

L^2 Discretization of Sturmian Wave Functions for Coulomb-like Potentials

A. L. FRAPICCINI,^{1,4} V. Y. GONZALEZ,^{2,4} J. M. RANDAZZO,^{1,4}
F. D. COLAVECCHIA,^{3,4} G. GASANEO^{1,4}

¹Departamento de Física, Universidad Nacional del Sur, 8000 Bahía Blanca, Argentina

²Departamento de Matemática, Universidad Nacional del Sur, 8000 Bahía Blanca, Argentina

³Centro Atómico Bariloche, 8400 San Carlos de Bariloche, Río Negro, Argentina

⁴Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina

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ABSTRACT: In this work we introduce a method to construct Sturmian functions for general interaction potentials in two-body problems. We expand these Sturmians on a finite L^2 space, using N Laguerre basis functions to obtain a discrete set of eigenvalues for positive and negative energies. Orthogonality and closure relations are thus rewritten for these expansions; completeness is achieved through increasing the basis size. We apply the method to the Coulomb and Herman and Skillman potential. We study the behavior of the functions obtained and their convergence for an overall range of energies. The Sturmian functions are applied to solve the Schrödinger equation for an active electron in a He-like system. © 2006 Wiley Periodicals, Inc. *Int J Quantum Chem* 107: 832–844, 2007

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1. Introduction

The theoretical study of a wide range of atomic and molecular properties can be carried out

Correspondence to: A. L. Frapiccini; e-mail: afrapic@uns.edu.ar
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through the representation of a particular physical magnitude by a functional basis set. Such functions are usually generated by solving the Schrödinger equation for the problem under study, or an approximated problem similar to the one of interest. The eigenfunctions obtained are those associated to the energy eigenvalues. However, in some cases, these functions are not suitable to a given problem and other basis sets are necessary or more convenient, e.g., for convergency reasons. As an alternative to energy eigenfunctions one could find solutions to the same wave equation treating the energy as a fixed

parameter and using other parameter appearing in the equation as eigenvalue [1,2]. These solutions for a particular set of boundary conditions, are referred to as Sturmian functions [1,3–5,7–9]

The Schrödinger Coulomb Sturmian functions (CSFs) for a two-body system are of particular interest in atomic physics. These functions are solutions of the two-body Schrödinger equation for a Coulomb potential, where the energy is fixed and the charge is considered as the eigenvalue. The CSFs form a discrete set for negative energies [1, 2] and have been widely used in atomic physics to determine atomic energy levels [10–12], or to expand the Coulomb Green function (see Ref. [13] and references therein). Meanwhile, at positive energies, they constitute a continuous spectrum [14, 15] running over the whole real axis, assuming that the CSFs satisfy standing-wave boundary conditions.

The fact that positive energy Sturmians with standing-wave boundary conditions have a continuous spectrum leads to continuous representations for physical operators. These expansions involve integrals on the Sturmian basis set, which requires the computation of quite cumbersome numerical integrals, which one would wish to avoid.

In this study, we work out an alternative to this approach. We propose the usual variable separation in the two-body Schrödinger equation in spherical coordinates and then expand the resulting radial Sturmian function in a finite set of L^2 functions. This set is based on Laguerre-type functions, that accurately mimic the boundary conditions of the problem. Within this L^2 space of size N , the problem is reduced to solve a matrix eigensystem for the charge eigenvalues, giving rise to a discrete spectrum of eigenvalues for the full energy range.

This work is organized as follows. In Section 2, we outline the general method for expanding the two-particle Sturmian functions in terms of Laguerre-type basis, and obtain orthogonality and closure relations restricted to an space of size N . In Section 3, we study the problem for the Coulomb potential $V(r) = Z/r$, and we give numerical and closed expressions for the expansion coefficients and the normalization constant. We also perform a comparison between the solutions here derived with the available for the exact Coulomb Sturmians [14, 15]. We also discuss the convergence of the functions with the basis size. In Section 4, we derive Sturmian functions for Herman and Skillman-type potentials, as an example of the application of the method for non-Coulomb models. We apply the method introduced in Section 2 to the determination of the

eigenvalues and eigenfunctions of this potential and compare our results with those corresponding to the Coulomb potential. Finally, in Section 5 we present a summary of our work, draw some conclusions, and suggest some applications. Atomic units are used unless otherwise stated.

