

## Discrete sets of Sturmian functions applied to two-electron atoms

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(Received 7 July 2008; published 9 February 2009)

We present a configuration-interaction (CI) method based on Sturmian functions. The components of this CI basis are the solutions of a two-body Sturmian eigenproblem, where the eigenvalues are related to the interacting potential in the two-body equation. Our method accommodates any arbitrary, physically sound, central potential in the Sturmian equations and different adequate asymptotic conditions. Computation of eigenvalues and eigenfunctions is performed by direct numerical discretization of the Sturmian equation. We apply this method to obtain bound states for two-electron systems. We show the convergence of the partial-wave expansion for the ground-states energies of the He atom and the  $H^-$  ion, and obtain very accurate results that are compared with other recent CI calculations.

DOI: [10.1103/PhysRevA.79.022507](https://doi.org/10.1103/PhysRevA.79.022507)

PACS number(s): 31.15.ac, 31.10.+z

### I. INTRODUCTION

The configuration-interaction (CI) method has been widely used to perform *ab initio* calculations of  $N$ -electron atomic and molecular systems [1–6]. Application of the CI procedure to atomic systems is based on the expansion of the solutions of the Schrödinger equation in terms of antisymmetrized products of atomic orbitals in spherical coordinates [5]. In most of CI applications, the nucleus is at rest in the center of the coordinate system and the electrons move in a central potential. Thus, by means of a multipole expansion of the interelectronic repulsion terms, the  $3N$ -dimensional differential equation (one variable for each electron's coordinate) can be transformed into a coupled set of  $N$ -dimensional differential equations, involving only the radial electron's coordinates.

The main advantage of the CI method compared with other approaches is its simplicity and flexibility, because *ab initio* calculations on two or more electron systems are relatively easy. On the other hand, the CI method converges slowly as a function of the number basis functions in the expansion. This small convergence rate occurs in the calculation of the energy as well as other mean values of a given atomic system, such as the average position of the electrons.

The CI method has been continuously improved along the years. Several versions of the theory have been proposed according to the type of basis elements and their asymptotic behavior [7–9], the optimization of the parameters, and the technique to solve the algebraic coupled equations.

Many basis sets in spherical coordinates have been proposed within the CI approach. A very effective scheme among the standard CI for atomic systems is based on Laguerre-type orbitals [5], also called Coulomb Sturmian functions (CSFs). These CSFs are discrete solutions of the radial Schrödinger equation with a pure Coulomb interaction where the energy is considered as a negative—externally fixed—parameter, and the Coulomb charge assumes the role of the eigenvalue.

The parameters of the CSF basis for two-electron CI systems are numerically optimized to obtain the best values for

the energies [6]. In the generalized Sturmian (GS) methodology of Avery and collaborators [1,2,4,10–12], the parameters are optimized by the diagonalization process itself and associated to the energies of the different states of the system. The GS methodology was shown to be efficient in obtaining atomic bound states for two- and three-electron atoms, as well as in molecular systems.

It has been stated that CSFs have the correct asymptotic behavior corresponding to the exact two-electron states (a fact that can substantially improve the convergence of a CI expansion) [4]. However, as we shall see in Sec. II, this is not entirely correct. These basis functions do not have all the same asymptotic behavior because it depends on the charge eigenvalue.

The main aim of this work is to develop a Sturmian-based CI method that overcomes most of the drawbacks summarized in the previous paragraphs. Here we present an alternative CI methodology based on one-electron SFs. These functions satisfy a two-body Sturmian equation which includes two central potentials: a long-range one modeling the general physical problem including the asymptotic region, plus a short-range potential used to describe the dynamics of the inner region where the chance to find both electrons is more important. The strength of the short-range potential is the eigenvalue of the problem. In this way, all the corresponding eigenfunctions obey the same long-range asymptotic condition. Based on physical considerations, we select the parametric values of the atomic energies in the one-electron Sturmian functions to construct a CI basis for two-electron problems. The asymptotic behavior of the basis is fixed by setting the long-range potential of the Sturmian equation to reproduce the asymptotic behavior of the atomic states. High-precision numerical methods [13,14] are used to solve the two-body radial Schrödinger equation and allows us to deal with a great variety of atomic central potentials. We exhibit the ability of the method by studying the partial-wave convergence of He and  $H^-$  ground states and by comparing our results with those obtained with CSFs by other authors.

The paper is organized as follows. In Sec. II we present the theory for the two-particle SFs and the numerical tech-

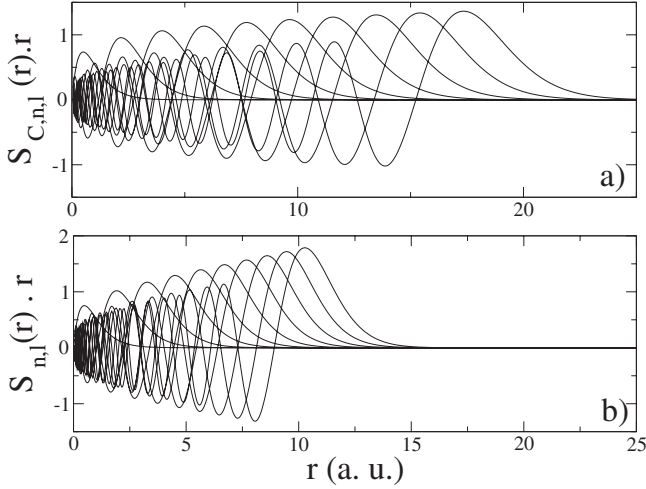


FIG. 1. First ten Coulomb Sturmian functions (CSFs) (a) and Sturmian functions (SFs) (b). Both correspond to the choice  $rV(r) = \exp(-\alpha r)$  and  $rU(r) = -Z$ . In panel (a) we set  $\alpha=0$ ,  $Z=0$ , and  $E = -11.52$  a.u. ( $\kappa=4.8$ ), while in (b) we set  $\alpha=0.375$ ,  $Z=2$ , and  $E = -1.42385$  a.u. We plot  $S_{n,l}$ , with  $n=1, 3, 5, \dots, 19$ , for  $l=0$ .

nique applied to solve the Sturmian equation. In Sec. III we develop the method further to solve the two-electron Schrödinger equation. In Sec. IV we apply the method to the somewhat simpler  $S$ -wave model for the He atom and then to the real He atom and  $H^-$  ion and also discuss the accuracy of the calculations. In Sec. V we draw some conclusions and envision other lines of future work.

