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Compact wave functions for four-electron atomic systems

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A procedure is developed to construct improved wave functions for the bound states in various four-electron atoms and ions. The bound state wave functions are improved in the sense that our trial wave functions are compact and accurate. We employ two independent four-electron spin functions $\chi_1=\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha$ and $\chi_2=2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\beta\alpha-\alpha\beta\alpha\beta$ in each trial wave function. Optimization of the nonlinear parameters is performed for each radial function. Our procedure is applied to obtain the total energies of the ground $^1S^e$ states in the following four-electron berylliumlike systems: Li^-, Be, B^+, C^{2+}, N^{3+}, O^{4+}, F^{5+}, Ne^{6+}, Na^{7+}, and Mg^{8+}. All our trial wave functions used in this study are very compact. In fact, each of these functions contains only 300 basis (radial) functions which are constructed from ten-dimensional gaussoids of the five-body relative coordinates r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}, and r_{45}.

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I. INTRODUCTION

In this study we consider the electronic structure of the ground $^1S^e$ states in a number of four-electron atoms and ions. Our goal is to construct very compact approximate wave functions for arbitrary four-electron atomic systems. Such functions must be "sufficiently accurate," i.e., the total energies and other bound state properties computed with these wave functions must be accurate enough to be useful in applications to various problems in atomic physics. In this work, we restrict ourselves to the consideration of the following systems: the negative Li^- ion, neutral beryllium atom Be, and a number of positively charged berylliumlike ions: $\mathrm{B}^+, \mathrm{C}^{2+}, \ldots, \mathrm{Mg}^{8+}$. Each of these systems contains four electrons and one heavy positively charged nucleus. All particles (i.e., electrons and nuclei) are considered as point particles with masses m_e and M and electric charges $q=-e$ and Qe, respectively. In atomic units, where $\hbar=1$, $m_e=1$, $|e|=1$, these values are $m_e=1$, $M=\frac{M}{m_e}$, $q=-1$, and Q, respectively. In fact, everywhere below in this study only atomic units are used. In these units the nonrelativistic Hamiltonian of an arbitrary four-electron berylliumlike system takes the form (see, e.g., [1])

$$H=-\frac{1}{2}\left[\sum_{i=1}^{4}\nabla_i^2+\frac{1}{M}\nabla_5^2\right]-\sum_{i=1}^{4}\frac{Q}{r_{i5}}+\sum_{i=1}^{3}\sum_{j=2(>i)}^{4}\frac{1}{r_{ij}}, \quad (1)$$

where the subscripts 1, 2, 3, 4 designate four electrons, while the subscript 5 means the positively charged nucleus. Also, in Eq. (1) $\nabla_i=(\frac{\partial}{\partial x_i},\frac{\partial}{\partial y_i},\frac{\partial}{\partial z_i})$ is the gradient operator of the ith particle $(i=1,2,\ldots,5)$. The notation r_{ij} stands for the (ij)-relative distance or coordinate between ith and jth particles, i.e., $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|=r_{ji}$, where $\mathbf{r}_i$ are the Cartesian coordinates of the ith particle. The notation M in Eq. (1) stands for the mass of the central (heavy) nucleus. For all atoms and ions considered in this study $M\gg 1$.

Our first aim is to determine the highly accurate solutions of the Schrödinger equation $H\Psi=E\Psi$ where H is the Hamiltonian, Eq. (1), while E is the eigenvalue (total energy) of the considered bound state and Ψ is the corresponding wave function. In fact, in this study we consider only the ground $^1S^e$ states in four-electron (berylliumlike) systems. The variational method developed here allows us to construct sufficiently accurate variational wave functions for an arbitrary four-electron atomic system. Note that all our trial wave functions are very compact and that in contrast with other methods our approach is relatively simple.