2. Method for Obtaining Sturmians

The time-independent Schrödinger equation has been used to obtain the energies and wave functions of almost any physical system in the quantum realm. In the case of two bodies interacting through the potential V , the center-of-mass motion can be extracted from the equation, giving

$$\left[-\frac{1}{2\mu} \nabla_r^2 - V \right] |\Psi\rangle = E |\Psi\rangle. \quad (1)$$

The first term of the left-hand side represents the relative kinetic energy of the system. Under physical boundary conditions, the solutions of Eq. (1) represent the energies E_ν and eigenstates $|\Psi_\nu\rangle$ of the system.

Instead, the Sturmian functions for a physical potential V are found to be solution of the Schrödinger equation

$$\left[-\frac{1}{2\mu} \nabla_r^2 - E \right] |\Psi\rangle = -\beta V |\Psi\rangle \quad (2)$$

subject to appropriate physical boundary conditions. In this case, the energy E is considered a fixed parameter, and β is the eigenvalue to determine. Since the Sturmian functions have been used mainly for Coulomb potentials, it is customary to call the β parameter as charges. However, in a general case, this parameter is related to the magnitude of the scaled potential βV . The solutions of (2) are the eigencharges β_ν that represent the scaled eigenpotentials and their corresponding eigenstates $|\Psi_\nu\rangle$ for a given, fixed energy E .

For a spherically symmetric potential, separation of variables can be performed by writing the Sturmian functions as the product of the radial and angular parts

$$\langle \mathbf{r} | \Psi_\nu \rangle = \frac{1}{r} S_{\nu,l}(r) Y_l^m(\theta, \phi), \quad (3)$$

where Y_l^m represents the spherical harmonics defined in, e.g., Ref. [17]. The radial part of the Sturmian functions then satisfies the equation

$$[H_l - E] |S_{\nu,l}\rangle = -\beta_\nu V |S_{\nu,l}\rangle, \quad (4)$$

where H_l is the radial kinetic energy operator:

$$H_l = -\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)}{2\mu r^2}. \quad (5)$$

For E real and negative, the two-boundary conditions

$$S_{v,l}(r) \rightarrow 0 \quad \text{for } r \rightarrow 0 \quad (6)$$

$$S_{v,l}(r) \rightarrow 0 \quad \text{for } r \rightarrow \infty \quad (7)$$

lead to an infinite discrete spectrum of eigenvalues β_v with $v = n = 1, 2, \dots$ [3,5]. The eigenfunctions $|S_{n,l}\rangle$ corresponding to the eigenvalues β_n are orthogonal with respect to the potential V

$$\langle S_{n',l}|V|S_{n,l}\rangle = \int_0^\infty dr S_{n',l}(r)V(r)S_{n,l}(r) = \delta_{n',n} \quad (8)$$

and satisfy the following closure relation:

$$\sum_{n=1}^\infty |S_{n,l}\rangle\langle S_{n,l}|V = \delta(r-r'). \quad (9)$$

For real and positive energy, we can impose the two-points boundary conditions:

$$S_{v,l}(r) \rightarrow 0 \text{ for } r \rightarrow 0 \quad (10)$$

$$S_{v,l}(r) \rightarrow \text{bounded for } r \rightarrow \infty, \quad (11)$$

which implies regularity at the origin and standing-wave boundary conditions at large distances. These two conditions do not lead to a discretization of the eigenvalue β_v ; then, the positive energy Sturmian have a continuous spectrum that covers the whole real axis $-\infty < \beta < \infty$. An example of functions satisfying these boundary conditions have been discussed by Szmytkowski [14] and Gasaneo and Colavecchia [15] for the two-body Coulomb problem. The orthogonality and closure relations satisfied by the eigenfunctions of Eq. (4) with the boundary conditions given by Eqs. (10) and (11) are

$$\langle S_{v',l}|V|S_{v,l}\rangle = \int_0^\infty dr S_{v',l}(r)V(r)S_{v,l}(r) = \delta(v'-v), \quad (12)$$

$$\int dv |S_{v,l}\rangle\langle S_{v,l}|V = \delta(r-r'). \quad (13)$$

The closure relations (9) and (13) show that each set of Sturmian functions, for negative and positive

energies separately, is a complete and orthogonal basis in the domain $0 \leq r < \infty$ [15,16]. However, aside for some particular potentials, there are no analytic solutions for the eigenvalue problem defined by Eq. (4) with the boundary conditions (6)–(7) or (10)–(11).

