult to develop a working procedure which can be used to
determine all bound states in few-electron atoms and ions, since, e.g., some methods are
good for weakly-bound, or Rydberg states, but not sufficiently accurate for the ground and
low-lying bound states and vice versa. Our method developed in [1] and in this study
allows one to investigate the both spectral series in the bound state spectra of the beryllium
atom and $^9$Be isotope-substituted atom. It provides relatively high numerical accuracy for
the both singlet and triplet bound states in the four-electron atoms and can be used for
rotationally excited bound states with arbitrary, in principle, angular momentum $L$. In
addition, our method was successfully applied to calculate different bound states in many
four-electron ions. Briefly, we can say that by using our method we can investigate the
general structure of the bound state spectra of the four-electron atomic systems. It is a
great advantage of our approach, since many methods used for these problems in earlier
studies allow one to determine only a very few lowest bound states (usually, some of the
$S$- and $P$-states). On the other hand, all Hartree-Fock based methods are not accurate
for excited and highly excited states. In application to four-electron atoms and ions these
methods often produce only approximate energies for the excited states.

IV. SPECTRAL DIAGRAM OF THE FOUR-ELECTRON BERYLLIUM ATOM

In this study we have determined the total energies of a large number of bound singlet
states in the Be-atom. Our computational results can be used to draw the energy levels of
all computed singlet (bound) states of the $^\infty$Be atom as functions of angular momentum $L$
of these states. In old books on atomic spectroscopy such pictures (or diagrams) were called
the ‘spectral diagrams’. In general, the spectral diagrams are 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 B$^+$, C$^{2+}$, N$^{3+}$ and other similar four-electron ions. The spectra of
the negatively charged ions, e.g., the Li$^-$ ion) contain only a very few bound states (usually one bound state \(26\)) and the corresponding spectral diagrams are very simple and not informative.

For neutral atoms and ions with the same nuclear charge \(Q\) the actual spectral diagrams are often used to discover and investigate effects related with the role of electron-electron correlations in different atomic states. For instance, from our spectral diagram one finds that the \(3^1D\)-state in the Be-atom is less bound than the analogous \(3^1S\)-state, while for the bound \(4^1D\)- and \(4^1S\)-states such an order of bound states is opposite. The true theory of electron-electron correlations in atoms must explain the actual order of the bound states (or energy levels) in the spectrum and approximately predict the energy differences between them.

In general, by performing numerical calculations of a large number of bound states in atomic systems one always needs to answer the two following questions: (1) predict the correct order of low-lying bound states, and (2) describe transition between the low-lying bound states and weakly-bound, or Rydberg states. To solve the first problem we can compare our results with the known experimental data for Be-atom \(2\). For the singlet states in the Be-atom the agreement between our computational results, the picture Fig.1 and data for the beryllium atom presented in \(2\) can be considered as very good. Combining the theoretical and experimental data we can predict the total order of states in the singlet and triplet series, as shown in Table III. It is also clear we have calculated only the non-relativistic (total) energies, i.e. all relativistic and lowest-order QED corrections were ignored. Note also that our CI-method is substantially more accurate than various procedures based on Hatree-Fock approximation, but it still provides a restricted description of the electron-electron correlations in actual atoms and ions. Nevertheless, the observed agreement with the actual bound state spectra of the triplet states in the Be atom (or \(^9\)Be atom) is very good for low-lying bound states.

Now, consider the second problem. As follows from the results of our calculations all bound singlet states with \(n \geq 6\) in the beryllium atom are the weakly-bound, or Rydberg states. On the other hand, all bound triplet states in the Be-atom with \(n \geq 4\) can be considered as the pre-Rydberg states. It follows from comparison of the total energies of the triplet \(4^3F\), \(5^3G\) states and singlet \(4^1F\), \(5^1G\) states (for more details, see \(1\)). On the other hand, it is clear that the ‘boundary’ principal quantum number \(n_R\) from which the
Rydberg states begin (for $n \geq n_R$) must be exactly the same for both spectral series in the four-electron atoms and ions.

In this study our main attention was given to the singlet bound states in the four-electron Be-atom. The triplet states in the Be-atom were considered in our paper [1] which also contains the spectral diagram of the bound triplet states in the Be-atom. For maximal convenience of the reader we also included the updated spectral diagram of the triplet states in our present analysis (see, Fig.2). In many cases it is useful to observe spectral diagrams for the both singlet and triplet series together and compare these diagrams with the analogous spectral diagrams for atoms which have bound state spectra represented as a combination of the two separate spectral series (singlet and triplet). For instance it is very interesting and informative to make such a comparison of the spectra of the beryllium and helium atoms (see, e.g., [25] and references therein).