II. VARIATIONAL WAVE FUNCTIONS

In our case the variational wave functions Ψ must be constructed for four-electron atomic systems with one heavy nucleus. In general, this is a very complex problem, since such a wave function includes a number of different terms in its spin part. For the ground $^1S^e$ state of the four-electron system there are two independent spin functions χ_1 and χ_2. The wave function of the ground $^1S^e$ state of the four-electron berylliumlike atom or ion can be written in the form (see, e.g., [2])

$$\Psi=\psi_{L=0}(A;\{r_{ij}\})\chi_1+\phi_{L=0}(B;\{r_{ij}\})\chi_2, \quad (2)$$

where $\psi_{L=0}(A;\{r_{ij}\})$ and $\phi_{L=0}(B;\{r_{ij}\})$ are the two independent radial parts (spatial parts) of the total wave function. The notations A and B in Eq. (2) designate the different sets of nonlinear parameters used in the two radial parts of the total wave function (radial wave functions, for short). As we mentioned above there are two independent spin functions for the ground $^1S^e$ states in four-electron atomic systems. Below, we shall choose the two independent spin functions χ_1 and χ_2 in Eq. (2) in the following form [2]:

$$\chi_1=\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha, \quad (3)$$

$$\chi_2=2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\beta\alpha-\alpha\beta\alpha\beta, \quad (4)$$

where α and β are the spin-up and spin-down single electron functions, i.e., $\hat{\sigma}_z\alpha=\alpha$ and $\hat{\sigma}_z\beta=-\beta$. In general, any two linear and pairwise orthogonal combinations of the χ_1 and χ_2 spin functions can also be considered as possible spin functions of the four-electron system with $\mathbf{S}^2=0$ and $S_z=0$, where $\mathbf{S}=\mathbf{s}_1+\mathbf{s}_2+\mathbf{s}_3+\mathbf{s}_4$ is the total electron spin. The most general

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form of the four-electron spin function which corresponds to the $\mathbf{S}^2=0$ and $S_z=0$ values can be represented in the following one-parametric form (see, e.g., [3] and references therein):

$$\chi_{00} = \sqrt{\frac{1}{3}} \sin\theta|\alpha\alpha\beta\beta\rangle + \left(\frac{1}{2}\cos\theta - \sqrt{\frac{1}{12}}\sin\theta\right)|\alpha\beta\alpha\beta\rangle - \left(\frac{1}{2}\cos\theta + \sqrt{\frac{1}{12}}\sin\theta\right)|\alpha\beta\beta\alpha\rangle - \left(\frac{1}{2}\cos\theta + \sqrt{\frac{1}{12}}\sin\theta\right)|\beta\alpha\alpha\beta\rangle + \left(\frac{1}{2}\cos\theta - \sqrt{\frac{1}{12}}\sin\theta\right)|\beta\alpha\beta\alpha\rangle + \sqrt{\frac{1}{3}}\sin\theta|\beta\beta\alpha\alpha\rangle, \tag{5}$$

where θ is the free angular parameter. In this equation the six basic spin functions are designated as the Dirac $|\text{ket}\rangle$ vectors, e.g., $|\alpha\alpha\beta\beta\rangle$. By choosing the different values of the angular parameter θ one finds a few different spin functions for an arbitrary four-electron system (but only two of them are really independent). For instance, by choosing $\theta=0$ and $\theta=\frac{\pi}{2}$ in the last formula one finds the spin functions χ_1 and χ_2 from Eqs. (3) and (4). Note that the effective methods for constructing different spin-isospin functions with the required permutation symmetry in various few-body systems have been developed in few-body nuclear physics. In this study, we shall use the two independent spin functions χ_1 and χ_2, Eqs. (3) and (4). Note that these two functions have been used earlier in computations of the ground state in the four-electron berylliumlike systems [2].

The radial parts $\psi_{L=0}(A;\{r_{ij}\})$ and $\phi_{L=0}(B;\{r_{ij}\})$ of the total wave function, Eq. (2), in this work are represented in the form [4,5]

$$\psi_{L=0}(A;\{r_{ij}\}) = \mathcal{P}_1 \sum_{k=1}^{N_A} C_k \exp\left(-\sum_{ij} \alpha_{ij}^{(k)} r_{ij}^2\right), \tag{6}$$

$$\phi_{L=0}(B;\{r_{ij}\}) = \mathcal{P}_2 \sum_{k=1}^{N_B} \tilde{C}_k \exp\left(-\sum_{ij} \alpha_{ij}^{(k)} r_{ij}^2\right), \tag{7}$$

