

COMPACT VARIATIONAL WAVE FUNCTIONS FOR BOUND STATES IN THREE-ELECTRON ATOMIC SYSTEMS

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The variational procedure to construct compact and accurate wave functions for three-electron atoms and ions is developed. The procedure is based on the use of six-dimensional Gaussoids written in the relative four-body coordinates r_{12} , r_{13} , r_{23} , r_{14} , r_{24} , and r_{34} . The nonlinear parameters in each basis function have been carefully optimized. Using these variational wave functions, we have determined the energies and other bound state properties for the ground 1^2S -states in a number of three-electron atoms and ions. The three-electron atomic systems considered in this work include the neutral Li atom and nine positively charged lithium-like ions: Be^+ , B^{2+} , C^{3+} , \dots , Na^{8+} , and Mg^{9+} . Our variational wave functions are used to determine the hyperfine structure splitting and field shifts for some lithium-like ions. The explicit formulas of the Q^{-1} expansion are derived for the total energies of these three-electron systems.

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1. INTRODUCTION

Our main goal in this work was to develop a variational procedure that can be used to construct compact but relatively accurate wave functions for an arbitrary three-electron atomic system, i. e., an atom and/or an ion. Recently, it was observed in numerous computations that variational expansions developed for the three-electron atoms and ions can be quite compact and accurate, if they are based on the use of four-body (or six-dimensional) Gaussoids [1] of the relative four-body coordinates r_{12} , r_{13} , r_{23} , r_{14} , r_{24} , and r_{34} . By compact and accurate, we mean that such a variational expansion contains a relatively small number of terms and that the accuracy of the computed energies and other bound state properties is comparable with (or even better than) the accuracy of analogous calculations based on the use of the Hylleraas basis set (see, e. g., [2, 3]). Our attention to the variational expansions based on the use of four-dimensional Gaussoids can be explained by their great convenience in applications to a significant number of atomic three-electron problems.

In this work, we try to achieve the best numerical

accuracy for the total (nonrelativistic) energies of some three-electron atomic systems. A number of bound state properties have also been determined. Our variational results are then compared with the analogous results obtained for these systems with the use of the Hylleraas basis set [2, 3] of comparable size (≈ 700 – 800 basis functions). In fact, we consider the ground 1^2S states in a number of three-electron atomic systems that include the Li atom and nine lithium-like ions: Be^+ , B^{2+} , C^{3+} , \dots , Na^{8+} , Mg^{9+} . We are primarily interested in the bound states properties of the ground states (or 1^2S states) in these systems. We note that each of the atoms and/or ions considered is a four-body atomic system, i. e., it has a very heavy (central) nucleus with electric charge $+Q$ and three electrons.

To determine the bound states in such systems, we apply the variational expansion written in six-dimensional Gaussoids [1]. Each basis function in this variational expansion depends on six interparticle coordinates r_{12} , r_{13} , r_{23} , r_{14} , r_{24} , and r_{34} and also contains six nonlinear parameters. We note that each of these interparticle coordinates $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is translationally and rotationally invariant, i. e., is a scalar that does not change under any translation and/or rotation of the four-body system. This means that the translations of the center of mass separate in these coordinates auto-

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matically. In particular, we can assume that the center of mass is at rest. We also note that the variational expansion written in six-dimensional Gaussoids [1] is a true correlated expansion of the wave function, i. e., all possible interparticle correlations in actual four-body wave functions must be reproduced correctly by this variational expansion if it includes a large number of basis functions.

It was very interesting to find that our variational wave functions can produce results/energies that are quite comparable with the best results obtained with the use of Hylleraas-type variational expansions for these atoms/ions [2, 3]. This shows the great potential and flexibility of modern computational methods based on the use of many-dimensional Gaussoids [1] for accurate solution of various atomic problems. In particular, the computed expectation values allow determining the hyperfine structure splitting and field component of the total isotope shift (field shift) in the three-electron atomic systems considered in this study. The energies of the three-electron atomic systems obtained in this study can be used to derive accurate analytic formulas for the Q^{-1} expansion.

In atomic units, where $\hbar = 1$, $|e| = 1$, and $m_e = 1$, the nonrelativistic Hamiltonian H of the three-electron atomic system takes the form

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{1}{2M}\nabla_4^2 - \frac{Q}{r_{14}} - \frac{Q}{r_{24}} - \frac{Q}{r_{34}} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}, \quad (1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$ are the six interparticle distances (relative coordinates), $(ij) = (ji) = (12), (13), \dots, (24), (34)$, and \mathbf{r}_i are the Cartesian coordinates of the four particles. In this equation, the notation

$$-\frac{1}{2}\nabla_i^2 = \frac{1}{2}\mathbf{p}_i^2, \quad i = 1, 2, 3, 4$$

means single-particle kinetic energies. Also, in this equation and everywhere below in this study, the subscripts 1, 2, 3 stand for three electrons e^- , and the subscript 4 always means a heavy nucleus with the mass M ($M \gg 1$) and a positive (nuclear) charge Q .

Our first goal is to determine the total energies and corresponding wave functions of the ground doublet ${}^2S_{1/2}$ state in the three-electron atom/ion with Hamiltonian (1). In other words, we need to obtain the highly accurate solutions of the corresponding Schrödinger equation $H\Psi = E\Psi$, where $E < 0$ and the bound-state wave function Ψ has the unit norm. For our present purposes, we assume that the nonrelativistic Schrödinger equation is exact. All lowest-order

relativistic ($\sim \alpha^2$) and QED ($\sim \alpha^3$) corrections to the nonrelativistic energies can be found with the use of the "exact" nonrelativistic wave functions and perturbation theory methods.