One aim of this report is to define a general method to find the Sturmian functions both for negative as well as positive energies for arbitrary, well-behaved, potentials. To this end, we consider a L^2 basis set of Laguerre-type functions with a free, real parameter λ :

$$\langle r|\varphi_{n,l}\rangle = \varphi_{n,l}(\lambda, r) = (2\lambda r)^{l+1} e^{-\lambda r} L_n^{2l+1}(2\lambda r), \quad (14)$$

with $L_n^\alpha(x)$ the generalized Laguerre polynomials [18]. We expand the Sturmian $|S_{v,l}^N\rangle$ for any energy in the subspace $\{\varphi_{n,l}\}_{n=0}^{N-1}$

$$|S_{v,l}^N\rangle = B_{v,l}^N \sum_{n=0}^{N-1} a_{n,l}^v |\varphi_{n,l}\rangle, \quad (15)$$

where we have explicitly stated the dependence of the Sturmian function on the parameter l and the basis size N . $B_{v,l}^N$ is the normalization constant and $a_{n,l}^v$ are the coefficients of the expansion. We need to point out that the Laguerre basis does not depend on the energy E , and therefore the entire energy dependence of the $|S_{v,l}^N\rangle$ Sturmian is contained on the $a_{n,l}^v$ coefficients. Replacing $|S_{v,l}^N\rangle$ as given by the expansion of Eq. (15) into Eq. (4) and projecting onto the basis, we obtain a set of equations given by

$$\begin{aligned} \sum_{n=0}^{N-1} \left[\frac{\lambda}{\mu} (n+l+1) \left\langle \varphi_{m,l} \left| \frac{1}{r} \right| \varphi_{n,l} \right\rangle \right. \\ \left. - \left(E + \frac{\lambda^2}{2\mu} \right) \langle \varphi_{m,l} | \varphi_{n,l} \rangle \right] a_{n,l}^v \\ = \beta_v \sum_{n=0}^{N-1} \langle \varphi_{m,l} | -V | \varphi_{n,l} \rangle a_{n,l}^v, \quad (16) \end{aligned}$$

which can be represented in matrix form as

$$\mathbf{M} \bar{\mathbf{a}} = \beta_v \mathbf{V} \bar{\mathbf{a}}, \quad (17)$$

where \mathbf{M} and \mathbf{V} are $N \times N$ square matrices with elements $M_{m,n} = \langle \varphi_{l,m} | H_l - E | \varphi_{l,n} \rangle$ and $V_{m,n} = \langle \varphi_{l,m} | -V | \varphi_{l,n} \rangle$, and $\bar{\mathbf{a}}$ is an N -dimensional vector with the coefficients of the expansion. The matrix elements

$M_{m,n}$ do not depend on the potential and are obtained in closed form as follows:

$$M_{m,n} = \delta_{m,n} \frac{\Gamma(2l + 2 + n)}{n!} \times \left[\frac{\lambda}{\mu}(n + l + 1) - \frac{\left(E + \frac{\lambda^2}{2\mu}\right)}{\lambda}(n + l + 1) \right] + \frac{\left(E + \frac{\lambda^2}{2\mu}\right)}{2\lambda} \left[(n + 1)\delta_{m,n+1} \frac{\Gamma(2l + 2 + n + 1)}{(n + 1)!} + (n + 2l + 1)\delta_{m,n-1} \frac{\Gamma(2l + 2 + n - 1)}{(n - 1)!} \right]. \quad (18)$$

The matrix elements $V_{m,n}$ should be obtained for each particular potential V . Equation (17) has a nontrivial solution if

$$\det(\mathbf{M} - \beta_v \mathbf{V}) = 0.$$

This condition gives a polynomial of degree N in β_v with roots labeled by $v = 1, 2, \dots, N$. This is a consequence of the restriction of the basis set to a subspace of N functions. Hence, we obtain a finite discrete set of eigenvalues β_v for both negative and positive energies. It follows that orthogonality and closure relation within this subspace are defined by

$$\langle S_{v',l}^N | V | S_{v,l}^N \rangle = \int_0^\infty dr S_{v',l}^N(r) V(r) S_{v,l}^N(r) = \delta_{v',v} \quad (19)$$

$$\sum_{v=1}^N |S_{v,l}^N\rangle \langle S_{v,l}^N| V = \delta^N(r - r'), \quad (20)$$

where δ^N is the representation of the Dirac delta in the N -subspace.