where N_A and N_B are the number of basis functions used, C_k and $\tilde{C}_k$ are the linear parameters of the variational expansions, Eq. (6) and (7), while $\{r_{ij}\}$ is designated the set of relative coordinates which are needed for complete description of the five-body systems. In fact, for all berylliumlike ions and atoms considered in this study the notation $\{r_{ij}\}$ stands for ten relative coordinates r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}, and r_{45}. In respect to this, the radial basis functions in Eqs. (6) and (7) are called the ten-dimensional gaussoids of the relative coordinates. This name was used in [4] where these basis functions were invented. The summation over $(ij)=(ji)$ in the exponents of Eqs. (6) and (7) is taken over all possible different pairs of particles. The projectors $\mathcal{P}_1$ and $\mathcal{P}_2$ produce the trial wave functions with the correct permutation symmetry between all electrons (see below). The symbol L in Eq. (6) is used for the total orbital angular momentum of the considered system. In fact, for the ground state of any Be-like system we always have $L=0$ and the total spin of such states equals zero. Furthermore, the parity of these states in the four-electron systems is even, in respect of which we shall henceforth designate these states as the ${}^1S^e$ states, or $1\,{}^1S^e$ states.

All numerical computations of the bound states in four-electron atomic systems include the nontrivial step of antisymmetrization upon all electronic variables, i.e., upon variables 1, 2, 3, and 4 in our present notations. The trial wave function Ψ, Eq. (2), must be antisymmetric upon all electron variables (variables 1, 2, 3, and 4 in our notations), i.e., $\hat{\mathcal{A}}\Psi=-\Psi$, where

$$\hat{\mathcal{A}} = \hat{e} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} - \hat{P}_{24} - \hat{P}_{34} + \hat{P}_{123} + \hat{P}_{132} + \hat{P}_{124} + \hat{P}_{142} + \hat{P}_{134} + \hat{P}_{143} + \hat{P}_{234} + \hat{P}_{243} - \hat{P}_{1234} - \hat{P}_{1243} - \hat{P}_{1324} - \hat{P}_{1342} - \hat{P}_{1423} - \hat{P}_{1432} + \hat{P}_{12}\cdot\hat{P}_{34} + \hat{P}_{13}\cdot\hat{P}_{24} + \hat{P}_{14}\cdot\hat{P}_{23} \tag{8}$$

is the complete four-particle antisymmetrizer. Here $\hat{e}$ is the identity permutation, while $\hat{P}_{ij}$ is the permutation of the ith and jth particles. Analogously, the operators $\hat{P}_{ijk}$ and $\hat{P}_{ijkl}$ are the permutations of three particles (i, j, and k) and four particles (i, j, k, and l), respectively. In actual variational computations, however, it is important to know the corresponding operator that symmetrizes the spatial parts of the total wave function. From the explicit form of the trial wave function Ψ, Eq. (2), it follows that in actual computations with the symmetric Hamiltonian and overlap matrices, only the four following permutation operators for spatial parts are important: $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$, $\mathcal{P}_{\phi\psi}$, and $\mathcal{P}_{\phi\phi}$. In reality, since $\mathcal{P}_{\psi\phi}=\mathcal{P}_{\phi\psi}$, one needs to use only three such operators $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$, and $\mathcal{P}_{\phi\phi}$. The explicit expressions for these operators are very complex and here we present only one such formula for the $\mathcal{P}_{\psi\psi}$ operator or projector

$$\mathcal{P}_{\psi\psi} = \frac{1}{4\sqrt{3}}(2\hat{e} + 2\hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} - \hat{P}_{24} + 2\hat{P}_{34} + 2\hat{P}_{12}\hat{P}_{34} + 2\hat{P}_{13}\hat{P}_{24} + 2\hat{P}_{14}\hat{P}_{23} - \hat{P}_{123} - \hat{P}_{132} - \hat{P}_{124} - \hat{P}_{142} - \hat{P}_{134} - \hat{P}_{143} - \hat{P}_{234} - \hat{P}_{243} - \hat{P}_{1234} - \hat{P}_{1243} + 2\hat{P}_{1324} - \hat{P}_{1342} - \hat{P}_{1432} + 2\hat{P}_{1423}). \tag{9}$$

The two other permutation operators $\mathcal{P}_{\psi\phi}$ and $\mathcal{P}_{\phi\phi}$ needed in actual computations have analogous structure and they are orthogonal to each other and to $\mathcal{P}_{\psi\psi}$. The use of these three projectors for matrix elements is equivalent to the operations with the trial wave functions with the correct permutation symmetry between all identical particles (electrons). Below, we present the explicit formulas for all matrix elements needed in computations with many-dimensional gaussoids.