This work has the following structure. The method used for construction of the approximate variational wave functions is discussed in Sec. 2. The most difficult part of this method for the many-electron problem is the proper antisymmetrization of the corresponding wave functions and matrix elements arising in calculations. This problem is also considered in Sec. 2. Section 3 contains a brief derivation of all analytic formulas for the matrix elements needed in highly accurate computations of four-body systems. Discussion of various optimization strategies used to optimize the nonlinear parameters in the variational wave functions can be found in Sec. 4. In Sec. 5, we then discuss the numerical results for some three-electron atomic systems obtained with the use of our method. We also consider the hyperfine structure splitting in the ground 1^2S states of three-electron atoms/ions. Another interesting application is related to the direct computation of the field component of the total isotope shift. The Q^{-1} expansion is applied to represent the energies of all three-electron atoms/ions (ground states) discussed in this study. Concluding remarks are given in Sec. 6.

2. THE METHOD

In general, any variational expansion of the ground doublet ${}^2S_{1/2}$ state in a three-electron atomic system must include the two independent spin functions (or configurations). In actual computations, such spin functions are chosen as

$$\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha, \quad \chi_2 = 2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha,$$

where α and β are the one-electron spin-up and spin-down functions, respectively (see, e.g., [4]). In other words, the wave function for the ground doublet ${}^2S_{1/2}(L=0)$ state of the three-electron atomic system 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 (radial parts) of the total wave function. The symbols A and B indicate that the two sets of nonlinear parameters associated with ψ and ϕ are optimized independently in our method. In actual computations, the radial parts in each of the two

terms in Eq. (2) can be approximated with the use of a variational expansion [1], e. g., for the $\psi_{L=0}$ part,

$$\psi_{L=0}(\{r_{ij}\}) = \mathcal{P}_s \sum_{k=1}^N C_k \exp \left(- \sum_{ij} \alpha_{ij}^{(k)} r_{ij}^2 \right), \quad (3)$$

where N is the number of basis variational functions used, C_k are the linear parameters of the variational expansion, and $\{r_{ij}\}$ is the set of relative coordinates that are needed for a complete description of the four-body system. In fact, for three-electron atoms/ions, the notation $\{r_{ij}\}$ stands for the six relative coordinates r_{12} , r_{13} , r_{23} , r_{14} , r_{24} , and r_{34} . The summation over $(ij) = (ji)$ in Eq. (3) is taken over all possible different pairs of particles. The projector \mathcal{P}_s produces the trial wave function with the correct permutation symmetry of all three electrons. The explicit form of the \mathcal{P}_s operator for a three-electron system depends on the corresponding spin state (see below). The symbol L in Eq. (3) is used for the total orbital angular momentum of the system. We note that for the ground ${}^2S_{1/2}$ states considered below, we always have $L = 0$, $S = 1/2$ (total spin), and $J = 1/2$ (total angular momentum).

We now discuss the permutation symmetry of the actual wave function. The two terms in the right-hand side of Eq. (2) must be completely antisymmetric with respect to the coordinates of the three electrons, i. e., the indexes 1, 2, and 3 in our notation. This means that $\hat{A}_e \Psi = -\Psi$, where Ψ is given by Eq. (2) and

$$\hat{A}_e = \hat{e} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{123} + \hat{P}_{132} \quad (4)$$

is the three-particle (electron) antisymmetrizer. Here, \hat{e} is the identity permutation, and \hat{P}_{ij} is the permutation of the i th and j th particles. Analogously, the operator \hat{P}_{ijk} is the permutation of the i th, j th, and k th particles. The same notation is used everywhere in what follows.

After the integration over electron spin coordinates, we find the four spatial projectors

$$\mathcal{P}_{\psi\psi} = \frac{1}{2\sqrt{3}} \left(2\hat{e} + 2\hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{123} - \hat{P}_{132} \right), \quad (5)$$

$$\mathcal{P}_{\psi\phi} = \frac{1}{2} \left(\hat{P}_{13} - \hat{P}_{23} - \hat{P}_{123} + \hat{P}_{132} \right), \quad (6)$$

$$\mathcal{P}_{\phi\psi} = \frac{1}{2} \left(\hat{P}_{13} - \hat{P}_{23} - \hat{P}_{123} + \hat{P}_{132} \right), \quad (7)$$

$$\mathcal{P}_{\phi\phi} = \frac{1}{2\sqrt{3}} \left(2\hat{e} - 2\hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23} - \hat{P}_{123} - \hat{P}_{132} \right), \quad (8)$$

where the indexes ψ and ϕ correspond to the notation used in Eq. (2). Each of these projectors produces matrix elements between the two radial basis functions in Eq. (2) with the correct permutation symmetry.

We note that the two projectors $\mathcal{P}_{\psi\phi}$ and $\mathcal{P}_{\phi\psi}$ coincide with each other. It can be shown that the three projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$, and $\mathcal{P}_{\phi\phi}$ are orthogonal to each other. We also note that in actual computations, only the upper triangular part of the Hamiltonian and overlap matrices are used. Therefore, only the three projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$, and $\mathcal{P}_{\phi\phi}$ are important in computations of the ground state of all three-electron systems considered in this study. In the next section, we derive analytic formulas for matrix elements in the basis of many-dimensional Gaussoids.

