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ON BOUND STATE COMPUTATIONS IN THREE- AND FOUR-ELECTRON ATOMIC SYSTEMS

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A variational approach is developed for bound state calculations in three- and four-electron atomic systems. This approach can be applied to determine, in principle, an arbitrary bound state in three- and four-electron ions and atoms. Our variational wave functions are constructed from four- and five-body Gaussoids that respectively depend on six ($r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34}$) and ten ($r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}$ and r_{45}) relative coordinates. The approach allows operating with different numbers of electron spin functions. In particular, the trial wave functions for the ^1S states in four-electron atomic systems include the two independent spin functions $\chi_1 = \alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha$ and $\chi_2 = 2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \alpha\beta\alpha\beta$. We also discuss the construction of variational wave functions for the excited 2^3S states in four-electron atomic systems.

1. INTRODUCTION

We consider the electronic structure of three- and four-electron atoms and ions. In particular, we undertake variational computations of the singlet ^1S states and triplet ^3S states in various four-electron atoms and ions. Below, by an atomic system, we mean a system that contains a number of electrons and one heavy nucleus. In the nonrelativistic approximation used in this study, the Hamiltonian of an arbitrary $(A-1)$-electron atomic system takes the form (see, e.g., [1])

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

where A is the total number of bodies in the atomic system. In a three-electron atomic system, $A = 4$. In this case, the subscripts 1, 2, 3 denote three electrons, while the subscript 4 denotes the positively charged atomic nucleus. For four-electron systems, $A = 5$ in Eq. (1), and the subscripts 1, 2, 3, 4 denote four electrons, while the subscript 5 denotes the positively charged nucleus. The Hamiltonian in Eq. (1) and all equations that follow are written in atomic units, where $\hbar = 1$, $m_e = 1$, and $e = 1$. Also,

$$\nabla_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right)$$

is the gradient operator of the ith particle ($i = 1, 2, \ldots, A$). The notation r_{ij} is for the relative distance/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. Also, M denotes the mass of the central (heavy) nucleus, and hence $M \gg 1$.

The main goal of this work is to discuss some important details of bound state calculations of three- and four-electron atoms and ions. In particular, special attention is given to the correct symmetrization of the four-electron trial wave functions that include more than one independent (electron) spin function, something not considered elsewhere in the modern literature. Formally, our main goal is to determine highly accurate solutions of the Schrödinger equation $H\Psi = E\Psi$, where H is the Hamiltonian in Eq. (1). It is clear that the permutation symmetry of the total wave function Ψ must be different for the singlet and triplet bound states in a four-electron system. The explicit construction of trial wave functions with the correct permutation symmetry between all three or all four electrons is the principal part of any accurate variational calculation of such atomic systems.

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In general, bound state computations of three-, four- and many-electron atomic systems with the use of a number of different spin functions (which, however, correspond to the same value of the total (electron) spin S_e and its z-projection $(S_e)_z$) are significantly more complicated than analogous calculations for two-electron helium-like atoms and ions. On the other hand, there is an obvious similarity in calculations of three- and four-electron atomic systems. Indeed, two different spin functions must be used for the ground (doublet) 1^2S states in three-electron atoms and ions. The same number of spin functions is needed for accurate computations of the ^1S states in four-electron atomic systems.

We note that in any four-electron atom and/or ion, all bound states are separated into two series of states: singlet states with the total electron spin $S_e = 0$, and triplet states with the total electron spin $S_e = 1$. In all previous works, only the ground singlet 1^1S state was considered. Accurate computations of the triplet states in four-electron atomic systems have been performed for a very few ions/atoms [2,3]. Moreover, in almost all previous computations of the singlet state in four-electron (beryllium-like) atoms and ions, only one spin function

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

was used. Here and everywhere below in this study, α and β are the spin-up and spin-down single-electron functions, i.e., $\hat{\sigma}_z\alpha = \alpha/2$ and $\hat{\sigma}_z\beta = -\beta/2$. The second independent spin function

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

has been ignored in almost all modern accurate computations of the singlet states in four-electron atomic systems. Bearing this in mind, we want to develop a method that can be used to perform bound state computations for the ^1S (singlet) and ^3S (triplet) bound states in arbitrary four-electron atoms and ions. Our method is not restricted with respect to the number of spin functions included. It works equally well in the cases where one, two, three, and even more independent spin functions are used.

2. VARIATIONAL WAVE FUNCTIONS

A central feature of any variational method is the construction of trial wave functions Ψ with the correct permutation symmetry. In general, such a trial wave function must include all electron and nucleus coordinates. Accurate wave functions explicitly depend on all scalar interparticle coordinates $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ in the atomic system. The use of a large number of relative coordinates complicates the explicit symmetrization of trial wave functions. Another complication follows from the presence of different (independent) terms in the spin part of the total wave function. For instance, we discuss the case of the singlet ^1S state in four-electron atomic systems. To compute this state in this study, we use the two independent spin functions

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

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

These two functions obey the relations

$$\mathbf{S}^2\chi_k = 0, \quad (\mathbf{S}_z)\chi_k = 0, \quad \langle\chi_i|\chi_k\rangle = D_k\delta_{ik}, \tag{2}$$

where $k = 1, 2$, D_k are normalization factors of the spin functions, and $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$ is the total electron spin of the four-electron system.

The total wave function of the $^1S(L = 0)$ state of the four-electron beryllium-like atom/ion is written in the form (see, e.g., [4, 5] and the references therein)

$$\Psi_{L=0} = \psi_{L=0}(A; \{r_{ij}\})\chi_1 + \phi_{L=0}(B; \{r_{ij}\})\chi_2, \tag{3}$$

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. For the wave function in Eq. (3), $\mathbf{S}^2\Psi = 0$ and $S_z\Psi = 0$. The radial parts $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ of the total wave function (3) are represented in the form [6]

$$\psi_{L=0}(A; \{r_{ij}\}) = \\ = \mathcal{P}_1 \sum_{k=1}^{N_A} C_k \exp\left(-\sum_{ij} \alpha_{ij}^{(k)} r_{ij}^2\right), \tag{4}$$

$$\phi_{L=0}(B; \{r_{ij}\}) = \\ = \mathcal{P}_2 \sum_{k=1}^{N_B} \mathcal{C}_k \exp\left(-\sum_{ij} \beta_{ij}^{(k)} r_{ij}^2\right), \tag{5}$$

where N_A and N_B are the numbers of basis functions used, C_k and $\mathcal{C}_k$ are the linear parameters of variational expansions, and $\{r_{ij}\}$ is the set of relative coordinates that are needed for complete description of five-body systems. The $\alpha_{ij}^{(k)}$ and $\beta_{ij}^{(k)}$ denote the nonlinear parameters associated with the r_{ij} relative coordinate in the kth basis function. For all beryllium-like ions and atoms considered in this paper, 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}. The radial basis functions in Eqs. (4) and (5) are called the five-body Gaussoids of ten relative coordinates. This name was used in [6], where these basis functions were invented for nuclear few-body systems.