III. MATRIX ELEMENTS

The computation of matrix elements with the five-body gaussoids, Eqs. (6) and (7), is well described in the literature (see, e.g., [4,5]). In fact, it is possible to obtain the universal formulas for all matrix elements which contain the total number of particles A in the system as an explicit parameter [4]. Let us present the explicit formulas for all matrix elements needed in computations. Below we shall use the following compact [4] notation

$$\langle\alpha| = \langle\alpha^{(k)}| = \exp\left(-\sum_{i>j=1}^{A}\alpha_{ij}^{k}r_{ij}^{2}\right)$$

and

$$|\beta\rangle = |\beta^{(\ell)}\rangle = \exp\left(-\sum_{i>j=1}^{A}\beta_{ij}^{\ell}r_{ij}^{2}\right), \tag{10}$$

where A is the total number of particles in the system. In this notation the overlap matrix element $\langle\alpha|\beta\rangle$ takes the form

$$\langle\alpha|\beta\rangle = \langle\alpha^{(k)}|\beta^{(\ell)}\rangle = \pi^{3(A-1)/2}D^{-3/2}, \tag{11}$$

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

$$b_{ii} = \sum_{j\neq i}^{A}(\alpha_{ij}^{k}+\beta_{ij}^{\ell}), \quad i=1,2,\ldots,A-1,$$

$$b_{ij} = -(\alpha_{ij}^{k}+\beta_{ij}^{\ell}), \quad i\neq j=1,2,\ldots,A-1. \tag{12}$$

In particular, the explicit expression for the (k,ℓ) matrix element of the $\hat{B}$ matrix in the case of $A=5$ is a 4×4 matrix. Analytical and/or numerical computations of the determinant of this matrix and all its first order derivatives is straightforward.

Now, consider the matrix elements of the potential energy V. For an arbitrary inter-particle potential which may be written as the sum of the central (pair) potentials, i.e., $W=\sum_{(ij)}V_{(ij)}(r_{ij})$, the formula for the appropriate matrix elements can be written in the form

$$\sum_{(ij)}\langle\alpha|V_{(ij)}(r_{ij})|\beta\rangle = \frac{4}{\sqrt{\pi}}\langle\alpha|\beta\rangle\sum_{ij}\int_{0}^{+\infty}V_{(ij)}\left(x\sqrt{\frac{D_{ij}}{D}}\right)\times\exp(-x^{2})x^{2}dx, \tag{13}$$

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 [4]. The formulas in [4] include the case of the Coulomb, Yukawa-type, exponential, oscillator, and many other potentials. For all such cases the expressions for lower bound estimates (E_L) have also been derived for an arbitrary A-particle system in [4]. The explicit analytical result for the matrix elements of the Coulomb potential energy is (in atomic units)

$$\sum_{(ij)}\langle\alpha|V_{ij}(r_{ij})|\beta\rangle = \sum_{(ij)}\langle\alpha|\frac{q_iq_j}{r_{ij}}|\beta\rangle = 2\sqrt{\frac{D}{\pi}}\langle\alpha|\beta\rangle\sum_{(ij)}\frac{q_iq_j}{\sqrt{D_{ij}}}, \tag{14}$$

where $(ij)=(ji)=(12),(13),(14),(15),\ldots,(35),(45)$ and $\langle\alpha|\beta\rangle$ is the overlap matrix element. In Eq. (14) the notation q_i $(i=1,2,\ldots,A)$ stands for the charges of the particles and $D_{ij}=\frac{\partial D}{\partial\alpha_{ij}}=\frac{\partial D}{\partial\beta_{ij}}$. The matrix elements of the kinetic energy take the form (in atomic units)

$$\langle\beta|T|\alpha\rangle = \frac{3}{2D}\left[\sum_{ijk=1}^{A}\frac{\alpha_{ik}\beta_{jk}}{m_k}(D_{ik}+D_{jk}-D_{ij})\right]\langle\beta|\alpha\rangle \tag{15}$$

where m_i $(i=1,2,\ldots,A)$ are the masses of the particles and $i\neq j\neq k$ in Eq. (15). The ensuing symmetrization of the given expressions in the case of identical particles does not present any difficulty.