3. MATRIX ELEMENTS

The computation of the matrix elements with the four-body (six-dimensional) Gaussoids, Eq. (3), is well described in the literature (see, e. g., [1, 5]). In fact, for an arbitrary A -body system, the universal formulas for all matrix elements can be obtained. These formulas contain the total number of particles A in the system as an explicit parameter. The first such formulas were established more than 25 years ago in nuclear few-body calculations (see [1] and the reference therein). This is an obvious advantage of the variational expansion based on Eq. (3) in comparison with other few-body expansions. We now present the explicit formulas for all matrix elements needed in computations. First, we introduce the compact notation [1]

$$\begin{aligned} \langle \alpha | &= \langle \alpha^{(k)} | = \exp \left(- \sum_{i>j=1}^A \alpha_{ij}^k r_{ij}^2 \right), \\ |\beta \rangle &= |\beta^{(\ell)} \rangle = \exp \left(- \sum_{i>j=1}^A \beta_{ij}^\ell r_{ij}^2 \right), \end{aligned} \quad (9)$$

where A is the total number of particles in the system. In our present case, $A = 4$. In this notation, the overlap matrix element $\langle \alpha | \beta \rangle$ becomes

$$\langle \alpha | \beta \rangle = \langle \alpha^{(k)} | \beta^{(\ell)} \rangle = \pi^{3(A-1)/2} D^{-3/2}, \quad (10)$$

where D is the determinant of the $(A-1) \times (A-1)$ matrix \hat{B} with the entries

$$\begin{aligned} b_{ii} &= \sum_{j(\neq i)}^A (\alpha_{ij}^k + \beta_{ij}^\ell), \quad j(\neq i) = 1, 2, \dots, A, \\ b_{ii} &= -(\alpha_{ij}^k + \beta_{ij}^\ell), \quad i \neq j = 1, 2, \dots, A-1. \end{aligned} \quad (11)$$

In particular, for $A = 4$, the (k, ℓ) entry of the \hat{B} matrix is a 3×3 matrix. Analytic and/or numerical computation of the determinant of this matrix and all its first-order derivatives is straightforward.

We now consider the matrix elements of the potential energy V . For an interparticle potential that can be written as the sum of the central (pair) potentials, i. e.,

$$W = \sum_{(ij)} V_{(ij)}(r_{ij}),$$

the analytic formula for the appropriate matrix elements can be written as

$$\sum_{(ij)} \langle \alpha | V_{(ij)}(r_{ij}) | \beta \rangle = \frac{4}{\sqrt{\pi}} \langle \alpha | \beta \rangle \times \sum_{ij} \int_0^\infty V_{(ij)} \left(x \sqrt{\frac{D_{ij}}{D}} \right) \exp(-x^2) x^2 dx, \quad (12)$$

where

$$D_{ij} = \frac{\partial D}{\partial \alpha_{ij}} = \frac{\partial D}{\partial \beta_{ij}}.$$

The explicit expressions for various interparticle potentials often used in bound-state calculations can be found in [1]. The formulas in [1] include systems with the Coulomb, Yukawa-type, exponential, oscillator, and many other potentials. For all such cases, the analytic expressions for lower-bound estimates (E_L) were also derived for an arbitrary A -particle system in [1].

In particular, matrix elements of the Coulomb potential energy are (in atomic units)

$$\sum_{(ij)} \langle \alpha | V_{ij}(r_{ij}) | \beta \rangle = \sum_{(ij)} \langle \alpha | \frac{q_i q_j}{r_{ij}} | \beta \rangle = 2 \sqrt{\frac{D}{\pi}} \langle \alpha | \beta \rangle \sum_{(ij)} \frac{q_i q_j}{\sqrt{D_{ij}}}, \quad (13)$$

where $(ij) = (ji) = (12), (13), (23), (14), (24), (34)$ and $\langle \alpha | \beta \rangle$ is the overlap matrix element. In Eq. (13), the q_i ($i = 1, 2, \dots, A$) stand for the charges of the particles. The matrix elements of the kinetic energy take the form (in atomic units)

$$\langle \beta | T | \alpha \rangle = \frac{3}{2D} \times \left[\sum_{i,j,k=1}^A \frac{\alpha_{ik} \beta_{jk}}{m_k} (D_{ik} + D_{jk} - D_{ij}) \right] \langle \beta | \alpha \rangle, \quad (14)$$

where m_i ($i = 1, 2, \dots, A$) are the masses of the particles and $i \neq j \neq k$. The symmetrization of the given

expressions to the case of identical particles does not present any difficulty.

In general, for an arbitrary self-adjoint operator \hat{X} , the corresponding bound state property (or the expectation value) is determined as

$$\langle X \rangle = \frac{\langle \psi | \hat{X} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (15)$$

where $|\psi\rangle$ is the wave function obtained in variational calculations. If $\hat{X} = f(r_{ij})$, then we find the following formula for the matrix elements:

$$\langle \alpha | f(r_{ij}) | \beta \rangle = \langle \alpha^{(k)} | f(r_{ij}) | \beta^{(\ell)} \rangle = \frac{4}{\sqrt{\pi}} \langle \alpha | \beta \rangle \int_0^\infty f \left(x \sqrt{\frac{D_{ij}}{D}} \right) \exp(-x^2) x^2 dx. \quad (16)$$

The one-dimensional integral in the last equation can be computed analogously for a large number of actual interparticle potentials. In particular, for $f(y) = y^{2n-1}$ ($n = 0, 1, 2, \dots$), it follows from Eq. (16) that

$$\langle \alpha | r_{ij}^{2n-1} | \beta \rangle = \frac{2}{\sqrt{\pi}} \langle \alpha | \beta \rangle n! \left(\frac{D_{ij}}{D} \right)^{(2n-1)/2}, \quad (17)$$

and for $f(y) = y^{2n}$ ($n = 0, 1, 2, \dots$), we have

$$\langle \alpha | r_{ij}^{2n} | \beta \rangle = \frac{(2n+1)!!}{2^n} \left(\frac{D_{ij}}{D} \right)^n \langle \alpha | \beta \rangle, \quad (18)$$

where $(2n+1)!!$ is the product $1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n+1)$. In the case where $f(y) = y^{-2}$ (i. e., $n = -1$ in Eq. (18)), the appropriate expression becomes

$$\langle \alpha | r_{ij}^{-2} | \beta \rangle = 2 \langle \alpha | \beta \rangle \frac{D}{D_{ij}}. \quad (19)$$

In some problems, the expectation values of the two-, three-, and many-particle delta-functions are important. The analytic formulas for the expectation values of various few-particle delta-functions can be found in [5].