The main advantage of the radial functions defined in Eqs. (4) and (5) follows from the fact that the formulas for all matrix elements do not depend explicitly on the total number of particles in the system. In other words, these formulas are essentially the same for three-, four-, five- and many-body systems, and are discussed in the next section.

The symbols A and B in Eqs. (4) and (5) mean that there are two different sets of nonlinear parameters: each of the basis functions in Eqs. (4) and (5) contains ten nonlinear parameters, which are optimized independently. The summation over $(ij) = (ji)$ in the exponents of Eqs. (4) and (5) is taken over all possible different pairs of particles. In general, the radial basis functions are not orthogonal to each other. The projectors $\mathcal{P}_1$ and $\mathcal{P}_2$ produce trial wave functions with the correct permutation symmetry between all electrons (see below). The symbol L in Eq. (4) is used for the total angular momentum of the considered system. For the ground state of any beryllium-like system, we always have $L = 0$ and the total electron spin of such states is equal to zero. Furthermore, the parity of these states in the four-electron systems is even. These states are therefore often denoted as ${}^1S^e$, or 1^1S^e states.

For the triplet ${}^3S$ states in four-electron atomic systems, there also exist two independent spin functions,

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

We note that there are, in fact, two independent triplets of the spin functions, and hence the total number of electron spin functions is $2 \times 3 = 6$. The above functions χ_1 and χ_2 correspond to the values $S_e = 1$ and $(S_e)_z = 1$. Using the explicit form of these two spin functions, we can construct the four remaining spin functions with $S_e = 1$ and $(S_e)_z = 0$ (two functions), and $S_e = 1$ and $(S_e)_z = -1$ (two functions). In actual calculations of the internal atomic structure, we can restrict ourselves to the use of the two spin functions χ_1 and χ_2 only. All the six spin functions are needed only in some special cases, e.g., if an external magnetic field is present.

It is interesting to find that the total variational wave function Ψ of three-electron atoms and ions is also represented in form (3). In this case, $\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha$, while the two independent radial parts depend on the six relative coordinates $r_{12}, r_{13}, r_{23}, r_{14}, r_{24}$, and r_{34} (here, the indices 1, 2, 3 refer to three electrons, and 4 to the nucleus). The radial basis functions can also be chosen in form (4) and (5). In this case, each of the radial basis functions contains six nonlinear parameters. We also note that for each of the spin functions, we have $S^2\chi_i = (3/4)\chi_i$ and $(S)_z\chi_i = (1/2)\chi_i$ (with $i = 1, 2$). Explicit constructions of the variational wave functions for three- and four-electron atomic systems are discussed below.

3. MATRIX ELEMENTS

Actual computation of matrix elements with the four- and five-body Gaussoids is Eqs. (4) and (5) is based on analytic formulas derived elsewhere (see, e.g., [6, 7]). It was mentioned already in [6] that the explicit expressions for all matrix elements needed for the solution of the Schrödinger equation depend on the total number of particles A in the system as a numerical parameter. In other words, the expressions for matrix elements in three-electron systems coincide with the corresponding formulas for matrix elements obtained for four- and five- and many-electron systems. Moreover, in some few-body systems, one of the electrons can be replaced by another particle, e.g., by μ^-, but such a replacement does not change the explicit formulas for matrix elements. Below, the symbol A denotes the total number of particles (i.e., bodies) in the system. An A-particle atomic system includes the $(A-1)$-electron subsystem plus one heavy nucleus. The A-particle muonic atom/ion contains the $(A-2)$-electron subsystem, one negatively charged muon μ^-, and one heavy nucleus.

The explicit formulas for all matrix elements needed in computations of A-particle atomic systems can be presented in a very brief form with the use of the compact notation

$$\begin{gathered}\langle\alpha| = \langle\alpha^{(k)}| = \exp\left(-\sum_{i>j=1}^{A} \alpha_{ij}^{k} r_{ij}^2\right), \\ |\beta\rangle = |\beta^{(\ell)}\rangle = \exp\left(-\sum_{i>j=1}^{A} \beta_{ij}^{\ell} r_{ij}^2\right).\end{gathered} \tag{6}$$

In this notation, the symbols $|\beta\rangle$ and $|\alpha\rangle$ (or $\langle\alpha|$ and $\langle\beta|$) denote the radial basis functions, differently from the meaning of α and β used in other sections of this paper, where they denote spin-up and spin-down functions.

In the notation defined in Eq. (6), the overlap matrix element $\langle\alpha|\beta\rangle$ is written in the form

$$\langle\alpha|\beta\rangle = \langle\alpha^{(k)}|\beta^{(\ell)}\rangle = \pi^{3(A-1)/2} D^{-3/2}, \tag{7}$$

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

$$\begin{aligned} b_{ii} &= \sum_{j\neq i}^{A}(\alpha^{k}_{ij}+\beta^{\ell}_{ij}), \quad i\neq j=1,2,\ldots,A-1, \\ b_{ij} &= -(\alpha^{k}_{ij}+\beta^{\ell}_{ij}), \quad i\neq j=1,2,\ldots,A-1. \end{aligned} \tag{8}$$

In particular, the explicit expression for the (k,ℓ) matrix element of the overlap matrix $\hat{S}$ for $A=5$ is the 4×4 matrix $\hat{B}$ with matrix elements b_{ij} defined in Eq. (8). Analytic and/or numerical computations of the determinant of this matrix and all its first-order derivatives are straightforward.