For an arbitrary self-adjoint operator $\hat{X}$ the corresponding bound state property (or the expectation value) is determined as follows:

$$\langle X\rangle = \frac{\langle\psi|\hat{X}|\psi\rangle}{\langle\psi|\psi\rangle}, \tag{16}$$

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

$$\langle\alpha|f(r_{ij})|\beta\rangle = \langle\alpha^{(k)}|f(r_{ij})|\beta^{(\ell)}\rangle = \frac{4}{\sqrt{\pi}}\langle\alpha|\beta\rangle\int_{0}^{+\infty}f\left(x\sqrt{\frac{D_{ij}}{D}}\right)\exp(-x^{2})x^{2}dx. \tag{17}$$

The one-dimensional integral in the last equation can be computed analytically for a large number of actual interparticle potentials. In particular, for $f(y)=y^{2n-1}$ $(n=0,1,2,\ldots)$ one finds from Eq. (17)

$$\langle\alpha|r_{ij}^{2n-1}|\beta\rangle = \frac{2}{\sqrt{\pi}}\langle\alpha|\beta\rangle n!\left(\frac{D_{ij}}{D}\right)^{(2n-1/2)} \tag{18}$$

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

$$\langle\alpha|r_{ij}^{2n}|\beta\rangle = \frac{(2n+1)!!}{2^{n}}\left(\frac{D_{ij}}{D}\right)^{n}\langle\alpha|\beta\rangle \tag{19}$$

where the notation $(2n+1)!!$ stands for the product $1\times3\times5\times\cdots\times(2n+1)$ (odd factorial). In the case when $f(y)=y^{-2}$ (i.e., $n=-1$ in the last formula) the appropriate expression takes the form

$$\langle\alpha|r_{ij}^{-2}|\beta\rangle = 2\langle\alpha|\beta\rangle\frac{D}{D_{ij}}. \tag{20}$$

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

The formulas for matrix elements presented above allow one to conduct accurate variational computations, in principle, for all many-body systems with a variety of interparticle interactions. In particular, the variational methods based on the use of many-dimensional gaussoids have been found to be very effective in applications to various few-electron systems. For atomic systems with four and more electrons, the method developed in [4] is, in fact, one of a very few accurate procedures which work effectively in such cases. In actual applications, however, this method becomes effective, if (and only if) the nonlinear parameters in Eqs. (6) and (7) are optimized carefully. The optimization of these parameters is discussed below.

Note that the approach developed in [4] was based on the method proposed in earlier work [6] (for nuclear three-body systems). In theoretical chemistry a similar approach has been developed by Singer [7] and Boys [8]. The last approach is, in fact, a different method from [4], since it does not include the integration upon internuclear coordinates.

Optimization of the nonlinear parameters

The radial parts of our trial wave functions, Eqs. (6) and (7), are represented as the variational sums of ten-dimensional (or five-body) gaussoids. All gaussoids have incorrect asymptotic behavior at very large interparticle distance in many-body Coulomb systems. This means that the variational expansion based on the use of Eqs. (2), (6), and (7) cannot provide very high accuracy for such systems. In fact, our variational expansion becomes accurate only if the nonlinear parameters $\{\alpha_{ij}^{(k)}\}$ in the radial functions Eqs. (6) and (7) are also varied or optimized. To perform accurate variational computations in various atomic systems with three, four, five, and many electrons we have developed a number of different optimization strategies. Some of these strategies are effective in calculations with a relatively small number of nonlinear parameters. Other strategies are applied when the total number of varied nonlinear parameters is not very large ($\approx$300–3000). In calculations with the large ($\geqslant$5000) and extremely large ($\geqslant$20 000) numbers of the varied nonlinear parameters one has to apply completely different optimization strategies. All such details are analyzed in our earlier study [9] and here we do not want to repeat that discussion. Instead, we discuss the principal difference between our optimization approach and methods used by other authors.

The most important difference is the use of two spin configurations in our computations. Briefly, this means that the nonlinear parameters in the radial functions which are associated with the second spin configuration are varied independently from analogous parameters in the radial functions associated with the first spin configuration. The variation of nonlinear parameters in the two parts of the trial wave functions provides additional flexibility and allows us to improve substantially the overall convergence rate of our method. Moreover, even very accurate and detailed optimization in the second part of the total wave function cannot produce any linear dependence between basis functions. Another advantage of our total wave function is related to the fact that it already contains two spin configurations which must be in the exact wave function. If accurate computations in few-electron atomic systems were performed with the use of only one spin function, then one finds a number of problems related with computations of some bound state properties, various reaction, and transition probabilities. The well known example is the accurate computation of the Fermi contact term [10] for three-electron atomic systems which is described in detail, e.g., in [11].