The formulas for matrix elements presented above allow conducting highly accurate variational computations, in principle, for various A -body systems ($A \geq 2$) with different interparticle interactions. The related procedures and methods based on Eq. (3) have been applied in highly accurate computations of many hundred of atomic, molecular, quasimolecular, and nuclear systems. In particular, the variational methods based on the use of many-dimensional Gaussoids were found to be very effective in applications to various few-electron systems. Moreover, for atomic systems with four and

more electrons, the method in [1] is one of a few highly accurate procedures that work effectively in such cases. We note that the approach developed in [1] was based on the method proposed in earlier work [6] (for three-body systems). In theoretical chemistry, a similar approach has been developed in [7, 8]. The last approach is, in fact, a method different from [1], because it did not include the integration over inter-nuclear coordinates. In applications to atomic and molecular problems, the methods analogous [1] were created only in the mid-1990s (see, e. g., [5, 9, 10]).

4. OPTIMIZATION OF THE NONLINEAR PARAMETERS

In general, the optimization of the nonlinear parameters in the trial wave functions is an important step in construction of highly accurate few-body wave functions. For variational expansions that include many-dimensional Gaussoids of the relative coordinates, e. g., Eq. (3), the optimization of nonlinear parameters plays even a greater role, because without such an optimization, only relatively poor total energies and very approximate wave functions can be produced. We note that optimization of the nonlinear parameters in a few-electron wave functions have been extensively discussed in earlier studies (see, e. g., [11, 12] and the references therein).

We note that many different optimization strategies are currently used to optimize the nonlinear parameters in the trial wave functions, Eq. (3). In this section, we briefly discuss the general principles and rules applied to the optimization of the nonlinear parameters in few-body wave functions. First, we assume that some trial wave function includes N nonlinear parameters $\alpha_1, \alpha_2, \dots, \alpha_N$, where $N \gg 1$. In actual applications, it is convenient to divide these parameters into a number of groups and perform numerical optimization in each group. This also allows the application of very powerful methods of parallel programming [13].

Second, all optimization procedures can be separated into the two following groups: (1) methods that can be used for fast, but approximate optimization of the nonlinear parameters, and (2) methods that provide relatively accurate optimization of large numbers of the nonlinear parameters. The methods of the first group include parabolic interpolation and Brent's optimization method in multidimensions [14]. These procedures allow constructing approximate wave functions that can be considered as the first approximation to highly accurate wave functions. The overall accuracy

of such wave functions is drastically improved at later stages. At these stages of the optimization procedure, Powell's method in multidimensions and/or the conjugate gradient method can be used [14]. These methods allow optimizing large numbers of nonlinear parameters at once. Various modifications of the simplex method and simulated annealing method also work well for optimization of the nonlinear parameters in Eq. (3). In fact, the same conclusion is true for the bound state computations in five- and six-body systems. Our results for such systems will be published elsewhere (also see the Conclusions).

A very important step in any optimization process is the increase in the total number of nonlinear parameters. The problem is formulated as follows. We suppose that we have the "original" wave function with N carefully optimized nonlinear parameters. At the next step, we want to increase the total number of such parameters from N to $N + N_s$, where $N + N_s$ is the total number of the nonlinear parameters in the "final" wave function. The crucial question here is to find the optimal strategy for the $N \rightarrow N + N_s$ increase. It is clear that N_s must be smaller than N . Moreover, for small N (10–60), the optimal value of N_s is approximately equal N . For larger N ($N \geq 300$ –600), the optimal value N_s rapidly decreases, e. g., $N_s \approx N/6$ for $N \approx 600$. During optimization of these additional N_s nonlinear parameters, the numerical values of the first N such parameters do not change. However, when all N_s new nonlinear parameters are well optimized, then it is very useful to perform the re-optimization of all the $N + N_s$ nonlinear parameters. Combinations of different optimization methods used for optimization and re-optimization of the nonlinear parameters allow constructing very compact and accurate variational wave functions. After a number of similar steps, we obtain a very accurate variational wave function with a relatively large number of nonlinear parameters ($N \approx 3000$ –9000 and even more). Such wave functions can be used to determine various bound state properties in a three-electron atomic system. The results of our variational computations are considered below.

5. RESULTS

Results of our calculations of the ground bound $1^2S(L=0)$ states in a number of three-electron atoms and ions are given in Tables 1 and 2. For simplicity, in calculations performed for Tables 1 and 2, all nuclear masses were assumed to be infinite. Table 1 contains the variational energies of the ground 1^2S states ob-

Table 1. The total energies E in atomic units for the ground 1^2S states of some lithium-like systems. For all these systems, $N = 800$ in Eq. (2)

	E		E		E		E
Li	-7.47805925	C ³⁺	-34.7755102	F ⁶⁺	-82.3303368	Mg ⁹⁺	-150.136196
Be ⁺	-14.3247623	N ⁴⁺	-48.3768970	Ne ⁷⁺	-102.682231	-	-
B ²⁺	-23.4246051	O ⁵⁺	-64.2285409	Na ⁸⁺	-125.284190	-	-

Table 2. The expectation values in atomic units of some properties for the ground bound 1^2S states of some three-electron ions: N denotes the positively charged nucleus and e denotes the electron