The formula for the appropriate matrix elements of the potential energy can be written as

$$\sum_{(ij)}\langle\alpha|V(r_{ij})|\beta\rangle = \frac{4}{\sqrt{\pi}}\langle\alpha|\beta\rangle\sum_{ij}\int_0^\infty V\left(x\sqrt{\frac{D_{ij}}{D}}\right)\times \\ \times\exp(-x^2)x^2dx, \tag{9}$$

where

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

with $(ij)=(ji)=(12), (13), (23), (14), (24), (34)$ for $A=4$ and $(ij)=(ji)=(12), (13), (14), (15), \ldots, (35), (45)$ for $A=5$. The explicit expressions for various interparticle potentials often used in bound state calculations can be found in [6]. The integral in the last formula is computed analytically in many actual cases, including the case of Coulomb, Yukawa-type, exponential, and oscillator potentials. The kinetic energy matrix elements take the form

$$\langle\alpha|T|\beta\rangle = \frac{3}{2D}\times \\ \times\left[\sum_{ijk=1}^{A}\frac{\alpha_{ik}\beta_{jk}}{m_k}(D_{ik}+D_{jk}-D_{ij})\right]\langle\alpha|\beta\rangle, \tag{10}$$

where m_i $(i=1,2,\ldots,A)$ are the masses of the particles and $i\neq j\neq k$. The explicit formulas for matrix elements of other operators written in the basis of many-dimensional Gaussoids can be found elsewhere (see, e.g., [6,7]).

If all formulas needed for matrix elements of the potential and kinetic energies are known, then the solution of the incident Schrödinger equation is reduced to the generalized eigenvalue problem

$$\sum_{\beta=1}^{N}\Big(H_{\alpha,\beta}-ES_{\alpha,\beta}\Big)C_\beta = 0 \tag{11}$$

for $\alpha=1,\ldots,N$, where N is the total number of basis functions used. Here,

$$H_{\alpha,\beta}=T_{\alpha,\beta}+V_{\alpha,\beta}=\langle\alpha|T|\beta\rangle+\langle\alpha|V|\beta\rangle$$

is the Hamiltonian matrix, $T_{\alpha,\beta}=\langle\alpha|T|\beta\rangle$ and $V_{\alpha,\beta}=\langle\alpha|V|\beta\rangle$ are respectively the matrices of the kinetic and potential energies. The $S_{\alpha,\beta}=\langle\alpha|\beta\rangle$ matrix in Eq. (11) is the overlap matrix (7). For nonorthogonal basis sets, the overlap matrix is a typical dense matrix, i.e., all of its elements differ from zero in general. Moreover, it can be shown that the overlap matrix $\langle\alpha|\beta\rangle$ is a symmetric, positive definite matrix. This means that all eigenvalues of the overlap matrix are positive.

4. ANTISYMMETRIZATION OF THE TRIAL WAVE FUNCTIONS

We consider the antisymmetrization of the trial wave functions and the related antisymmetrization of the corresponding matrix elements derived in the previous section. As mentioned above, the correct antisymmetrization is a central part of the construction of explicitly correlated, trial wave functions. In general, such a wave function depends on all electron–nucleus and electron–electron coordinates. In two-electron atoms and ions, the antisymmetrization of the total wave function is a trivial problem, since the wave function of the two-electron system is always represented as a product of a radial and a two-electron spin functions. Moreover, only singlet and triplet spin functions are possible in any two-electron atom and/or ion. The singlet states have the spin function $\chi_1=\alpha\beta-\beta\alpha$, and the triplet states have three spin functions $\chi_2^{(1)}=\alpha\alpha$, $\chi_2^{(2)}=\alpha\beta+\beta\alpha$, and $\chi_2^{(3)}=\beta\beta$. For the singlet spin function, $S^2\chi_1=0$ and $S_z\chi_1=0$, and for the triplet spin functions, $S^2\chi_2^{(i)}=2\chi_2^{(i)}$ and $S_z\chi_2^{(i)}=\kappa_i\chi_2^{(i)}$, where $\kappa_1=1$, $\kappa_2=0$, and $\kappa_3=-1$.

We note that the singlet spin function χ_1 is antisymmetric with respect to the electron variables. Therefore, its product with a symmetric radial function produces a function that is totally antisymmetric with respect to all electron variables. It is clear that such a function can be regarded as a total wave function with the correct permutation symmetry between two electrons. For triplet states, the corresponding radial function must be antisymmetric with respect to all electron (spatial) coordinates.

In contrast with two-electron systems, the antisymmetrization of three-electron wave functions is a significantly more complex process because not one but a number of different independent spin functions exist for the same spin state. This statement is true even for the doublet states with $S = 1/2$ and $S_z = \pm 1/2$ in any three-electron atomic system. In actual computations, such spin functions are usually chosen to be orthogonal to each other. For instance, any variational expansion written for the doublet ^2S states in a three-electron atomic system must include the two independent spin functions $\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha$. The total wave function for the ground doublet $1^2S(L=0)$ state of the three-electron atomic system is written as (see, e.g., [8, 9])

$$\Psi_{L=0} = \psi_{L=0}(A;\{r_{ij}\})(\alpha\beta\alpha - \beta\alpha\alpha) + \\ + \phi_{L=0}(B;\{r_{ij}\})(2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha), \quad (12)$$

where $\psi_{L=0}(A;\{r_{ij}\})$ and $\phi_{L=0}(B;\{r_{ij}\})$ are the two independent spatial parts. The symbols A and B indicate that the two sets of nonlinear parameters associated with ψ and ϕ are optimized independently.

We note that each of these two spin functions χ_1 and χ_2 satisfies the equations

$$\mathbf{S}^2\chi_k = S(S+1)\chi_k = \frac{3}{4}\chi_k, \quad (\mathbf{S})_z\chi_k = \frac{1}{2}\chi_k, \quad (13)$$

where $k = 1, 2$, $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3$ is the total electron spin of the three-electron system, and $\mathbf{S}_z$ is its z-projection. Equations (13) indicate clearly that the two spin functions χ_1 and χ_2 are equally important in this variational method. Therefore, we cannot neglect any of these spin functions *a priori*. This means that in any of our calculations for a three-electron atomic system, we have to appropriately use the two different radial functions and two spin configurations χ_1 and χ_2. The explicit construction of the trial wave functions for three-electron atomic systems with two independent spin functions is more complicated than in the case of one spin function, and the solution to this problem is based on the method of projection operators discussed below.