We use atomic units ( $m=\hbar=e=1$ ) throughout.

## II. TWO-BODY STURMIAN FUNCTIONS

### A. Theory

The aim of this section is to present the general theory of two-particle Sturmian functions as well as the method we use to solve the Sturmian equation (see Fig. 1).

The starting point of the problem is the two-body Schrödinger equation

$$\left[ -\frac{1}{2}\nabla_{\mathbf{r}}^2 + U(r) - E \right] \Psi_{\nu}(\mathbf{r}) = -\beta_{\nu} V(r) \Psi_{\nu}(\mathbf{r}), \quad (1)$$

where  $\nu$  stands for all quantum numbers. The potential  $U$ , which we shall name *auxiliary* from now on, is either a long-range—e.g., Coulomb—potential or a central short-range potential. The potential  $V$  plays an important role in our discussion, and it will be referenced as the *generating potential*. It is a central short-range potential, which vanishes in the outer region  $r > R$ .

The physical boundary conditions associated with the Schrödinger equation are

$$r\Psi_{\nu}(\mathbf{r}) \rightarrow 0 \quad \text{for } r \rightarrow 0, \quad (2)$$

$$r\Psi_{\nu}(\mathbf{r}) \rightarrow \text{bounded for } r \rightarrow \infty. \quad (3)$$

The Sturmian problem is defined by Eq. (1) and the conditions (2) and (3), taking the energy  $E$  as a fixed parameter

and  $\beta_{\nu}$  as the eigenvalue. The solutions of this Sturmian equation represent, in the outer region, a particle of energy  $E$  moving in the outer region of the potential  $U$ .

The auxiliary and generating potentials only depend on the radial coordinate  $r$ , and hence Eq. (1) is separable in spherical coordinates. With a standard notation, we propose the following definition for  $\Psi_{\nu}(\mathbf{r})$ :

$$\Psi_{\nu}(\mathbf{r}) = \frac{1}{r} S_{n,l}(r) Y_{l,m}(\theta, \varphi). \quad (4)$$

Thus, we only have to solve

$$[T_r + U(r) - E] S_{n,l}(r) = -\beta_{n,l} V(r) S_{n,l}(r) \quad (5)$$

for  $S_{n,l}(r)$ , where  $T_r$  is the radial kinetic energy operator:

$$T_r = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2}. \quad (6)$$

The boundary condition (2) sets the regularity of the Sturmian functions at the origin of coordinates, where the potentials  $V$  and  $U$  might be divergent. The boundary condition (3) is responsible for the discretization of the eigenvalues  $\beta_{n,l}$  for negative values of the energy  $E$ , which can be labeled with a discrete index  $n=1, 2, 3, \dots$ . Note that the asymptotic behavior of the wave function is controlled by the auxiliary potential  $U$ . For large distances, where the potential  $V$  vanishes, the radial Sturmian equation (5) reduces to

$$[T_r + U(r) - E] S_{n,l}(r) = 0 \quad \text{for } r > R. \quad (7)$$

Therefore, the solutions  $S_{n,l}(r)$  of the radial Sturmian equation will present all the same asymptotic behavior. On the one hand, if  $U$  is also a short-range potential ( $U=0$  for  $r > R$ ), the asymptotic solutions of (7) will be proportional to

$$\exp(-\kappa r) \quad \text{for } r \rightarrow \infty, \quad (8)$$

where  $\kappa = \sqrt{2|E|}$ . On the other hand, if  $U$  is solely Coulombic in the region  $r > R$  [i.e., with the well defined form  $U(r) = -Z/r$  for  $r \rightarrow \infty$ ], then the solutions of (7) will behave as [15]

$$\exp\left(-\kappa r + \frac{Z}{\kappa} \ln(2\kappa r)\right) \quad \text{for } r \rightarrow \infty. \quad (9)$$

One can write down the conditions (8) and (9) as

$$\left[ \frac{dS_{n,l}(x)}{dx} + \kappa S_{n,l}(x) \right]_{x=r} = 0, \quad r \rightarrow \infty, \quad (10)$$

$$\left[ \frac{dS_{n,l}(x)}{dx} + \left( \kappa - \frac{Z}{\kappa x} \right) S_{n,l}(x) \right]_{x=r} = 0, \quad r \rightarrow \infty, \quad (11)$$

respectively. The condition (10) was given by Ovchinnikov and Macek, but is adapted here to negative energies [16]. The condition (11) is the extension to long-range potentials. In this work we assume that the energy  $E$  is negative.

Note at this point that these Sturmian functions can be reduced to the Coulomb Sturmian ones setting  $U=0$  and  $V = -\frac{e^{-\varepsilon r}}{r}$  in the limit  $\varepsilon \rightarrow 0$ . As described by many authors (see,

e.g., [16]), the definition of  $\beta_{n,l}$  in terms of the negative energy is  $\beta_{n,l}=n\kappa$ , while the asymptotic behavior of the CSFs  $S_{C,n,l}(r)$  for large  $r$  is

$$S_{C,n,l}(r) \rightarrow \exp[-\kappa r + n \ln(2\kappa r)] = (2\kappa r)^n \exp(-\kappa r). \quad (12)$$

Let us now emphasize the main difference between the set of Sturmian functions  $S_{n,l}$  and the Coulomb Sturmian functions  $S_{C,n,l}(r)$ . Equation (9) is the asymptotic behavior of the solutions of the Sturmian equation with boundary conditions (2) and (11). These functions have a fixed and well-defined logarithmic factor modifying the exponentially decaying behavior  $\exp(-\kappa r)$  of the bound states, which is the same for all basis elements. However, this logarithmic term changes from one CSF basis element to another; see Eq. (12). This dependence of the asymptotic behavior on the charge itself is an important issue to be considered in the use of these functions in many-electron atoms. As we will demonstrate in the following sections, the unique (and adequate) asymptotic behavior of the SFs improves the convergence of the basis respect to the CSFs.