System	Be ⁺	N ⁴⁺	F ⁶⁺	Na ⁸⁺	Mg ⁹⁺
$\langle r_{eN} \rangle$	1.0337900	0.50177267	0.37520415	0.29983894	0.27250821
$\langle r_{ee} \rangle$	1.7556665	0.83467918	0.62096465	0.49471506	0.44911832
$\langle r_{eN}^2 \rangle$	2.169235	0.4760186	0.2619051	0.1656895	0.1363986
$\langle r_{ee}^2 \rangle$	4.357836	0.9554660	0.5253921	0.3322342	0.2734526
$\langle r_{eN}^3 \rangle$	6.22822	0.614080	0.248100	0.124094	0.092487
$\langle r_{ee}^3 \rangle$	13.1398	0.131745	0.534416	0.267931	0.199856
$\langle r_{eN}^4 \rangle$	21.067	0.93406	0.27715	0.10961	0.07396
$\langle r_{ee}^4 \rangle$	45.453	2.07411	0.62001	0.24630	0.16646
$\langle r_{eN}^{-1} \rangle$	2.6579629	4.9088461	6.4089498	7.9089947	8.6590077
$\langle r_{ee}^{-1} \rangle$	1.0820108	2.1106599	2.7936624	3.4761518	3.8173010
$\langle r_{eN}^{-2} \rangle$	18.99849	62.76864	106.1185	160.8033	192.3956
$\langle r_{ee}^{-2} \rangle$	2.965660	10.67731	18.48395	28.42356	34.19330
$\langle -(1/2)\nabla_e^2 \rangle$	4.7749205	16.1256311	27.4434408	41.7613938	50.0453940
$\langle \delta_{eN} \rangle$	11.66345	68.41104	149.25557	277.49827	362.58613
$\langle \delta_{ee} \rangle$	0.52773	3.63633	8.30797	15.8744	20.9625
$\langle \delta_{eeN} \rangle$	78.3097	3011.32	14709.58	52324.7	90034.1

tained in calculations, and Table 2 includes the expectation values of many bound state properties computed for these ions. In Table 2, we restrict ourselves to the consideration of the following ions in their 1^2S states: Be⁺, N⁴⁺, F⁶⁺, Na⁸⁺, and Mg⁹⁺. The properties of the last two ions have not been considered previously. For the other light three-electron atoms and ions (Li, B²⁺, C³⁺, O⁵⁺, and Ne⁷⁺), our results are very close to the expectation values obtained in [2], and we do not want to repeat them here.

In general, the convergence rates observed in our calculations for the variational energies of the ground 1^2S states in these ions (see Table 1) were relatively high. The total energies obtained in this study have been determined to the accuracy that is quite compa-

rable to the accuracy of the best variational computations performed with the use of the Hylleraas-type basis set [2, 3], where the same (or comparable) number of basis functions was used ($N \approx 700$).

All properties in Table 2 are given in atomic units. The physical meaning of all expectation values in Table 2 is generally quite clear from the notation used, and we have to make only a few following remarks. The notation $\langle \delta_{eN} \rangle$, $\langle \delta_{ee} \rangle$, and $\langle \delta_{eeN} \rangle$ is for the expectation values of the electron–nucleus, electron–electron, and three-particle delta functions. The expectation values $\langle \delta_{ee} \rangle$ and $\langle \delta_{eeN} \rangle$ have never been determined for three-electron atomic systems in earlier studies. The expectation values of the three-electron and four-particle delta-functions (i. e., $\langle \delta_{eee} \rangle$ and $\langle \delta_{eeeN} \rangle$) are equal to

zero identically for all considered three-electron atoms and ions in their 1^2S states. This follows from the spin symmetry of the total wave function. In general, the variational expansion in Eq. (3) describes the three-electron atoms and ions as slightly more diffuse systems than does the Hylleraas expansion. This explains some small deviations of our results from the results obtained with the use of the Hylleraas basis set [2, 3]. Overall, the agreement between the two groups of results can be considered very good.

We note that some of the expectation values given in [2] were defined differently. For instance, in modern works, the $\langle r_{ee}^{-1} \rangle$ expectation value means the average electron–electron repulsion, i. e., the value computed per one electron. The analogous notation $\langle 1/r_{ij} \rangle$ used in [2] means the sum of three electron–electron repulsions. It is, in fact, the total electron–electron repulsion energy, rather than the electron–electron repulsion determined per one electron. This means that $\langle 1/r_{ij} \rangle$ [2] = $3\langle 1/r_{ee} \rangle$ (this work). Similar deviations can be found for other bound state properties computed in [2]. In fact, at that time similar definitions were used by many other authors, e. g., Pekeris used them for the electron–nuclear properties in the He atom.

In general, our procedure has the two following advantages in comparison with the Hylleraas method. First, in our computations for Tables 1 and 2, all nuclear masses were assumed to be infinite. But the use of finite nuclear masses is also very easy and straightforward, because it requires only a one-line change in the code. For instance, in some calculations performed for Table 1, we obtained the total energy $E \approx -14.3247607$ a.u. for the ${}^\infty\text{Be}^+$ ion. Now, using the nuclear masses $M({}^9\text{Be}^+) = 16419.7014 m_e$ and $M({}^{10}\text{Be}^+) = 18244.5534 m_e$, we find $E({}^9\text{Be}^+) \approx -14.3238608$ a.u. and $E({}^{10}\text{Be}^+) \approx -14.3239508$ a.u. from the results of the direct computations. All bound state properties for the finite-mass isotopes are computed at the same moment. Such calculations are direct, simple, and do not require any computation of some additional expectation values of slowly convergent operators. The second advantage has an even greater value in actual applications. In our method, the non-linear parameters in Eqs. (2) and (3) can be varied independently. The linear dependence between different radial basis functions from the ψ and ϕ families (see Eq. (2)) is very rare and can be ignored in actual computations. In contrast, for a Hylleraas basis set, an additional procedure must be developed for eliminating all linearly dependent basis functions [15]. For large basis sets, this is not an easy task.