4.1. Three-electron atomic systems. Doublet states

We suppose that our trial wave function for a three-electron atomic system is written in form (12). In real applications, however, only the trial functions that have the correct permutation symmetry between all identical particles, i.e., electrons, are accepted. This means that the two terms in the right-hand side of Eq. (12) must be completely antisymmetric with respect to spin and spatial coordinates of the three electrons, i.e., with respect to the indices 1, 2, and 3 in our notation. In other words, we must have $\hat{\mathcal{A}}_e\Psi = -\Psi$, where Ψ is given by Eq. (12) and $\hat{\mathcal{A}}_e$ is the three-particle antisymmetrizer [10, 11]

$$\hat{\mathcal{A}}_e = \frac{1}{6}(\hat{e} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{123} + \hat{P}_{132}). \quad (14)$$

Here, $\hat{e}$ is the identity permutation and $\hat{P}_{ij}$ is the permutation of the ith and jth particles. Analogously, the operator $\hat{P}_{ijk}$ is the permutation of the ith, jth and kth particles. The same notation is used everywhere in what follows.

By using the three-particle antisymmetrizer in Eq. (14), we can construct a trial wave function with the correct permutation symmetry. In reality, we need not the wave function itself but the matrix elements with the correct permutation symmetry. We describe the approach that allows obtaining properly symmetrized matrix elements. First, we note that the expectation value of an arbitrary totally symmetric operator W is written in the form

$$\langle \hat{\mathcal{A}}_e \sum \psi_i(A_i;\{r_{ij}\})\chi_i | W | \hat{\mathcal{A}}_e \times \\ \times \sum \psi_j(A_j;\{r_{ij}\})\chi_j\rangle, \quad (15)$$

where χ_i are the spin functions ($i = 1, \ldots, N_s$). The spin functions χ_1 and χ_2 are assumed to be orthogonal to each other, i.e., $\langle\chi_i|\chi_j\rangle = \delta_{ij}$. The notation $\psi_i(A_i;\{r_{ij}\})$ is for the corresponding radial functions that depend on all relative coordinates $\{r_{ij}\}$ and nonlinear parameters A_i. These radial functions can be arbitrary, and are not necessarily orthogonal to each other. The operator W is a differential operator written in the relative coordinates. It is assumed to be totally symmetric with respect to all inter-electron permutations.

Next, we note that the totally symmetric operator W commutes with the $\hat{\mathcal{A}}_e$ operator in Eq. (14). Moreover, the operator $\hat{\mathcal{A}}_e$ is an orthogonal projector [12], i.e., $(\hat{\mathcal{A}}_e)^2 = \hat{\mathcal{A}}_e$ and $(\hat{\mathcal{A}}_e)^* = \hat{\mathcal{A}}_e$, where B^* is the operator conjugate to B. If the operator W is independent of spin variables, then these properties of $\hat{\mathcal{A}}_e$ allow reducing Eq. (15) to the form

$$\sum_i\sum_j \langle\psi_i(A_i;\{r_{ij}\})|W|\hat{\mathcal{A}}_e\psi_j(A_j;\{r_{ij}\})\rangle \times \\ \times \langle\chi_i|\hat{\mathcal{A}}_e|\chi_j\rangle. \quad (16)$$

This expectation value can be rewritten in another form with the use of the matrix notation

$$[\Theta(W)]_{ij} = \langle\chi_i|\hat{\mathcal{A}}_e|\chi_j\rangle[W\hat{\mathcal{A}}_e]_{ij}, \quad (17)$$

where $[\ldots]_{ij}$ denotes the (ij) matrix element of the corresponding matrix. The matrix elements of $\Theta(W)$ computed on any basis set of spatial three-electron wave functions have the correct permutation symmetry between all identical particles. The size of the $[\Theta(W)]_{ij}$ matrix is equal to the number of spin functions used in calculations.

First, we compute the matrix elements of the $\hat{\mathcal{A}}_e$ operator. Based on Eq. (17), this operator can be written in the form $\Theta(\hat{e})$, where $\hat{e}$ is the unit operator. We note that $\hat{\mathcal{A}}_e$ can be written as

$$\hat{\mathcal{A}}_e = \sum_{abc} s_{abc} \hat{P}_{abc}, \tag{18}$$

where s_{abc} are integers and $\hat{P}_{abc}$ are the interparticle permutations in the system of three identical particles. The sum in Eq. (18) is computed over all interparticle permutations possible in three-body systems, as in Eq. (14). The (ij) matrix element of $\hat{\mathcal{A}}_e$ in our basis is

$$[\hat{\mathcal{A}}_e]_{ij} = \sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle \hat{P}_{abc}. \tag{19}$$

In the case of the (ij) matrix element of the $\Theta(W)$ operator, we find

$$[\Theta(W)]_{ij} = \sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle W \hat{P}_{abc} = \\ = W \Big[\sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle \hat{P}_{abc} \Big]. \tag{20}$$

We note that both the expectation value $\langle \chi_i | \hat{P}_{abc} | \chi_j \rangle$ and s_{abc} are integers for all abc, while the operator P_{abc} is a projector that acts on the spatial coordinates of the three electrons $(a \to b \to c)$. In other words, the $\hat{\mathcal{A}}_e$ operator is represented as a finite sum of all spatial permutations $\hat{P}_{abc}$ with integer coefficients equal to the products of the s_{abc} in Eq. (18), and the $\langle \chi_i | \hat{P}_{abc} | \chi_j \rangle$ expectation values. The computation of all expectation values

$$\langle \chi_i | \hat{P}_{abc} | \chi_j \rangle = \langle \chi_i | \hat{P}_{abc} \chi_j \rangle$$

can be regarded as the integration over electron spin coordinates.