V. CONCLUSION

We have considered the bound state spectrum of the singlet states in the four-electron Be-atom. Analogous spectrum of the bound triplet states in the four-electron Be-atom has been presented and discussed in our earlier study [1]. The results of both studies reproduce the complete ‘optical’ spectrum of the four-electron Be-atom. The observed agreement between our computational results and actual singlet/triplet spectrum of the Be atom [2] can be considered as very good. Formally, it is the first case in the literature when quite complicated bound state spectrum of some few-electron atom (or element) has been obtained and studied by using only computational methods. It should be mentioned that our success in this study is based on our computational approach which has three following advantages: (1) it can be applied for accurate computations of all bound states in the spectrum, including rotationally excited states and weakly-bound, Rydberg atomic states, (2) it provides overall accuracy which is beyond the level provided by various method based on the Hartree-Fock approximation, (3) such an accuracy does not decrease for the excited $LS$-states in the spectrum. A unique combination of these three factors makes our computational method a unique tool to study the bound state spectra in different few-electron atom and ions. Our results for three-electron atom(s) and ions can be found in [21].

The results of our studies allowed us to draw the spectral diagrams of the singlet and
triplet spectra of the four-electron Be atom. Such spectral diagrams for Be-atom can now be compared with analogous spectral diagrams of other light atoms and ions. Theoretical comparison of the atomic spectra of the Be and He atoms seems to be very interesting, since each of these two spectra contains two independent series of bound states (singlet and triplet). On the other hand, it would be very interesting to compare the bound state spectrum of the neutral Be-atom with the analogous spectra of the four-electron ions, e.g., B$^+$, C$^{2+}$, N$^{3+}$, etc. The corresponding spectral diagrams of these atomic species are very similar to each other, but a few differences between them and $Z$-dependence of these differences makes such a study extremely interesting and very promising to improve our understanding of the electron-electron correlations in the four-electron atomic systems.

VI. ACKNOWLEDGMENTS

We would like to thank James Sims and Stanley Hagstrom for providing us with numerical results from Hylleraas-CI calculations on the Be atom which have serve to check our Be computer program, and to Carlos Bunge for valuable advise about the construction of $LS$ and degenerate configurations. One of us (F.L.) greatly acknowledges his PhD supervisor Leticia González at the University of Vienna for her scientific support.
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FIG. 1 – The energy levels of the singlet states in the beryllium atom. The threshold energy (or ionization limit) $E(\text{Be}^+)$ coincides with the total energy of the ground $2^2S$-state of the three-electron Be$^+$ ion.
FIG. 2 – The energy levels of the triplet states in the beryllium atom. The threshold energy (or ionization limit) $E(\text{Be}^+)$ coincides with the total energy of the ground $2^2S$-state of the three-electron Be$^+$ ion.
TABLE I – List of the different $L$ configurations employed in the CI calculations of the $S$, $P$, $D$, $F$, and $G$ states. In all configurations $M = 0$. Here it is taken into account that the exponents within a shell have been kept equal.

| State | $L$ | $M$ | Configurations |
|-------|-----|-----|-----------------|
| $S$   | 0   | 0   | $ssss$, $sspp$, $spps$, $ppss$, $pppp$, $ssdd$, $sdds$, $ddss$, $sppd$, $dpps$, $sdpp$, $ppds$, $ppdd$, $dddd$, $dppp$, $ssff$, $ppff$, $dfdf$, $ffss$, $ffpp$, $ffdd$ |
| $P$   | 1   | 0   | $sssp$, $spss$, $sppp$, $ppsp$, $sddp$, $ddsp$, $sfsp$, $ffsp$, $sspd$, $spds$, $pdss$, $pdpp$, $pddd$, $pdfp$, $pppd$, $dfpd$, $fsps$, $psps$, $pppp$, $ssdd$, $sdds$, $ddss$ |
| $D$   | 2   | 0   | $sssd$, $sdss$, $sppd$, $ppsd$, $sddp$, $ddsp$, $sfsp$, $ffsd$, $ssps$, $spps$, $ppps$, $pppp$, $ssdd$, $sdds$, $ddss$ |
| $F$   | 3   | 0   | $sssf$, $sfss$, $sppf$, $ppsf$, $sddf$, $ddsf$, $ffsf$, $ggsf$, $hhhsf$ |
| $G$   | 4   | 0   | $sssg$, $sgss$, $sppg$, $ppsg$, $sddg$, $ddsg$, $ffsg$, $ggsg$, $hhsg$ |
| $H$   | 5   | 0   | $sssh$, $shss$, $spph$, $ppsh$, $sddh$, $ddsh$, $ffsh$, $ggsh$, $hhsh$ |
| $I$   | 6   | 0   | $sssi$, $siss$, $sppi$, $ppsi$, $sddi$, $ddsi$, $ffsi$, $gssi$, $hhsi$, $iisi$ |
TABLE II – The total energies in a.u. of some low-lying singlet states of the $\infty$Be atom determined with the use of the CI method and comparison with the non-relativistic values of the bibliography. The total energies of the bound states in the upper part of this Table are lower than the ionization threshold of the $\infty$Be atom ($E_{\infty \text{Be}^+} = -14.324\ 763\ 176\ 47$ a.u.). N is the number of configurations used in calculations.