The computed expectation values can be used to

determine various atomic properties. In general, the numerical values of these properties are known from numerous experiments. There are many interesting atomic properties in three-electron ions, but we restrict ourselves to the computation of the field component of the total isotope shift, which is determined for some of the three-electron ions mentioned in this study. The hyperfine structure splitting is computed for some of these ions that have nonzero nuclear spin. Another actual problem is the application of the Q^{-1} expansion to represent the total energies of these ions.

5.1. Field shift

Here, we consider the field component of the total isotope shift in three-electron atoms/ions. We note that in many works, the field component of the total isotope shift is also called the field shift, for brevity. The field shift is related to the extended nuclear charge distribution that produces the non-Coulomb field at the distances close to the nucleus. In general, the largest deviations between the point Coulomb and actual potentials can be found at the distances close to the atomic nucleus, i. e., for distances $r \approx r_e \ll \Lambda \ll a_0$, where

$$r_e = \frac{e^2}{m_e c^2} = \alpha^2 a_0 \approx 2.81794093 \text{ fm}$$

is the classical electron radius and $\Lambda = \alpha a_0$ is the Compton wave length. Here and below, $\alpha = 7.297352568 \cdot 10^{-3}$ is the fine structure constant and $a_0 \approx 5.29177249 \cdot 10^{-11}$ m is the Bohr radius. It is clear that the field shift is important only for $s(\ell = 0)$ electrons, which have a finite probability to be within the nuclear volume. The general theory of the field shift has been discussed extensively in a number of works (see, e. g., [16–18]).

In our previous work [19], we obtained the following expression for the field shift (in atomic units) in light atoms and ions:

$$\begin{aligned} E_M^{fs} &= \frac{2\pi}{3} Q \rho_e(0) R^2 \frac{\lambda+3}{\lambda+5} = \frac{2\pi}{5} Q \rho_e(0) R^2 \frac{1+\lambda/3}{1+\lambda/5} = \\ &= \frac{2\pi}{5} Q \alpha^4 \langle \delta(\mathbf{r}_{eN}) \rangle \left(\frac{R}{r_e} \right)^2 \xi, \quad (20) \end{aligned}$$

where Q is the nuclear charge and R is the nuclear radius. The parameter λ and the related factor

$$\xi = \frac{1 + \lambda/3}{1 + \lambda/5} \approx 1$$

in these equations describe the actual charge/proton distribution in the nucleus [13]. All numerical values

Table 3. The nuclear sizes, field shifts E_M^{fs} , nuclear spin I (\hbar), and nuclear magnetic moment μ_N for the ${}^6\text{Li}$ and ${}^7\text{Li}$ atoms and for some three-electron ions (in atomic units)

Ion	$(\langle R^2 \rangle)^{1/2}$, fm	E_M^{fs}	Ion	I	μ_N	H_{FS}
${}^6\text{Li}$	2.56	$3.47372 \cdot 10^{-8}$	${}^6\text{Li}$	0.82205	1	-4552.7697
${}^7\text{Li}$	2.41	$2.89818 \cdot 10^{-8}$	${}^7\text{Li}$	3.25644	3/2	-16031.2730
${}^9\text{Be}^+$	2.519	$8.37010 \cdot 10^{-8}$	${}^9\text{Be}^+$	-1.1776	3/2	14662.0371
${}^{10}\text{Be}^+$	2.45	$4.514187 \cdot 10^{-7}$	${}^{14}\text{N}^{4+}$	0.40376	1	-33151.8140
${}^{11}\text{B}^{2+}$	2.37	$4.086263 \cdot 10^{-7}$	${}^{15}\text{N}^{4+}$	-0.28319	1/2	31002.7812
${}^{14}\text{N}^{4+}$	2.54	$1.097511 \cdot 10^{-7}$	${}^{19}\text{F}^{6+}$	2.62887	1/2	-627940.296
${}^{15}\text{N}^{4+}$	2.580	$2.13881 \cdot 10^{-6}$	${}^{22}\text{Na}^{8+}$	1.746	3	-452393.558
${}^{19}\text{F}^{6+}$	2.900	$3.03744 \cdot 10^{-6}$	${}^{23}\text{Na}^{8+}$	2.21752	3/2	-656646.547
${}^{24}\text{Mg}^{9+}$	3.08	$4.75319 \cdot 10^{-6}$	${}^{25}\text{Mg}^{9+}$	-0.85545	5/2	297797.145

for the physical constants used in this study were chosen from [20, 21]. In general, the nuclear radius $R \approx r_e$ and its value depends on the total number of nucleons A in the nucleus ($R \propto A^{1/3}$). In other words, the field shift formally corresponds to the α^4 -correction to the energy levels, i. e., to the second-order relativistic correction. The values of the field shifts computed for the different three-electron ions can be found in Table 3. All nuclear sizes used in our present computations were chosen from [22]. In calculations performed for Table 3, we have selected zero value for the parameter λ ($\xi = 1$), i. e., the uniform (r -independent) proton density distribution is assumed in each of the nuclei.

5.2. Hyperfine splitting

In the doublet 2S states of any three-electron atomic system, the spin of the outermost electron may interact with the nuclear spin \mathbf{I}_N in the cases where $\mathbf{I}_N \neq 0$. For three-electron atomic systems with a nonzero nuclear spin, it is possible to observe the difference between the two states with the respective total angular momenta $I_N - 1/2$ and $I_N + 1/2$. Here and below, $I_N = \max|\mathbf{I}_N|$ is the nuclear spin. Such a difference between the two energies is called the hyperfine structure splitting, or hyperfine splitting for brevity. For the 2S states in three-electron atomic systems with the nonzero nuclear spin I_N , the following expression (Fermi–Segré formula) for the hyperfine splitting H_{FS} holds in the lowest-order approximation [23]

$$H_{FS} = \frac{8\pi\alpha^2}{3} \mu_B \mu_N g_e g_N \langle \delta(\mathbf{r}_{eN}) \rangle \times \frac{1}{2} [F(F+1) - I_N(I_N+1) - S(S+1)], \quad (21)$$

where $\langle \delta(\mathbf{r}_{eN}) \rangle = \langle \delta_{eN} \rangle$ is the electron–nuclear delta-function computed for the considered electron state, the total electron spin $S = 1/2$ for the doublet states, I_N is the nuclear spin ($I_N \geq 1/2$), and $F = |\mathbf{F}|$, where \mathbf{F} is the total angular momentum operator for the whole three-electron atom/ion (i. e., electrons plus the nucleus). For $S = 1/2$ and a nuclear spin $I_N \neq 0$, the hyperfine splitting can be observed between the states with $F = I_N - 1/2$ and $F = I_N + 1/2$.