Based on Eq. (20), we can introduce the operator

$$\mathcal{P} = \mathcal{D} \sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle \hat{P}_{abc}, \tag{21}$$

where $\mathcal{D}$ is a normalization constant. The numerical value of $\mathcal{D}$ is determined by the idempotency of $\mathcal{P}$, $\mathcal{P}^2 = \mathcal{P}$. The explicit use of this operator substantially simplifies the formulas in what follows. For instance, the (α, β) matrix element of any arbitrary totally symmetric operator W can be written as

$$\langle \mathcal{P}\alpha | W | \mathcal{P}\beta \rangle = \langle \alpha | \mathcal{P} W \mathcal{P} | \beta \rangle = \\ = \langle \alpha | W \mathcal{P} | \beta \rangle = \langle \alpha | W | \mathcal{P}\beta \rangle, \tag{22}$$

where α and β are nonsymmetric basis functions. This matrix element has the correct permutation symmetry between all electrons. This is the main advantage of constructing the orthogonal spatial projector $\mathcal{P}$ in explicit form.

In actual computations of the doublet ^2S states in three-electron atomic systems after the integration over electron spin coordinates, we find the four spatial projectors

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

$$\mathcal{P}_{\psi\phi} = \frac{1}{2} \Big(\hat{P}_{13} - \hat{P}_{23} - \hat{P}_{123} + \hat{P}_{132} \Big), \tag{24}$$

$$\mathcal{P}_{\phi\psi} = \frac{1}{2} \Big(\hat{P}_{13} - \hat{P}_{23} - \hat{P}_{123} + \hat{P}_{132} \Big), \tag{25}$$

$$\mathcal{P}_{\phi\phi} = \frac{1}{2\sqrt{3}} \Big(2\hat{e} - 2\hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23} - \hat{P}_{123} - \hat{P}_{132} \Big), \tag{26}$$

where the indices ψ and ϕ correspond to the notation for radial functions used in Eq. (12). Each of these projectors produces matrix elements between the two radial basis functions from Eq. (12) 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 also be shown that the three projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$, and $\mathcal{P}_{\phi\phi}$ are orthogonal to each other. In actual computations, only the upper triangles 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 bound doublet ^2S states in all three-electron atomic systems.

The approach described above allows constructing the spatial parts of the total variational wave functions with the correct permutation symmetry between all identical particles in a three-electron atomic system. In our previous work, we have also found (see [2, 5]) that the same approach works perfectly for all four-, five- and many-electron systems. Moreover, the symmetry of the electron spin functions can also be different, e.g., for the singlet and triplet states in four-electron systems. Below, the variational wave functions for the singlet and triplet states in four-electron atomic systems are constructed explicitly. The explicit formulas for the spatial parts of trial wave functions are derived with the use of the corresponding spatial projectors.

4.2. Four-electron atomic systems. Singlet states

Numerical computations of bound states in four-electron atomic systems include the nontrivial step of antisymmetrization of all electron variables, i.e., variables 1, 2, 3, and 4 in the trial wave function Ψ. The variational wave function Ψ of any singlet ${}^1S(L=0)$ state in a four-electron atomic system is represented in the form

$$\begin{aligned}\Psi_{L=0} &= \psi_{L=0}(A;\{r_{ij}\})\times \\ &\times(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha)+ \\ &+\phi_{L=0}(B;\{r_{ij}\})(2\alpha\alpha\beta\beta+2\beta\beta\alpha\alpha- \\ &-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\beta\alpha-\alpha\beta\alpha\beta), \quad (27)\end{aligned}$$

where $\psi_{L=0}(A;\{r_{ij}\})$ and $\phi_{L=0}(B;\{r_{ij}\})$ are the two independent spatial parts of the total four-electron wave function. The symbols A and B indicate that the two sets of nonlinear parameters associated with ψ and ϕ are optimized independently. Such a trial wave function must be antisymmetric with respect to all electron variables, i.e., $\hat{\mathcal{A}}_e\Psi=-\Psi$, where

$$\begin{aligned}\hat{\mathcal{A}}_e &= \hat{e}-\hat{P}_{12}-\hat{P}_{13}-\hat{P}_{23}-\hat{P}_{14}-\hat{P}_{24}-\hat{P}_{34}+\hat{P}_{123}+ \\ &+\hat{P}_{132}+\hat{P}_{124}+\hat{P}_{142}+\hat{P}_{134}+\hat{P}_{143}+\hat{P}_{234}+ \\ &+\hat{P}_{243}-\hat{P}_{1234}-\hat{P}_{1243}-\hat{P}_{1324}-\hat{P}_{1342}-\hat{P}_{1423}- \\ &-\hat{P}_{1432}+\hat{P}_{12}\hat{P}_{34}+\hat{P}_{13}\hat{P}_{24}+\hat{P}_{14}\hat{P}_{23} \quad (28)\end{aligned}$$

is the total four-particle antisymmetrizer. In addition to the notation explained above, $\hat{P}_{ijkl}$ is the permutation of the particles i,j,k,l.

Using the procedure described in the previous section, we can find explicit formulas for the corresponding spatial projectors. In fact, using the explicit form [27] of the trial wave function Ψ constructed for singlet states in four-electron systems and integrating over electron spin coordinates, we find the four spatial projectors

$$\begin{aligned}\mathcal{P}_{\psi\psi} &= \frac{1}{4\sqrt{3}}\Big(2\hat{e}+2\hat{P}_{12}-\hat{P}_{13}-\hat{P}_{23}-\hat{P}_{14}-\hat{P}_{24}+2\hat{P}_{34}+ \\ &+2\hat{P}_{12}\hat{P}_{34}+2\hat{P}_{13}\hat{P}_{24}+2\hat{P}_{14}\hat{P}_{23}-\hat{P}_{123}-\hat{P}_{132}- \\ &-\hat{P}_{124}-\hat{P}_{142}-\hat{P}_{134}-\hat{P}_{143}-\hat{P}_{234}-\hat{P}_{243}-\hat{P}_{1234}-\hat{P}_{1243}+ \\ &+2\hat{P}_{1324}-\hat{P}_{1342}-\hat{P}_{1432}+2\hat{P}_{1423}\Big), \quad (29)\end{aligned}$$