Finally, we would like to remind the reader that the eigenfunctions  $\Psi_\nu(\mathbf{r})$  which are solutions of Eq. (1), with conditions (2) and (3), satisfy potential-weighted orthogonality conditions. We choose the normalization constant such that the orthonormality condition

$$\langle \Psi_{\nu'} | V | \Psi_\nu \rangle = \int d\mathbf{r} \Psi_{\nu'}^*(\mathbf{r}) V(\mathbf{r}) \Psi_\nu(\mathbf{r}) = \delta_{\nu',\nu} \quad (13)$$

and the closure relation

$$\sum_\nu \Psi_\nu^*(\mathbf{r}') \Psi_\nu(\mathbf{r}) V(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') \quad (14)$$

are satisfied.

### B. Numerical solutions of the radial Sturmian equation

There exists only a small number of interaction potentials for which analytical solutions of Eq. (5) are known in closed form [17]. Moreover, in most cases only the  $l=0$  solution is known. Thus, to be able to generate Sturmian basis sets for general potentials, it is necessary to develop a numerical method to solve Eq. (5) for the radial Sturmian functions.

To this end, we propose a discretization of the wave function  $S_{n,l}(r)$ :

$$S_{n,l}(r_i) \cong S_i, \quad i = 0, 1, \dots, N_r - 1, \quad (15)$$

in the uniform radial grid  $r_i = i \Delta r$  (the quantum numbers  $l$  and  $n$  are suppressed for brevity). The function  $S_i$  is then defined up to a given radius  $R = N_r \Delta r$ , such that  $V(r) = 0$  for  $r > R$ . Within the finite-difference scheme, we can approximate the second-order derivative in Eq. (5) up to  $O(\Delta r^2)$  by

$$\frac{d^2 S_{n,l}(r_i)}{dr^2} = \frac{1}{\Delta r^2} [S_{i+1} - 2S_i + S_{i-1}] + O(\Delta r^2) \quad (16)$$

and Eq. (5) reads

$$\begin{aligned} -\frac{1}{2} \frac{1}{\Delta r^2} S_{i+1} - \frac{1}{2} \frac{1}{\Delta r^2} S_{i-1} + \left[ \frac{1}{\Delta r^2} + \frac{l(l+1)}{2r_i^2} + U(r_i) - E \right] S_i \\ = -\beta_{n,l} V(r_i) S_i + O(\Delta r^2). \end{aligned} \quad (17)$$

We write this finite recurrence relation in matrix form as

$$[\mathbf{H} - E\mathbf{I}]\mathbf{s} = -\beta_{n,l}\mathbf{V}\mathbf{s}, \quad (18)$$

where  $\mathbf{s}$  is the vector with elements  $S_i$ ,  $i = 1, \dots, N_r$ ,  $\mathbf{I}$  is the identity matrix, and  $\mathbf{V}$  is the diagonal matrix with elements  $V_{ii} = V(r_i)$ . The symmetric tridiagonal matrix  $\mathbf{H}$  has off-diagonal elements  $H_{i,i-1} = H_{i,i+1} = -\frac{1}{2} \frac{1}{\Delta r^2}$ , while the diagonal ones are

$$H_{ii} = h_i = \frac{1}{\Delta r^2} + \frac{l(l+1)}{2r_i^2} + U(r_i). \quad (19)$$

The boundary condition given by (2) is applied to the Sturmian functions by setting  $S_{-1} = 0$  numerically. At  $r = R$ , box boundary conditions can be set by the condition  $S_{N_r+1} = 0$ , which makes the basis useful for bound states whose radial dimensions are considerably smaller than  $R$ . Alternatively, the exponentially decreasing behavior given by Eq. (9) can be imposed on the Sturmian functions. To this end, we need a linear relation between  $S_{N_r}$  and  $S_{N_r+1}$ . Assuming that the wave functions behave as (9) except maybe for a constant multiplying factor, we can obtain such a linear relation through the ratio between  $S_{N_r+1}$  and  $S_{N_r}$ :

$$\begin{aligned} C_{N_r} &= -\frac{1}{2} \frac{1}{\Delta r^2} \frac{S_{N_r+1}}{S_{N_r}} \\ &= -\frac{1}{2} \frac{1}{\Delta r^2} \frac{\exp\left[-\kappa r_{N_r+1} + \frac{Z}{\kappa} \ln(2\kappa r_{N_r+1})\right]}{\exp\left[-\kappa r_{N_r} + \frac{Z}{\kappa} \ln(2\kappa r_{N_r})\right]} \\ &= -\frac{1}{2} \frac{1}{\Delta r^2} \exp\left(-\kappa \Delta r + \frac{Z}{\kappa} \ln \frac{r_{N_r+1}}{r_{N_r}}\right). \end{aligned} \quad (20)$$

Thus, an approximate solution with the exact boundary condition can be obtained from Eq. (18), making the replacement

$$h_{N_r} \rightarrow h_{N_r} + C_{N_r}. \quad (21)$$

If we multiply Eq. (18) from the left by the inverse of the diagonal potential matrix  $\mathbf{V}^{-1}$ , we obtain a standard tridiagonal eigenvalue problem, whose eigenfunctions have impenetrable-box boundary conditions at the origin and impenetrable-box boundary condition or exponentially decaying behavior at  $R$  given by Eq. (9). These eigenvalues are obtained by means of iterative algorithms [18], based on sequential orthogonal rotations of the tridiagonal matrix. These procedures concentrate the computational effort on a given number of eigenvalues in increasing order of magnitude. Calculation of the corresponding eigenvectors is performed through inverse iteration algorithms [19]. Once the values of all eigenvectors have been obtained for each grid point  $r_i$ , we

apply a spline interpolation to define the basis function for any value  $r$  in the entire region  $0 < r < R$ .

To obtain more accurate results, we have also developed a finite-difference scheme of order  $O(\Delta r^4)$ , which leads to a pentadiagonal matrix eigenvalue problem [20]. In Sec. III we will compare the precision of the calculation of the atomic energies with the basis evaluated with both the  $O(\Delta r^2)$  and  $O(\Delta r^4)$  schemes.