TABLE I. The nonrelativistic energies of the ground states of some berylliumlike systems computed with the use of the trial wave function, Eq. (2). The nuclear masses are infinite for all atomic systems mentioned in this table.

System	E (a.u.)	System	E (a.u.)
Li^-	−7.5005825	O^{4+}	−68.4112548
Be	−14.6672858	F^{5+}	−88.1005581
B^+	−24.3487629	Ne^{6+}	−110.290464
C^{2+}	−36.5346987	Na^{7+}	−134.980025
N^{3+}	−51.2224986	Mg^{8+}	−162.170163

Let N_i be the total number of radial functions associated with the χ_i spin function, where $i=1,2$. By varying the nonlinear parameters in radial functions associated with each spin configurations we have arrived to the following conclusion. If the sum $N_1+N_2=N$ is fixed and nonlinear parameters in each basis function are varied, then the minimal energy is reached at $N_1 \approx N_2 \approx \frac{N}{2}$. In fact, for our wave functions with 300 radial functions (see below) we have found that the optimal ratio between numbers of radial functions N_1 and N_2 is $\approx 2:1$. The opposite ratio $\approx 1:2$ also produces the total energies which are close to optimal (minimal) values. In contrast with this, in almost all previous works on four-electron atomic systems only one spin function χ_1 was used.

IV. NUMERICAL RESULTS

Let us discuss some numerical results obtained for a number of four-electron (berylliumlike) systems, in particular Li^-, Be, $\mathrm{B}^+, \ldots, \mathrm{Na}^{7+}$, Mg^{8+}; note that the negative Li^- ion is the first stable four-electron system in the sequence. Our main interest in this study is related to the total energies computed with the use of very compact variational wave functions. The analogous atomic systems with only three electrons were considered in similar studies [12] (see also [9]). However, the three-electron negatively charged helium ion (He^- ion) is not bound and one must begin the sequence of three-electron systems with a neutral species, namely Li atom.

In our present computations we have used trial wave functions with 300 basis functions each. The first 200 basis functions correspond to the χ_1 spin function, while the last 100 basis functions correspond to the χ_2 spin function. The nonlinear parameters in each basis function (ten such parameters per each basis function) have been varied independently (see the discussion above). All nonlinear parameters were assumed to be positive. A possibility to use some negative nonlinear parameters in Eqs. (6) and (7) does exist [13], but it was not used in our actual calculations. The results of our calculations can be found in Table I which contains the total energies of all systems considered in this work (in a.u.). In calculations for Table I we have assumed that all nuclear masses are infinite, i.e., $M=\infty$ in Eq. (1). This is not a principal restriction for our method. For instance, for the ground state of the ${}^{\infty}\mathrm{Li}^-$ ion one finds from Table I $E=E({}^{\infty}\mathrm{Li})$ $=-7.500\,582\,03$ a.u. With the same wave function, but using the actual ^{7}Li nuclear mass $M(^7\mathrm{Li})=12\,786.3927m_e$ [14,15], one finds the following total energy for the ground $^1S^e$ state of the $^7\mathrm{Li}^-$ ion: $E=-7.499\,971\,41$ a.u.. In fact, all such computations with the finite nuclear masses formally require only a one-line change in the code. However, the following fast and very approximate re-optimization of nonlinear parameters is feasible and can significantly improve the overall accuracy of the wave function constructed for atomic systems with the finite nuclear mass.

Note that the first computations of the bound states in four-electron atoms or ions with the use of correlated electron wave functions were started by Sims and Hagstrom in 1971 [16]. The ground state energies of many four-electron atoms and ions have been determined in a number of earlier studies (see, e.g., [2,16–24]). By analyzing our total energies determined with the use of very compact wave functions, one finds that these energies are lower (and even much lower) than the values obtained in [2,16–24] (see also references mentioned in these works). The only exception is the ground state energy of the $^{\infty}$Be atom computed in [24] (see also [22]). Currently, to obtain the energy comparable with their value we need to use 600–700 basis wave functions with well optimized nonlinear parameters.

In general, our results obtained for four-electron atomic systems are very comparable (and even better) than analogous results obtained with the use of other methods. This shows a great potential of our current procedure and compact wave functions for accurate solutions of the bound state problems in four-electron atomic systems. In turn, this opens a new avenue for the use of these compact (but accurate) wave functions in various problems related with the analysis of electron density distribution in different four-electron atomic systems and atomic excitations in such systems.