$$\begin{aligned}\mathcal{P}_{\psi\phi} &= \frac{1}{4}\Big(\hat{P}_{13}-\hat{P}_{23}-\hat{P}_{14}+\hat{P}_{24}+\hat{P}_{123}-\hat{P}_{132}-\hat{P}_{124}+ \\ &+\hat{P}_{142}+\hat{P}_{134}-\hat{P}_{143}-\hat{P}_{234}+\hat{P}_{243}+ \\ &+\hat{P}_{1234}-\hat{P}_{1243}-\hat{P}_{1342}+\hat{P}_{1432}\Big), \quad (30)\end{aligned}$$

$$\mathcal{P}_{\phi\psi}=\mathcal{P}_{\psi\phi}, \quad (31)$$

$$\begin{aligned}\mathcal{P}_{\phi\phi} &= \frac{1}{4\sqrt{3}}\Big(2\hat{e}-2\hat{P}_{12}+\hat{P}_{13}+\hat{P}_{23}+\hat{P}_{14}+\hat{P}_{24}- \\ &-2\hat{P}_{34}+2\hat{P}_{12}\hat{P}_{34}+2\hat{P}_{13}\hat{P}_{24}+2\hat{P}_{14}\hat{P}_{23}- \\ &-\hat{P}_{123}-\hat{P}_{132}-\hat{P}_{124}-\hat{P}_{142}-\hat{P}_{134}-\hat{P}_{143}- \\ &-\hat{P}_{234}-\hat{P}_{243}+\hat{P}_{1234}+\hat{P}_{1243}- \\ &-2\hat{P}_{1324}+\hat{P}_{1342}+\hat{P}_{1432}-2\hat{P}_{1423}\Big). \quad (32)\end{aligned}$$

In reality, because $\mathcal{P}_{\psi\phi}=\mathcal{P}_{\phi\psi}$, we need to use only three such operators $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$, and $\mathcal{P}_{\phi\phi}$. The use of these three projectors for matrix elements allows producing matrix elements with the correct permutation structure among all four identical particles. We note that all such matrix elements are computed only between the corresponding spatial basis functions and do not include any spin function. The explicit formulas for the complete set of singlet spatial projectors for four-electron atomic systems, Eqs. (29)–(32), have not been presented in previous publications. The first bound state computations of four-electron atomic systems with the use of completely correlated wave functions were performed in [13]. Since then, many authors have conducted such calculations for singlet states in various four-electron systems (see, e.g., [5] and the references therein).

4.3. Four-electron atomic systems. Triplet states

The trial wave function of the triplet ${}^3S$ state in the four-electron atomic system can also be represented in the form with the two independent spin functions $\chi_1=\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha$ and $\chi_2=2\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha-\alpha\beta\alpha\alpha$. The variational expansion takes the form

$$\begin{aligned}\Psi &= \psi_{L=0}(A;\{r_{ij}\})(\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha)+ \\ &+\phi_{L=0}(B;\{r_{ij}\})(2\alpha\alpha\beta\alpha-\beta\alpha\alpha\alpha-\alpha\beta\alpha\alpha), \quad (33)\end{aligned}$$

where $\psi_{L=0}(A;\{r_{ij}\})$ and $\phi_{L=0}(B;\{r_{ij}\})$ are the radial parts of the total wave function. Here, $\{r_{ij}\}$ denotes the complete set of fifteen interparticle (spatial) coordinates, and the symbols A and B denote the corresponding sets of nonlinear parameters. Optimization of nonlinear parameters in the A and/or B sets is performed independently. The trial wave function in Eq. (33) contains two electron spin functions χ_1 and χ_2 that correspond to the $S=1$ and $S_z=1$ values.

For triplet states, using the explicit form of the χ_1 and χ_2 functions, we can easily find the four other spin functions that correspond to the $S = 1$ and $S_z = 0$, and to $S = 1$ and $S_z = -1$ values. For instance, in the case of the $\chi_1 = \chi_1^{(+1)}$ spin function, the two spin functions

$$\chi_1^{(0)} = \alpha\beta\alpha\beta + \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha,$$

$$\chi_1^{(-1)} = \alpha\beta\beta\beta - \beta\alpha\beta\beta$$

respectively correspond to $S = 1$ and $S_z = 0$, and to $S = 1$ and $S_z = -1$. The three spin functions $\chi_1^{(+1)}$, $\chi_1^{(0)}$, $\chi_1^{(-1)}$ form a regular triplet of spin functions. An analogous triplet of spin functions can be constructed for the χ_2 spin function. To describe experimental situations without an external magnetic field, we need to use the spin functions associated with one value of S_z, e.g., $S_z = 1$. We therefore always choose

$$\chi_1 = (\alpha\beta - \beta\alpha)\alpha\alpha = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha,$$

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

(see Eq. (33) above).

In calculations with trial wave function (33), the explicit formulas for all three radial projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\phi\psi}(= \mathcal{P}_{\psi\phi})$, and $\mathcal{P}_{\phi\phi}$ must be known. However, numerical calculations using a wave function with two spin functions are computationally intensive and were not attempted in the current study. Accordingly, we did not attempt to derive the associated projectors. Instead, we performed some computations of the triplet states in four-electron atomic systems with the use of one spin function $\chi_1 = \chi_1^{(+1)} = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha$ only. The variational expansion in Eq. (33) is then written in the form

$$\Psi = \psi_{L=0}(A; \{r_{ij}\})(\alpha\beta - \beta\alpha)\alpha\alpha = \\ = \psi_{L=0}(A; \{r_{ij}\})(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha). \quad (34)$$