### III. METHOD FOR TWO-ELECTRON SYSTEMS

The Schrödinger equation for two-electron atomic systems is

$$\left[ -\frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} - E \right] \Psi(\mathbf{r}_1, \mathbf{r}_2) = 0. \quad (22)$$

We make use of a CI-style expansion to obtain the solution, where an eigenstate of the total angular momentum operator is written as a superposition of independent electron functions. The solution of this three-body Schrödinger equation is written as

$$\Psi_S^{L,M}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\nu}^N a_{\nu}^{L,M,S} \Phi_{\nu,S}^{L,M}(\mathbf{r}_1, \mathbf{r}_2), \quad (23)$$

where  $\nu = \{l_a, l_b, n_a, n_b\}$  represents the angular momentum and radial quantum numbers of the electronic configurations  $a$  and  $b$ . The coefficients of the expansion  $a_{\nu}^{L,M,S}$  depend on the quantum numbers  $\nu$ , as well as on the total spin  $S$ , angular momentum  $L$ , and its projection  $M$  along a fixed axis  $\hat{\mathbf{z}}$ . The basis elements  $\Phi_{\nu,S}^{L,M}(\mathbf{r}_1, \mathbf{r}_2)$  are written in terms of our Sturmian functions:

$$\Phi_{\nu,S}^{L,M}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{A}_S \frac{S_{n_a, l_a}(r_1)}{r_1} \frac{S_{n_b, l_b}(r_2)}{r_2} \mathcal{Y}_{l_a, l_b}^{L,M}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2). \quad (24)$$

The operator  $\mathcal{A}_S$  is defined as

$$\mathcal{A}_S F(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [F(\mathbf{r}_1, \mathbf{r}_2) + (-1)^S F(\mathbf{r}_2, \mathbf{r}_1)] \quad (25)$$

and introduces the symmetry of the Pauli exclusion principle according to the spin state considered ( $S=0$  for singlets and  $S=1$  for triplets). The functions  $S_{n_a, l_a}(r_i)$  and  $S_{n_b, l_b}(r_i)$  ( $i=1, 2$ ) are one-electron radial solutions of Eq. (5) with parameters  $\{n_a, l_a, E_a, Z_a\}$  and  $\{n_b, l_b, E_b, Z_b\}$ , respectively.

Note that since the parameters involved in the radial equation (5) can be different for each atomic configuration  $a$  or  $b$ , also the potentials  $U$  and  $V$  can have different functional behaviors. In such a case we should label them as  $U_i$  and  $V_i$ , where  $i=a, b$ . For the atomic systems considered in this report (see next sections), it is convenient to assume the same functional behavior for each electronic configuration, while  $U$  is a pure Coulomb potential—i.e.,  $Z_a=Z_b=Z$  and  $U_a=U_b=-Z/r$ .

The angular terms of Eq. (24) are bispherical harmonic functions [21], which can be written as a linear combination of products of the spherical harmonics  $Y_{l,m}$ . For a given  $L$ ,

the indices  $l_a$  ( $l_b$ ) run over the values that satisfy the triangular selection rule  $|L-l_a| \leq l_b \leq |L+l_a|$  ( $|L-l_b| \leq l_a \leq |L+l_b|$ ) and parity conservation  $(-1)^\Pi = (-1)^{l_a+l_b}$ , where  $\Pi=1, 0$ . To avoid redundancies in the expansion (which can produce instabilities in the linear system to be solved), we let  $n_a$  and  $n_b$  run from 1 to their numerical limits  $N_a$  and  $N_b$ , except when  $l_a=l_b$ , where  $n_b$  starts at  $n_b^0 = n_a + [1 - (-1)^S]/2$ .  $N$  is the number of basis elements employed in the expansion of Eq. (23), and the basis achieves theoretical completeness in the limit  $N \rightarrow \infty$ .

Inserting Eq. (23) into Eq. (22) and making use of Eq. (5), we get

$$\begin{aligned} \sum_{\nu} a_{\nu} \left[ \frac{1}{r_{12}} - V_e(r_1, r_2) \right] \Phi_{\nu,S}^{L,M}(\mathbf{r}_1, \mathbf{r}_2) \\ = \sum_{\nu} a_{\nu} (E - E_a - E_b) \Phi_{\nu,S}^{L,M}(\mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (26)$$

where  $V_e$  is the operator which acts over  $\Phi_{\nu,S}^{L,M}$  as

$$\begin{aligned} V_e(r_1, r_2) \Phi_{\nu,S}^{L,M}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{A}_S (\beta_{n_a, l_a} V(r_1) + \beta_{n_b, l_b} V(r_2)) \\ \times \frac{S_{n_a, l_a}(r_1)}{r_1} \frac{S_{n_b, l_b}(r_2)}{r_2} \mathcal{Y}_{l_a, l_b}^{L,M}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2). \end{aligned} \quad (27)$$

One can see from (26) that the kinetic energy operators are removed from (22) because they are exactly diagonalized by the Sturmian functions. Besides, we recall that the auxiliary potentials were defined as Coulomb potentials  $-Z/r_i$  and are also removed from Eq. (22).

Projecting from the left onto the basis elements  $\Phi_{\nu', S}^{L,M}$ , we end up with the  $N \times N$  generalized eigenvalue problem

$$[\mathbf{V}_{12} - \mathbf{V}_e] \mathbf{a} = \tilde{E} \mathbf{O} \mathbf{a}, \quad (28)$$

which can be cast into the standard eigenvalue problem

$$\mathbf{H} \mathbf{a} = \tilde{E} \mathbf{a}. \quad (29)$$

where  $\mathbf{H} = \mathbf{O}^{-1} [\mathbf{V}_{12} - \mathbf{V}_e]$ .  $\mathbf{V}_{12}$  is the matrix with elements  $\langle \Phi_{\nu', S}^{L,M} | \frac{1}{r_{12}} | \Phi_{\nu, S}^{L,M} \rangle$ , the matrix  $\mathbf{V}_e$  has elements  $\langle \Phi_{\nu', S}^{L,M} | V_e | \Phi_{\nu, S}^{L,M} \rangle$ , and  $\mathbf{O}$  is the overlap matrix, whose elements are  $\langle \Phi_{\nu', S}^{L,M} | \Phi_{\nu, S}^{L,M} \rangle$ . From the eigenvalues  $\tilde{E}$  we extract the unknown eigenenergies as  $E = \tilde{E} + E_a + E_b$ .

Since the matrix elements of  $\mathbf{V}_e$  and  $\mathbf{O}$  are separable in the coordinate, the six-dimensional integrals involved in these calculations can be reduced to 2 three-dimensional ones. Besides, the angular part of each of these three-dimensional integrals can be performed analytically. Calculation of the matrix elements  $\mathbf{V}_{12}$  involves a six-dimensional integral, which can be separated by means of a multipole decomposition of the interelectronic repulsion term  $\frac{1}{r_{12}}$  [22]. The angular part of the  $\mathbf{V}_{12}$  matrix elements has an analytical expression in terms of the Clebsch-Gordan coefficients. The two-dimensional radial integrals can be split into 2 one-dimensional integrals through a numerically stable decomposition [23]. All remaining radial integrals are computed numerically by means of Gauss-Legendre quadratures.