To conclude this section we want to construct a few approximate formulas for the Q^{-1} expansion (Q is the nuclear charge) for the total energies of the four-electron atomic systems. Our total energies determined for different four-electron atoms (see Table I) will be used as the test points to obtain a number of first coefficients in the $E(Q)$ expansion. Note that in contrast with [25] our $E(Q)$ expansion is written for the total energy, rather than for ionization potential. The explicit formula is written as a Laurent expansion (here and below $Q \geqslant 3$), i.e., it takes the form

$$E(Q) = a_2Q^2 + a_1Q + a_0 + b_1Q^{-1} + b_2Q^{-2} + b_3Q^{-3} + b_4Q^{-4} + \cdots, \tag{21}$$

where numerical values of the coefficients $a_2, a_1, a_0, b_1, b_2, b_3, \ldots$ must be determined from fitting the results of accurate numerical computations to Eq. (21). Note that the principal part of the expansion Eq. (21) includes only integer powers of Q^{-1}. Such an expansion essentially follows from the Poincaré's theorem applied to the Schrödinger equation with the Hamiltonian, Eq. (1). For degenerate bound states the expansion analogous Eq. (21) must also include the noninteger powers of Q (so-called Puiseux series [26]). However, this is not the case for the ground $1\,^1S^e$ states in four-electron atomic systems. The coefficients $a_2, a_1, a_0, b_1, b_2, b_3, \ldots$ determined with our variational energies for four-electron atoms or ions can be found in Table II. In fact, in this work we have used the formula, Eq. (21), with four, five, and six terms in it. Numerical values of the first, second, and third coefficients a_2, a_1, and a_0 coincide well with the values (-1.25, ≈ 1.55, and ≈ -0.8) obtained from computations with large numbers of basis functions. These values can also be established by considering the asymptotic case of large Q in which only three leading terms in Eq. (21) survive.

TABLE II. The coefficients of the Q^{-1} expansion constructed for the total energies of the ground $1\,^1S$ states in four-electron ions, Eq. (2). Expansions with $N=4$, 5, and 6 terms are considered.

a_2	−1.24916893	−1.25023612	−1.24960246
a_1	1.53995665	1.56666629	1.54629748
a_0	−0.72961516	−0.96119275	−0.71363865
b_1	−0.44483674	0.38132362	−1.04034589
b_2		−1.02933292	2.83411527
b_3			−3.98341752

V. CONCLUSIONS

In this work we have developed a variational method which allows one to construct very compact and relatively accurate wave functions for the four-electron atomic systems. Moreover, in contrast with other methods our procedure is relatively simple in applications and can be used for an arbitrary four-electron atomic system. Our variational expansion is written in the basis of ten-dimensional gaussoids, each of which contains ten relative coordinates $r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}, r_{45}$ and ten corresponding nonlinear parameters. In our method the two spin functions (χ_1 and χ_2; see above) are used on an equal footing. This means that the nonlinear parameters in all spatial terms associated with χ_1 spin function are varied independently from analogous variations in all spatial terms associated with χ_2 spin function. Briefly, we can say that the terms associated with the second spin function χ_2 used in our variational expansion allow us to improve drastically the overall convergence rate of the method. Finally, we can construct, in principle, very compact and accurate wave functions for an arbitrary four-electron atom or ion. It should be mentioned that in almost all previous works related to the beryllium atoms and berylliumlike ions only one spin function (χ_1) has been used in computations.

Finally, we want to note that the current accuracy of our compact wave functions ($\approx$300 basis functions) is sufficient for applications to various atomic problems: photodetachment, electron scattering, atomic excitations during various nuclear reactions and decays, etc. The wave functions used in previous studies require significantly larger numbers of basis functions to achieve comparable accuracy. In future studies we will try to generalize our procedure to computation of rotationally excited states in four-electron atoms or ions. Another possible direction is the analysis of the bound states in five-electron atomic systems. However, the ground bound state in boronlike atoms or ions is the doublet ^2P state (more precisely, the $^2P_{1/2}$ state, while analogous $^2P_{3/2}$ state is quasistable [27]). Currently, it seems to be a situation which may complicate our variational computations of the five-electron atomic systems.

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