Now, we need to obtain the spatial part of the total wave function with the correct permutation symmetry between all identical particles 1, 2, 3, and 4. The corresponding spatial projector is obtained by calculating the explicit expression for the spin expectation value

$$\mathcal{P}_{\psi\psi} = \mathcal{C} \sum_{abcd} s_{abcd} \langle (\alpha\beta - \beta\alpha)\alpha\alpha | \hat{P}_{abcd} | \times \\ \times (\alpha\beta - \beta\alpha)\alpha\alpha \rangle \hat{P}_{abcd}, \quad (35)$$

where $\mathcal{C}$ is a normalization factor and the integers s_{abcd} are defined from the explicit form of the total four-particle antisymmetrizer $\hat{\mathcal{A}}_e$ in Eq. (28). After some algebra, we find the explicit formula for the corresponding spatial projector

$$\mathcal{P}_{\psi\psi} = \frac{1}{2\sqrt{6}} \Big(2\hat{e} + 2\hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} - \hat{P}_{24} - \\ - 2\hat{P}_{34} - 2\hat{P}_{12}\hat{P}_{34} - \hat{P}_{123} - \hat{P}_{124} - \hat{P}_{132} - \hat{P}_{142} + \\ + \hat{P}_{134} + \hat{P}_{234} + \hat{P}_{243} + \hat{P}_{143} + \hat{P}_{1432} + \hat{P}_{1234} + \\ + \hat{P}_{1243} + \hat{P}_{1342} \Big). \quad (36)$$

This projector creates the spatial part of an arbitrary matrix element needed in bound state computations of the triplet ^3S states in an arbitrary four-electron atomic system. Such a matrix element has the correct permutation symmetry among all four identical particles (electrons). Explicit formulas for the spatial projectors corresponding to the triplet states have not been published previously.

Using the formulas presented above, we can perform accurate computations of triplet bound states in various four-electron atomic systems. As follows from our results of such calculations (see, e.g., [2]), the method described above allows determining various expectation values in four-electron atomic systems to a relatively high numerical accuracy. In particular, such expectation values can be computed for all positive and negative powers of the relative coordinates r_{ij}. In general, the expectation value of any regular function of the ten relative coordinates r_{ij} can be computed to a very good numerical accuracy. Analogous expectation values containing delta-functions of the relative coordinates and their products with the regular functions of the relative coordinates also do not present any problem for numerical computations. Real problems arise in computations of expectation values that include products of delta-functions with the corresponding electron spin functions, e.g., $\langle \alpha_i \delta_{Ni} \rangle$ and $\langle \alpha_i \beta_j \delta_{Ni} \delta_{Nj} \rangle$, where N refers to the nucleus and i to the ith electron. The first expectation value $\langle \alpha_i \delta_{Ni} \rangle$ represents the single-electron density of α-electrons on the atomic nucleus. Analogous expectation values can be computed in the case of β-electrons. A very poor convergence of such expectation values means that another spin function must be included in computations. In Eq. (33), such a spin function is called the second (electron) spin function χ_2.

5. GENERALIZATION TO THE FIVE- AND SIX-ELECTRON ATOMIC SYSTEMS

The method described above allows constructing the properly antisymmetrized trial functions for three- and four-electron atomic systems. Formally, our method can be generalized to the five-, six-, and many-electron atomic systems. However, its direct generalization is very difficult, since the proper antisymmetrization of the trial basis functions and their linear combinations becomes extremely difficult in the case of many-electron atoms with $A-1 \geq 5$ electrons. To construct the trial wave functions for five-, six-, and many-electron atoms, different interparticle permutations must be applied to a nonsymmetrized basis function. The presence of a very large number of terms in each wave function drastically complicates the explicit expressions for the spatial projectors mentioned above. For instance, such a spatial projector constructed for the B atom (five-electron atom) must include 120 different terms. Some of these terms can be equal to zero identically, but in any case the total number of remaining terms is still very large. Therefore, it is important to develop some effective methods that can be used to operate with a very large number of terms in trial wave functions. Our current hopes rely on the two following methods. The first is based on the use of various symbolic-algebra computational platforms such as Maple [14]. In this approach, all integrations over spin variables can be performed analytically. The expressions for all spatial projectors are never written explicitly, but they are used internally by this computational platform. We also note that for some basis sets, the action of any interparticle permutation $\hat{P}_{abc\ldots}$ on the basis wave functions reduces to the permutation of the corresponding nonlinear parameters in these functions. In particular, this is the case for the variational expansion defined by Eqs. (4) and (5). This means that actual permutations of the nonlinear parameters in the basis wave functions can always be applied instead of the permutation of the relative coordinates. This drastically simplifies the explicit construction of the totally symmetrized trial wave functions. The permutation of the nonlinear parameters in the basis wave functions can be combined with the analytic integration over spin variables in the total wave function. This can be used in the future methods.

The second method is based on the relations that exist for the spin functions in three-, four-, and many-electron systems. For instance, the second spin function χ_2 used in numerical computations of the triplet states of four-electron systems is obtained from the χ_2 spin function known for the doublet states in three-electron systems. Formally, we can write $\chi_2(1,2,3,4) = \chi_2(1,2,3)\alpha(4)$, where $\alpha(4)$ is the spin function of the additional (fourth) electron. The notation $\chi_2(1,2,3)$ is for the second spin function of the doublet state in the three-electron system, and $\chi_2(1,2,3,4)$ means the second triplet spin function of the four-electron system. A similar relation exists between another (first) triplet spin function of the four-electron atomic systems, $\chi_1(1,2,3,4)$, and $\chi_1(1,2,3)$ used above (see Eq. (12)) for the doublet states in three-electron atoms/ions. By studying this and other similar relations between spin functions, we can find some useful connections between the spatial projectors constructed for three- and four-electron systems. This approach can also simplify methods and algorithms to be developed in the future for systems with five or more electrons.

6. NUMERICAL RESULTS

To illustrate our method in applications to actual three- and four-electron atomic systems, we briefly describe the results of variational computations of bound states in the three-electron Be^+ ion in its 1^2S state and the four-electron Be atom in its 1^1S and 2^3S states. For simplicity, all nuclear masses were assumed to be infinite in such calculations. A separate group of calculations have been performed for the 2^3S electron state in the six-body oxygen–muonic ion $\mathrm{O}^{8+}\mu^-e_4^-$. This positively charged ion ($q=+3$) is a well-bound atomic system that contains the composite "nucleus" ($\mathrm{O}^{8+}+\mu^-$) with the overall "nuclear" charge $+7$ and four atomic electrons. Below, we consider the $^{16}\mathrm{O}$ nucleus only. In our calculations of the $\mathrm{O}^{8+}\mu^-e_4^-$ ion, we used $M = 29156.9457m_e$ for the mass of the oxygen-16 nucleus and $m_\mu = 206.768262m_e$ [15, 16].