We now apply formula (21) to evaluate the hyperfine splitting in the $1^2S(L = 0)$ states of the three-electron atomic systems. In atomic units, we have $\mu_B = 1/2$, $g_e = -2.002319304386$ [20], and $\mu_N = \mu_B(m_e/M_p)$, where $M_p = 1836.15267261m_e$ [20]. For light nuclei with $I_N \neq 0$, we also have $g_N = \mu_N/I_N$, where the product $\mu_N = g_N I_N$ is the so-called nuclear magnetic moment [20]. The values of μ_N and I_N for various nuclei can be found in data tables. Finally, we find (in MHz)

$$H_{FS} = -400.11870397143 \langle \delta(\mathbf{r}_{eN}) \rangle \times \frac{\mu_N}{I_N} \left[F(F+1) - I_N(I_N+1) - \frac{1}{4} \right], \quad (22)$$

where $F = I_N - 1/2$, $I_N + 1/2$ and $\langle \delta(\mathbf{r}_{eN}) \rangle = \langle \delta_{eN} \rangle$ (in a.u.) is the expectation value of the electron–nucleus delta-function. To transform the results from atomic units to MHz, the conversion factor 1 a.u. = 6.57968392061 MHz must be used. To produce these formulas, we used the fact that in atomic units,

Table 4. The coefficients of the Q^{-1} expansion constructed for the total energies of the ground 1^2S states in three-electron ions, Eq. (2). Expansions with $N = 4, 5,$ and 6 terms are considered. The results shown in the right column are obtained with the use of data in [32] for the first ten systems (Li-Mg⁸⁺)

a_2	-1.1248490528	-1.1250404995	-1.1249892386	-1.1249895979
a_1	1.0192512593	1.0240427795	1.0223950181	1.0224083939
a_0	-0.3805253825	-0.4220687503	-0.4020425473	-0.4022271767
b_1	-0.0949183497	0.0532889241	-0.0617188349	-0.0605633054
b_2	-	-0.1846549797	0.1278835626	0.1245391345
b_3	-	-	-0.3222436143	-0.3186502304

the Bohr magneton equals $1/2$ exactly. Also, in these equations, $g_N = \mu_N/I_N$, where the nuclear magnetic moment μ_N is expressed in the nuclear magnetons

$$\frac{e\hbar}{2m_p c} = \frac{m_e}{m_p} \mu_0,$$

where μ_0 is the Bohr magneton. The maximal value of the nuclear moment μ_N is presented in the tables of nuclear data (see, e. g., [21] and the references therein).

We note that the splitting between the two levels with $F = I_N + 1/2$ and $F = I_N - 1/2$ is written as (in MHz)

$$H_{FS} = -400.11870397143 \langle \delta(\mathbf{r}_{eN}) \rangle \times \frac{\mu_N(2I_N + 1)}{I_N}, \quad (23)$$

where $I_N \neq 0$ and $\langle \delta(\mathbf{r}_{eN}) \rangle$ is expressed in atomic units. Our theoretically predicted values of the hyperfine splitting for some of the three-electron atoms/ions in their 1^2S states can be found in Table 3. The agreement with the known experimental values for hyperfine splittings in the ⁶Li and ⁷Li atoms is quite good for the first approximation (see a discussion in [24], which also contains an extensive collection of references for the Li atom calculations). The formulas for the hyperfine splitting in Eqs. (21)–(23) correspond to the lowest-order approximation. To obtain a better approximation, one needs to determine various corrections to the Fermi–Segré formula, which are discussed, e. g., in [16].

5.3. The Q^{-1} expansion of the total energies

The accurate ground-state energies of the lithium atom and positively charged lithium-like ions obtained in this study allow producing the explicit formulas for the Q^{-1} expansion (Z^{-1} expansion) of the total energies $E(Q)$ of these systems. In other words, we consider the Q^{-1} expansion of the eigenvalues $E(Q)$, where

$H\Psi = E(Q)\Psi$ and the Hamiltonian H is taken in the form of Eq. (1) with $M = \infty$. In this case, the total energies of three-electron atoms/ions are analytic functions of the nuclear charge Q only. For the ground 1^2S states in lithium-like systems, the expansion for the energy function $E(Q)$ can be written as a Laurent expansion of the form (here and below, $Q \geq 3$)

$$E(Q) = a_2Q^2 + a_1Q + a_0 + b_1Q^{-1} + b_2Q^{-2} + b_3Q^{-3} + b_4Q^{-4} + \dots, \quad (24)$$

where numerical values of the coefficients $a_2, a_1, a_0, b_1, b_2, b_3, \dots$ must be determined from the results of numerical computations. We note that the principal part of the expansion in Eq. (24) includes only integer powers of Q^{-1} . Such an expansion essentially follows from the Poincaré theorem (see, e. g., [25]) applied to the Schrödinger equation with Hamiltonian (1). For degenerate bound states, the expansion analogous to Eq. (24) must also include noninteger powers of Q (so-called Puiseux series [26]). The analogous Q^{-1} (or Z^{-1}) expansions were found to be very useful for the two-electron ions (see, e. g., [27, 28]).