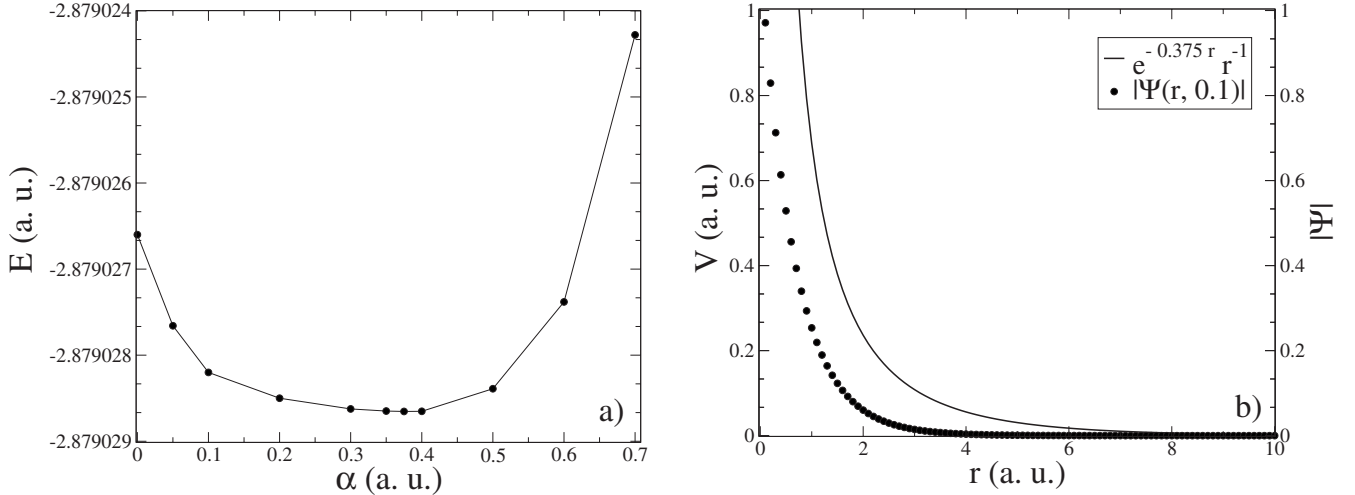


FIG. 2. (a) Ground-state energy obtained for He in the  $S$ -wave model, as a function of the parameter  $\alpha$  of the Yukawa potential  $V = \exp(-\alpha r)/r$ , which generates the Sturmian basis. The calculations were done with 20 Sturmian functions for each radial coordinate. (b) Behavior of the ground-state wave function of the He atom in the  $S$ -wave model, as a function of one of the coordinates, when the other one is fixed at 0.1 a.u. The figure also shows the behavior of the Yukawa potential with  $\alpha=0.375$  [a value close to the minimum in the curve shown in (a)]. See text for details.

#### IV. APPLICATIONS TO THE He AND $H^-$ SYSTEMS

In this section we apply the methodology described above to the study of two-electron atomic systems. We will focus the discussion on the role of the basis parameters in the calculation of the ground states of He and  $H^-$  systems.

##### A. Choice of basis parameters

There are a few basis parameters to be defined before performing any calculation. The range of the generating potential  $V$ , e.g., is set according to the system to be studied. As we shall see below, the introduction of this finite-range potential is mainly responsible for the improvement of the convergence rate of the method. Other basis parameters to be set are the asymptotic charges, included in the basis through the auxiliary potential  $U$ , and the energies. For symmetric states such as the He ground state, we may find adequate a symmetric basis with  $E_a = E_b = E_0/2$  and  $Z_a = Z_b = 2$ , where  $E_0$  is an *a priori* estimate of the energy. For asymmetric states, the choice  $E_a \neq E_b$  and/or  $Z_a \neq Z_b$  obtained from physical assumptions could be more adequate.

Note that the value  $E_0$  can be redefined after the diagonalization procedure and fed back in again iteratively until convergence. It is not the aim of this work to perform these kinds of calculations because we found that better absolute accuracy can always be reached increasing the basis size. Therefore, we study here the optimization of the range of the potential, the number of basis elements, and the grid size. We make use of a simple  $S$ -wave model of two-electron atoms to show the flexibility of the basis set and the convergence properties of our method.

Let us start our analysis with the choice of the parameters for the basis generation. Any simple model can be used to set up the initial values of the basis parameters. The GS expansion with only one basis element given in Ref. [10] could be considered as a good starting point. Within this approach, the

approximate solution for the ground state of a two-electron atom is

$$\phi_\nu(r_1, r_2) = \frac{k_\mu^3}{\pi} e^{-k_\mu(r_1+r_2)}, \quad (30)$$

where  $k_\mu$  is found to be

$$k_\mu = \frac{p_0}{\sqrt{2}} = Z - \frac{5}{16}. \quad (31)$$

The energy of the system is  $E_{app} = -\frac{p_0^2}{2}$ . For He atoms,  $Z=2$  and the model gives  $E_{app}^{(He)} \approx -2.8477$  a.u., while  $k_\mu^{(He)} = 1.6875$  a.u. For the  $H^-$  ion,  $Z=1$ , the energy  $E_{app}^{(H^-)} \approx -0.4726$  a.u., and  $k_\mu = 0.6875$  a.u. We set our Sturmian basis to have energies  $E_1 = E_2 = E_{app}/2$  as the starting point of the calculations.

It should be noticed that not only does the energy of the basis have to be set to an initially optimized value, but also the range of the potential  $V$  of Eq. (1). The generating potential has to go to zero at large distances fast enough so that the asymptotic behavior of the SFs corresponds to the behavior of the atomic state—i.e., an electron moving in a purely Coulomb potential of optimal charge. After some tests, the short-range potential that we found most adequate is the Yukawa potential  $V(r) = \exp(-\alpha r)/r$ . The parameter  $\alpha$  defines the range of the potential and can be varied according to the state in study. All Sturmian functions obtained with this potential have the same asymptotic behavior, which is determined by the auxiliary potential.