| State | N    | This work | $E(FCI)$ | Ref. | N       | $E(nr)$ | Ref. |
|-------|------|-----------|----------|------|---------|---------|------|
| $2^1S$ | 947  | -14.665194484958 | $\approx 2m$ | 4    | 4096    | -14.6673564949 | 10   |
| $3^1S$ | 898  | -14.415012524285 | -14.41795727 | 5    | 10000   | -14.418240328 | 11   |
| $4^1S$ | 927  | -14.360087560495 |          |      | 10000   | -14.370087876 | 11   |
| $5^1S$ | 962  | -14.351957151995 |          |      | 10000   | -14.351511654 | 11   |
| $2^1P$ | 1210 | -14.469466899537 | -14.47300965 | 5    | 7400    | -14.473451358 | 12   |
| $3^1P$ | 1230 | -14.384169592733 | -14.39278828 | 5    | 7400    | -14.393143504 | 12   |
| $4^1P$ | 1453 | -14.350385199711 |          |      | 7400    | -14.361938370 | 12   |
| $5^1P$ | 1215 | -14.298031990164 |          |      | 7400    | -14.347876248 | 12   |
| $3^1D$ | 860  | -14.399799844571 | -14.40436(6) | 14   | 4200    | -14.40823703(40) | 13   |
| $4^1D$ | 1754 | -14.351935051094 | -14.37344241 | 5    | 4200    | -14.37382438(30) | 13   |
| $5^1D$ | 1131 | -14.329064248785 |          |      | 4200    | -14.35398265(50) | 13   |
| $4^1F$ | 2210 | -14.352207136124 |          |      |         |         |      |
| $5^1F$ | 1625 | -14.326782502407 |          |      |         |         |      |
| $5^1G$ | 1676 | -14.336099101160 |          |      |         |         |      |
| $6^1H$ | 1443 | -14.326855859049 |          |      |         |         |      |
| $7^1I$ | 1242 | -14.314857832724 |          |      |         |         |      |
**TABLE III** – Order of bound states in the Be atom from the theoretical calculations and experimental observations of spectral lines [2]. The symbol ‘<’ denotes here lower energy.

| n  | order in singlet series | order in triplet series |
|----|-------------------------|-------------------------|
| 13 | $13^1D < 13^1P$         | $13^3D$                 |
| 12 | $12^1D < 12^1P$         | $12^3D$                 |
| 11 | $11^1D < 11^1S < 11^1P$ | $11^3D$                 |
| 10 | $10^1D < 10^1S < 10^1P$ | $10^3D$                 |
|  9 | $9^1D < 9^1S < 9^1P$    | $9^3D$                  |
|  8 | $8^1D < 8^1S < 8^1P$    | $8^3P$                  |
|  7 | $7^1D < 7^1S < 7^1P < 7^1F < 7^1G < 7^1H < 7^1I$ | $7^3D < 7^3F < 7^3S$ |
|  6 | $6^1D < 6^1S < 6^1P < 6^1F < 6^1G < 6^1H$ | $6^3P < 6^3D < 6^3F < 6^3S$ |
|  5 | $5^1D < 5^1S < 5^1P < 5^1F < 5^1G$ | $5^3P < 5^3D < 5^3F < 5^3G < 5^3S$ |
|  4 | $4^1D < 4^1S < 4^1P < 4^1F$ | $4^3P < 4^3D < 4^3F < 4^3S$ |
|  3 | $3^1S < 3^1D < 3^1P$    | $3^3P, 3^3P'\alpha < 3^3D < 3^3S$ |
|  2 | $2^1S < 2^1P$           | $2^3P < 2^3S$           |

*Here we denote the duplet of states with same n energy level.*