The coefficients $a_2, a_1, a_0, b_1, b_2, \dots$ in formula (24) can be determined numerically from the results of accurate computations performed for a number of three-electron atomic systems. To compute the coefficients $a_2, a_1, a_0, b_1, b_2, \dots$ in Eq. (24), we have used our best variational results obtained for all three-electron ions (ground states) mentioned in Table 1. Only for the ground 1^2S state of the $^\infty\text{Li}$ atom, we have used the most accurate energy known from the modern literature $E(^\infty\text{Li}) = -7.4780606323904$ a.u. [29]. Paper [29] also contains most of the recent references for highly accurate computations of the 1^2S state in the $^\infty\text{Li}$ atom. The coefficients in Eq. (24) determined with these energies can be found in Table 4. In our calculations, we used Eq. (24) with four, five, and six unknown coefficients. In principle, the more accurate results (ener-

gies) expected to be obtained in future variational computations of three-electron ions ought to provide better numerical accuracy for all coefficients in Eq. (24).

6. CONCLUSION

We have computed the ground bound 1^2S states in various three-electron atomic systems. The systems discussed in this study include the neutral Li atom and Be^+ , B^{2+} , C^{3+} , ... Na^{8+} , Mg^{9+} ions. The variational wave functions used in this study are represented as the sums of six-dimensional Gaussoids written in the four-body relative coordinates r_{12} , r_{13} , r_{23} , r_{14} , r_{24} , and r_{34} . The overall accuracy of our results is quite comparable with the accuracy produced by the best Hylleraas-type expansions with the comparable number of basis functions ($N \approx 700\text{--}800$). Such a conclusion was quite unexpected, because the actual convergence rate of any Hylleraas-type expansion is significantly higher than the analogous convergence rate for the three-dimensional Gaussoids.

In fact, at the beginning of this project, we expected that our best results would be substantially different from the results obtained with the use of exponential and/or Hylleraas basis functions. Such a difference can be found, e. g., when exponential and/or Hylleraas basis functions and three-dimensional Gaussoids are applied to the bound-state computations in two-electron atomic system, e. g., to the ground 1^1S state of the $^\infty\text{He}$ atom. For instance, in our calculations of the ground 1^1S state of the $^\infty\text{He}$ atom in [30] we obtained the total energy

$$E = -2.903\,7243\,7703\,4119\,5831\,1034 \text{ a. u.},$$

where 21 decimal digits are stable. By using the variational expansion based on six-dimensional Gaussoids in relative coordinates (with 4000 terms), it is very difficult to obtain even 12 correct decimal digits. But for three-electron atomic systems, the overall accuracy of our results was quite comparable with the accuracy produced by the Hylleraas expansions of comparable size, i. e., if the same (or approximately the same) number of basis vectors are used.

There are three different reasons that can be used to explain this result. First, we have varied all nonlinear parameters in each basis function and for each spin configuration used in calculations. In calculations with the Hylleraas basis set, this is impossible to achieve due to the rapidly increasing linear dependence between basis vectors. Second, the overall convergence rate of Hylleraas basis set is relatively low for three-electron

atomic systems, e. g., it cannot be compared with the case of two-electron atoms and ions. The gap in convergence rates observed for our six-dimensional Gaussoids and the Hylleraas basis set is much smaller for three-electron systems than for two-electron atoms and ions. Third, in the current version of the Hylleraas method, the variation of nonlinear parameters is very primitive and nonaccurate. Moreover, it is impossible to vary the nonlinear parameters in each Hylleraas basis function. Also, the nonlinear parameters in radial basis functions used with the second spin configuration cannot be varied as real independent parameters. If these problems with the Hylleraas basis set can be fixed, then, probably, the gap observed for convergence rates of the two methods will be restored.

On the other hand, in some recent calculations, the Hylleraas basis set included very large (≥ 3500) [31] and extremely large ($N \geq 10.000$) [29] numbers of radial basis functions. The accuracy of such complex calculations is obviously better than our current accuracy achieved with only 700–800 (different) basis functions. However, we note that the area of applications for the Hylleraas basis set is very restricted. It cannot be used, in principle, for arbitrary four-body system, e. g., for bi-positronium Ps_2 , the $d\text{t}\mu\mu$ molecule and/or the $^1\text{H}_2$ molecule. Our variational expansion based on Eq. (3) works successfully for an arbitrary four-body system.

By using our compact and accurate wave functions determined in this study, we have obtained the numerical values of some atomic properties that can be measured in modern experiments. In particular, for all three-electron systems mentioned in this work, we evaluate the field component of the total isotopic shift. The hyperfine structure splittings for the ground (doublet) 1^2S states are also determined numerically for nuclei that have a nonzero nuclear spin. An analytic formula for the Q^{-1} expansion is derived to represent the total energies of the three-electron atomic systems.

We note that our current procedure can easily be generalized to the four-electron atomic systems (atoms and ions). The trial wave functions constructed for the ground 1^1S^e states in the four-electron atoms/ions contain two independent spin configurations [31]

$$\chi_1 = \alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha,$$

$$\chi_2 = 2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \alpha\beta\alpha\beta.$$

Our current variational energy of the ground state in the O^{4+} ion computed with 700 radial basis functions (400 + 300) is -68.411508315 a.u. This energy is much better than the value obtained in [33]. The generalization of our method to the P -, D -, F -, and

other bound states with $L \geq 1$ in the three- and four-electron atomic systems is straightforward. However, highly accurate computations of the ground doublet $^2P_{1/2}$ and $^2P_{3/2}$ states of the five-electron B atom is not an easy task due to a very complex permutation symmetry of the five-electron wave function. But, in principle, our computer codes work for an arbitrary six-body system, and hence there appears to be no barrier to the application of this approach to the B atom.

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