The effect of the use of a short-range potential to generate the eigenfunctions is shown in Fig. 2(a). It displays the result of a calculation of the ground-state energy of the He atom in the  $S$ -wave model, as a function of the parameter  $\alpha$  of the Yukawa potential [remember that in our case  $V_a = V_b = \exp(-\alpha r)/r$ ] and where the value of the individual-electron

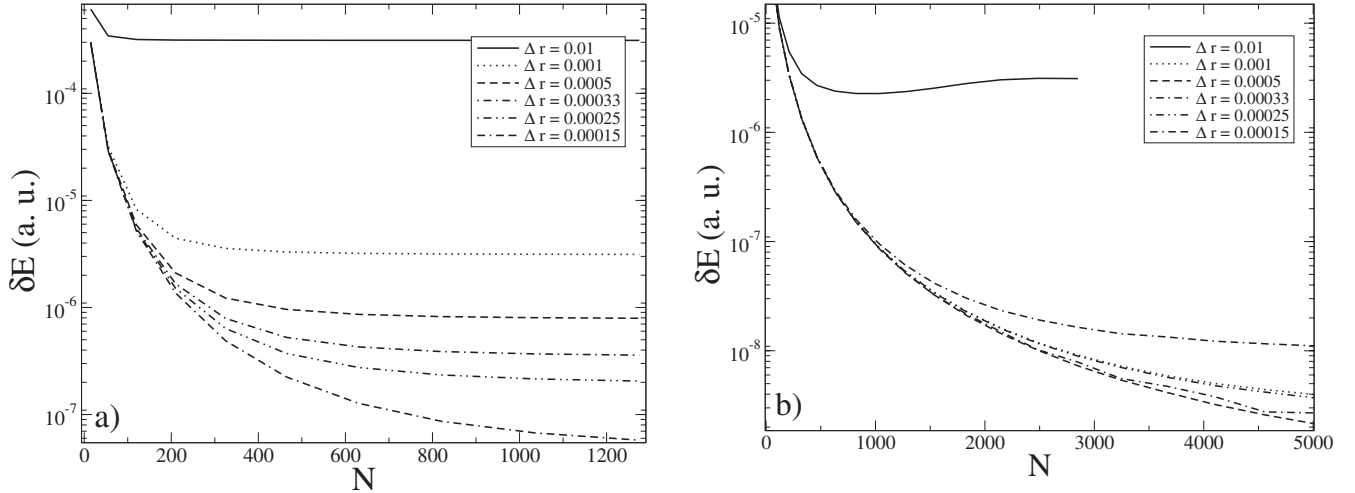


FIG. 3. Performance of the different numerical finite-difference schemes as a function of the basis size  $N$  for various grid sizes  $\Delta r$ . We define  $\delta E$  as the difference between the computed  $S$ -wave He ground-state energy and  $E_{acc} = -2.879028767$  a.u., a very accurate result obtained by Goldman [24]. (a)  $O(\Delta r^2)$  scheme [Eq. (17)] and (b)  $O(\Delta r^4)$  scheme (Ref. [20]). The best value obtained was  $-2.8790287655$  a.u., with  $N=5565$ .

energies is  $E_{app}/2$ . We can see that the curve has a minimum close to  $\alpha=0.375$ . For any value of the eigenvalue  $\beta$ , all the SFs reach their asymptotic behavior at approximately  $r \approx 6$  a.u., where  $V \approx 0.018$  a.u. This is consistent with the size of the He ground state in the  $S$ -wave model [see Fig. 2(b)].

Note that the energy increases rapidly when  $\alpha$  increases, because the basis is not efficient to describe large regions of the space. In that case, the ground state cannot be efficiently represented and the basis becomes formally inadequate. On the other hand, as  $\alpha \rightarrow 0$  the potential becomes Coulombic (long range) and the basis range is much larger. This is reflected by the fact that the energy reaches a well-defined value, which corresponds to that obtained with CSFs.

### B. Numerical precision

As already mentioned, we obtain the basis by numerical methods, so that their inaccuracy is a source of error in applications for two-electron wave function calculations.

We first note that the calculation of the two-body basis elements involves the diagonalization of a tridiagonal or pentadiagonal matrix. The eigenvalue problem consumes small memory resources, and it can be solved using very large grids, of the order of  $N_r \sim 10^5$ , in present personal computers. If we choose, for example, a radial domain of 50 atomic units and we set  $N_r = 5 \times 10^5$ , the grid step size is  $\Delta r = 10^{-4}$ . This means that the second derivative term of Eq. (16) has a local error of order  $10^{-8}$ . This error decreases if we represent states with spatial dimensions smaller than 50 a.u. or increases for highly excited states. However, values of  $\Delta r$  too small often lead to a loss of numerical precision, due to the iterative eigenvalue and eigenvector algorithm, as illustrated in the next paragraphs.

A practical test to study the precision of a two-electron calculation is the evaluation of the He ground-state energy in the  $S$ -wave model, with different radial grid sizes  $\Delta r$ . We first recall that the numerical error  $\varepsilon_r$  implicit in the finite-

difference method depends on  $\Delta r$ . The matrix elements of Eq. (28) involve the integration of the basis functions and their implicit error. We use Gauss-Legendre quadrature, which by far exceeds the precision of the numerical SFs. It immediately follows the error in the matrix elements of Eq. (29) is also of order  $\varepsilon_r$ , and then our eigenvalue problem can be written as

$$(\mathbf{H} + \mathbf{R})\mathbf{a} = \tilde{E}\mathbf{a}, \quad (32)$$

where  $\mathbf{R}$  is an error matrix with elements of order  $\varepsilon_r$ . If  $\mathbf{a}'$  are the exact eigenvectors (those that would be obtained if  $\varepsilon_r=0$ ), it can be shown [8,23] that they satisfy the condition

$$\begin{aligned} |\mathbf{a}'^t \mathbf{H} \mathbf{a} - \mathbf{a}'^t \mathbf{H} \mathbf{a}'| &\leq \sqrt{\sum_{j=1}^N R_{jj}^2} + \max(|R_{jj}|) \\ &\leq \max(|R_{jj}|)(\sqrt{N} + 1) \\ &= \varepsilon_r(\sqrt{N} + 1), \end{aligned} \quad (33)$$

where  $N$  is the size of the matrix  $\mathbf{H}$ . Figure 3 shows the differences between the calculated  $S$ -wave energy and the 21 digits of absolute accuracy value given by Goldman [24], versus the order of the matrix  $\mathbf{H}$ .