Numerical results of our computations are given in the Table, where we list the total energies E and some other bound state properties expressed in atomic units. The electron state of each atomic system is shown in the following brackets. For the $\mathrm{O}^{8+}\mu^-e_4^-$ ion, the notation 2^3S_e stands for the triplet electron state. The muonic quasinucleus $\mathrm{O}^{8+}+\mu^-$ is in its ground 1^1S state. This is always assumed, but not shown in our notation. For each energy shown, only nine decimal digits are presented. In general, optimization of the nonlinear parameters in variational expansions (4) and (5) always decreases the total energies. On the other hand, small variations in a few last decimal digits are not critically important for our present purposes.

As follows from the Table, our method provides very good numerical accuracy for doublet states in three-electron atoms and ions. This method also works perfectly for singlet and triplet four-electron atomic systems. It is very likely that the analogous procedure can be developed for five-, six-, and many-electron atomic systems. However, for atomic systems with five and more electrons, a number of additional problems occur

Table. The nonrelativistic energies and other properties determined for the S states in some three- and four-electron atoms, ions, and muonic ions (in atomic units)

	Be^{+} (1^2S)	Be (1^1S)	Be (2^3S)	$\mathrm{O}^{8+}\mu^{-}e_4^{-}$ (2^3S_e)
E	−14.3247627	−14.6673323	−14.4300595	−6619.33457
$\langle r_{eN}^{-1}\rangle$	2.65796	2.10684	2.03603	4.77655
$\langle r_{ee}^{-1}\rangle$	1.08200	0.72912	0.61933	1.26072
$\langle r_{eN}\rangle$	1.03379	1.49297	2.63085	0.98798
$\langle r_{ee}\rangle$	1.75565	2.54516	4.70847	2.43483

and direct generalization of our method is very difficult (see a discussion in the previous section).

We also note that the overall convergence rates of radial variational expansions (4) and (5) for three- and four-electron atomic systems are comparable with each other. This seems to be very strange, but we need to remember that the number of nonlinear parameters in each basis function rapidly increases as the total number of bodies A in the system increases. For four-electron atomic systems, each of these basis function contains ten nonlinear parameters (each of them varied independently), while for three-electron atomic systems, there are only six such parameters in each basis function. Briefly, this means that the overall "flexibility" of the four-electron trial function is comparable with the analogous "flexibility" of the three-electron trial functions.

7. CONCLUSION

We have considered the problem of accurate computations of bound states in three- and four-electron atomic systems. The method developed in this study allows constructing variational wave functions for an arbitrary bound state in three- and four-electron atomic systems. All such trial wave functions have the correct permutation symmetry (with respect to all permutations of identical particles, i.e., electrons). It is important to note that the total number of independent spin functions can be varied in our method. Numerical computations can start with the use of one electron spin function only. The second spin function can be introduced later to improve the overall convergence of the results. Our procedure can be generalized to bound states with a nonzero angular momentum L. Such a generalization is straightforward, but it requires extensive use of additional notation, application of special methods developed in the theory of angular momentum, and substantial explanations. Variational calculations of the bound $P(L = 1)$ states in five-electron atomic systems will be considered in our next study. The ground state of the B-atom is the $P(L = 1)$ state.

Our method is based on explicit constructions of the total wave functions for various bound states in three- and four-electron atomic systems. The unified procedure has been applied to an example of each type of system. The central part of the procedure is the construction of spatial projectors with the correct permutation symmetry between all identical particles (electrons). This method was originally developed for three-electron atomic systems in [8] (see also [9]). We generalized this procedure to the cases where a number of different spin functions are used in computations. In addition, we have constructed spatial projectors needed in calculations of the singlet and triplet bound states in four-electron atomic systems. Currently, the total energies and other properties of bound states in four-electron atomic systems can be determined to the accuracy that is better than the accuracy of old bound state calculations performed for two-electron atomic systems [17]. In general, using various optimization strategies for nonlinear parameters in the trial wave functions allows very accurate variational energies and highly accurate wave functions to be obtained. Such wave functions can be used in accurate computations of different bound state properties, including various relativistic and QED corrections.

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REFERENCES

1. L. D. Landau and E. M. Lifshitz, *Quantum Mechanics. Non-Relativistic Theory*, Oxford, England, Pergamon Press (1977).

2. A. M. Frolov and D. M. Wardlaw, Phys. Rev. A **79**, 064501 (2009).

3. F. G. Galvez and E. Buendia, J. Chem. Phys. **117**, 6071 (2002).

4. C. Froese Fisher, J. Phys. B **26**, 855 (1993).

5. A. M. Frolov and D. M. Wardlaw, Phys. Rev. A **78**, 042506 (2008).

6. N. N. Kolesnikov and V. I. Tarasov, Yad. Fiz. **35**, 609 (1982), [Sov. J. Nucl. Phys. **35**, 354 (1982)].

7. A. M. Frolov and D. M. Wardlaw, Zh. Eksp. Teor. Fiz. **135**, 667 (2009).

8. S. Larsson, Phys. Rev. **169**, 49 (1968).

9. F. W. King, Phys. Rev. A **40**, 1735 (1989).

10. M. I. Petrachen and E. D. Trifonov, *Applications of Group Theory in Quantum Mechanics*, Dover Publ., Inc., New York (2009), ch. XV–XIX.

11. V. Heine, *Group Theory in Quantum Mechanics*, Dover Publ., Inc., New York (1993), ch. II–IV.

12. P. R. Halmos, *Finite-Dimensional Vector Spaces*, D. Van Nostrand Company Inc., New York (1958), ch. III.

13. J. S. Sims and S. A. Hagström, Phys. Rev. A **4**, 908 (1971).

14. A product of Waterloo Maple Inc., Waterloo, Ontario, Canada (see: http://www.maplesoft.com).

15. *The NIST Reference on Constants, Units and Uncertainty*, http://physics.nist.gov/cuu/Constants/index.html.

16. *CRC Handbook of Chemistry and Physics*, ed. by D. R. Lide, CRC Press, Inc., Boca Raton, Florida (2004).

17. H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Springer-Verlag, Berlin (1957).