Figure 3(a) shows the results evaluated with the finite-difference method of Eq. (17). We see that all eigenvalues are below the limit imposed by inequality (33) and that all curves tend to a stationary value which decreases as  $\Delta r$  decreases. In the curve corresponding to  $\Delta r=0.01$  in Fig. 3(b), the decreasing behavior is interrupted for  $N \geq 1000$  and it increases from there onward. Curves for small  $\Delta r$  do not present such behavior, and the discrepancies from the Goldman's value are smaller than those of Fig. 3(a). However, we have to point out, unlike the results found in Fig. 3(a), calculations with  $\Delta r=0.0005$  and a  $O(\Delta r^4)$  scheme reach the smallest discrepancy for  $N=5050$  and then increase as  $\Delta r$  decreases [Fig. 3(b)]. This anomalous behavior could be

TABLE I. Partial-wave analysis of the He ground state.  $L_i$  ( $i=a,b$ ) is the maximum angular momentum quantum numbers considered for each electron. The second and third columns show calculations with 20 SFs and CSFs per  $L_i$ , respectively, while the fourth column uses 40 CSFs. We also show our best variational value (BVV) (see text).

$L_i$	He ground-state energy (in atomic units)		
	Present work	Ref. [6]	Ref. [23]
0	-2.879 028 654	-2.879 028 507 ( $\lambda=4.8$ )	-2.879 027 97
1	-2.900 515 957	-2.900 515 873 ( $\lambda=7.8$ )	-2.900 513 86
2	-2.902 766 371	-2.902 766 378 ( $\lambda=10.1$ )	-2.902 762 09
3	-2.903 320 378	-2.903 320 527 ( $\lambda=12.1$ )	-2.903 313 21
4	-2.903 517 659	-2.903 517 973 ( $\lambda=14.0$ )	-2.903 506 82
5	-2.903 604 533	-2.903 605 022 ( $\lambda=15.5$ )	-2.903 589 25
6	-2.903 648 475	-2.903 649 142 ( $\lambda=17.1$ )	-2.903 628 16
7	-2.903 672 975	-2.903 673 821 ( $\lambda=18.7$ )	-2.903 661 00
8	-2.903 687 656	-2.903 688 677 ( $\lambda=20.1$ )	
9	-2.903 696 951	-2.903 698 142 ( $\lambda=21.5$ )	
10	-2.903 703 098	-2.903 704 451 ( $\lambda=22.9$ )	
11	-2.903 707 307	-2.903 708 815 ( $\lambda=24.2$ )	
12	-2.903 710 272	-2.903 711 927 ( $\lambda=25.5$ )	
BVV ( $L_i=12$ )	-2.903 712 009		
Exact [25]	-2.903 724 377		
Exact, $L_i=0$ [24]	-2.879 028 767		

traced back in the inverse-iteration algorithms which are used to evaluate the eigenfunctions, whose performance worsens when  $\Delta r$  is too small.

In summary, the theoretical limit of our calculation is  $\Delta r^4(\sqrt{N}+1)$ , which for  $\Delta r=0.0005$  and  $N=5050$  corresponds to the very small value of  $4.5 \times 10^{-12}$ . However, by incidence of the iterative methods, the absolute accuracy reduces finally to about  $1 \times 10^{-9}$ .

### C. Partial-wave results

In Table I we show the ground-state energy of the He as a function of the maximum angular momentum  $L_i$  ( $0 \leq l_i \leq L_i$ ) ( $i=a,b$ ) for each configuration. These results were obtained with 20 SFs per angular momentum quantum number  $l_i$ , generated by the Yukawa potential with  $\alpha=0.375$ , the abscissa of the minimum of the curve shown in Fig. 2. Also, we set the parametric energy in the Sturmian equation (1)  $E_i = E_{app}/2 = -1.483 85$  a.u. for both electrons, obtained from Avery's model. The calculation was performed up to  $L_i=12$ , for which the maximum (symmetrized) basis size was  $N=2520$ . We use 30 000 equally spaced radial grid points to generate the basis, starting from  $r=0$  and ending at  $r=15$  a.u., which corresponds to  $\Delta r=0.0005$ . According to the discussion of the previous section, we can estimate an absolute accuracy of  $1 \times 10^{-9}$  for the total energies. We compare our results with those of Fomouou and collaborators [23], which were obtained with 40 radial CSFs per  $l_i$  for each electron, and also with those of Bromley and Mitroy [6], who used 20 radial functions per  $l_i$  for each electron. Those authors used a symmetric basis composed of products of Laguerre-type orbitals (CSFs) with special choices of the

scaling parameter  $\lambda$ . In the work of Fomouou *et al.*, that parameter is fixed to a particular value, while in the work of Bromley and Mitroy it is varied separately for each  $l_i$  [6] (12 variational parameters for the best value obtained with 20 single-electron orbitals per  $l_i$  for  $L_i=12$ ). In both cases the use of Laguerre basis functions implies that the asymptotic behavior of the basis is not the one associated with the state that they are expanding, since the Coulombic logarithmic phase associated with the CSFs changes from one basis element to the other (see Sec. II A). This is not the case of our basis set where all the elements have the same asymptotic behavior, an exponential factor times a logarithmic phase.

Note that we obtain better results for  $L_i=0$  than those of Bromley and Mitroy (for the  $L_i=0$  and  $L_i=1$  partial-wave terms) and than those of Fomouou *et al.* (for all partial waves), even though we have just only one optimal parameter ( $\alpha$ ). To obtain better values for  $L_i$  up to 12, we have to perform a new optimization over  $\alpha$  and/or other parameters. We found that a new optimization over  $\alpha$  was not sufficient to reproduce the accuracy of Bromley and Mitroy, so that we also vary the energy of the SF basis. We found that by setting  $\alpha=0.795$  and  $E=1.05$  a.u., the energy for the 12 partial-wave energy terms is  $-2.903 712 009$  a.u., which is in better agreement with the exact value than all the calculations we are comparing with. It should also be noted that this last calculation was performed adjusting both the asymptotic behavior of the basis set ( $E$ ) and the region where it is applied through  $\alpha$ . The optimization of these two physical basis parameters is enough to avoid the complete optimization procedure implemented by Bromley and Mitroy. Moreover, this optimization is possible within our method also by taking the charge of  $U$  as an optimization parameter. To exactly reproduce the re-

TABLE II. Partial-wave analysis of the  $H^-$  ground state.  $L_i$  ( $i = a, b$ ) is the maximum angular momentum quantum numbers considered for each electron. The numerically exact value is taken from Ref. [26]. See text for discussion.

$L_i$	$E_i$	$\alpha$	H <sup>-</sup> ground-state energy (in atomic units)	
			Present work	Ref. [23]
0	-1.25	0.425	-0.514 496 258	-0.514 496 14
1	-1.15	0.425	-0.526 584 655	-0.526 584 10
2	-1.05	0.45	-0.527 438 491	-0.527 437 44
3	-1.05	0.9	-0.527 625 592	-0.527 623 91
4	-1.05	0.9	-0.527 688 280	-0.527 686 18
5	-1.05	0.9	-0.527 715 221	-0.527 712 15
Exact [26]			-0.527 751 016 35	

sults of Bromley and Mitroy (and those of Fomouo also) we should set  $\alpha=0$ ,  $Z=0$ ,<sup>1</sup> and  $E=-\lambda^2/2$  in the Sturmian equation for each partial wave. However, according the values of  $\lambda$  given in Table I, the best choices of the basis energies would range from  $E=-11.52$  a.u. for  $l_i=0$  to  $E=-325.125$  a.u. for  $l_i=12$ , values that are not related to the asymptotic behavior of the He ground state at all.

We can see from the results presented in Table I that our method achieves better He ground-state energy values than Fomouo and collaborators, even when we are using half of the basis elements per electron than they use. This improvement in the convergence respect to their basis is not evident in the  $H^-$  case shown in Table II, where we used also 40 SFs for each electron per  $L_i$  to obtain comparable results, although our method provides another significant figure. This is because the spatial extension of the fundamental  $H^-$  state is larger than in the case of He. Then, the best choice of  $\alpha$  for the Sturmian energy parameter given by Avery’s model (0.2363) is very small (we used  $\alpha=0.05$  to obtain the results of Table II). Hence the basis of Fomouo and collaborators does not differ too much from our Sturmian set. They use a  $\lambda$  parameter (which they call  $k$ ) of 1.0, which can be associated with an energy of 0.5, twice our value. We also remark that Avery’s model for the  $H^-$  system is not very realistic, because it does not give an adequate model for the bound state of the  $H^-$  ion [10]. Through an optimization procedure we found the best energy value for  $L_i=0$  to be  $-0.514 496 301 1$  a.u. with an energy basis parameter equal to  $-0.0075$ .

Excited-state energies can also be obtained easily with the diagonalization procedure presented here. However, we note that the region used to evaluate these states has to be large enough. With a larger  $R$  both ground and excited states are properly obtained. An optimization of the basis energy as suggested by Avery can be easily implemented, leading to a very good energies and states [4]. Although in the calculations presented in this report we always use symmetric basis sets, it could be better for other states and systems to choose

different sets of parameters for each electron, especially in the case of asymmetric states such as the highly excited states of two-electron atoms or even also for the  $H^-$  bound state. We emphasize that our method can easily accommodate these asymmetric conditions, and its application to the study of excited and scattering states will be soon presented elsewhere.

## V. CONCLUDING REMARKS

We have proposed a method to deal with two-electron atomic systems based on Sturmian functions. Although in this paper we centered our attention on bound states, our theoretical approach is also valid for continuum ones. To the best of our knowledge, a method to generate Sturmian functions for any type of central potentials both for positive and negative energies has not been presented before; this constitutes one of the main results of our paper.

We presented the set of Sturmian functions and the methodology developed to generate them. The method allowed us to generate Sturmian functions for *any* type of central potential. In particular, the system of functions proposed in this report is the solution of a Schrödinger equation with an interaction potential written as a sum of two terms. The first term (the auxiliary potential) includes either short- or long-range potentials. The second term (the generating potential), which is a short-range potential, is specifically used to generate the set of Sturmian eigenvalues and eigenvectors. The asymptotic behavior of the functions is defined by the auxiliary potential. Different types of boundary conditions can be fixed at large distances, which is another advantage of our method. The well-known Coulomb Sturmian functions constitute just one particular case and can be easily obtained within our approach.

A properly symmetrized product of one-electron Sturmian functions was used to generate the basis of the configuration space for two-electron systems. The three-body problem was then reduced to a standard eigenvalue problem for the coefficients of the expansion.

To exhibit the benefits of a CI scheme with these Sturmian functions, we explored different ground states common in atomic physics. First, since our method enables us to set the range of the generating potential freely, we analyzed the optimization of this parameter in the context of the spherically symmetric  $S$ -wave model He. The accuracy of the basis set was also analyzed in this particular system for different numerical schemes. We have clearly shown that the optimization of this potential leads to an enhancement of the rate of convergence of the energies and wave functions. This was verified by comparing our results obtained with those of Fomouo *et al.* [23] and Bromley and Mitroy [6].

To perform a partial-wave analysis, we studied the bound states of the He atom and the  $H^-$  ion. We showed that using a much smaller basis than Fomouo *et al.* [23], we could get better energies for the He case. Besides, our energies were more accurate than those presented by Bromley and Mitroy [6] for the same basis size, even when they used different variational parameters for each partial wave. Our optimized result for the  $H^-$  ground-state energy is in excellent agreement with the exact result, beyond the standard CSFs of

<sup>1</sup>Actually, if  $\alpha=0$ , the value of  $Z$  has no effect, since in that case it will always be related to  $E$  and  $\beta$  through  $\beta+Z=\sqrt{-2E}$ .



Foumouo and co-workers. However, the improvement was not as significant as in the case of the He system, because the optimal Sturmian functions are similar to the CSFs.

Calculations with different Sturmian basis for each electron's coordinate (asymmetric basis sets) require further studies and will be presented elsewhere. Furthermore, the use of other generating potentials could be more convenient for those purposes, and that will be a matter of future investigations.

## ACKNOWLEDGMENTS

We would like to thank to Professor J. Avery and Professor U. Ancarani for a careful reading of the manuscript and for their encouraging comments about our work. This work has been supported by Grants No. PICTR 2003/00437 and No. PICT 04/20548 of the ANPCYT (Argentina), Grant No. PIP 5595 of Conicet, and Grant No. PGI 24/F038 of Universidad Nacional del Sur (Argentina).

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