The coefficients $a_{n,l}^v$ are found by solving the system Eq. (16), and the normalizations $B_{v,l}^N$ are evaluated by means of the orthogonality relation Eq. (19), by setting $v' = v$.

In this way we obtain a discrete set of functions independently of the sign of the energy. Completeness of the set of Sturmians is achieved as the size of the basis N increases toward infinity, that is, $\delta^N \rightarrow \delta$ as $N \rightarrow \infty$.

The functions of Eq. (15) corresponding to each of the eigenvalues that result from the diagonalization process described clearly satisfy the boundary conditions (6) and (10) for positive and negative energies. The basis functions $\langle r | \varphi_{n,l} \rangle$ are regular at the origin and therefore they lead to a regular function $\langle r | S_{v,l}^N \rangle$. In contrast, to see how $|S_{v,l}^N\rangle$ fulfill the boundary

conditions (7) and (11) requires a more careful discussion about the expansion on the basis functions $|\varphi_{n,l}\rangle$. As can be seen from Eq. (15), $\langle r | S_{v,l}^N \rangle$ includes N functions $\langle r | \varphi_{n,l} \rangle$. These are basically polynomials up to order $N + l + 1$, times an exponentially decaying function $e^{-\lambda r}$. Thus, $\langle r | S_{v,l}^N \rangle$ vanishes at large distances: the distance at which the exponential decreasing dominates, depends on the number of basis functions N independent of the behavior of the function, $|S_{v,l}\rangle$, that is being expanded.

When dealing with negative energies, the Sturmian functions $\langle r | S_{v,l} \rangle$ vanish at large distances due to the exponential $e^{-\sqrt{2\mu E}r}$ [31]. Then, when representing $|S_{v,l}\rangle$ in terms of $|\varphi_{n,l}\rangle$, care must be taken of including sufficient basis functions in such a way that $|S_{v,l}\rangle$ is properly represented by the pointwise expansion in its asymptotic region. The exponentially decreasing behavior imposed by the basis, i.e., by N and $e^{-\lambda r}$, must occur at distances from the origin that are larger than the exponentially decreasing behavior observed in the function $|S_{v,l}\rangle$.

For positive energies the situation is different. The boundary condition of Eq. (11) is a bounded $\sin(x)$ function for both to short- and long-range potentials [15]. The Sturmian $|S_{v,l}\rangle$ satisfying the boundary conditions (10) and (11) are not L^2 functions and do not decay exponentially at any distance, even though its expansion $\langle r | S_{v,l}^N \rangle$ does. For those cases where analytic expressions for $|S_{v,l}\rangle$ are available, it is possible to show that in the limit $N \rightarrow \infty$ the expansion in terms of $|\varphi_{n,l}\rangle$ correctly reproduces the whole function up to infinity. This has been done and applied by Broad [23–26] and Yamani and Reinhardt [22] for the case of eigenenergies and eigenvectors of free particles and Coulomb interacting particles. However, for finite N , the expansion will decay as dictated by N and $e^{-\lambda r}$. For short-range potentials the asymptotic region of $\langle r | S_{v,l} \rangle$ is reached when r is beyond of the region of the action of the potential. Passing that r , $\langle r | S_{v,l} \rangle$ will behave as $\sin(x)$ function of constant amplitude. Thus, to have a proper L^2 representation of $|S_{v,l}\rangle$, i.e., $|S_{v,l}^N\rangle$, the size of the basis should be at least sufficiently large to be able to properly represent the function up to the region where $|S_{v,l}\rangle$ has reached its asymptotic limit. When the function $|S_{v,l}\rangle$ is applied to practical calculation, it might be possible to find situations where the description of the function is also needed at values of the coordinate which are far beyond from the region of the action of the potential and where the asymptotic form is already reached. For those cases, N should be large enough to describe $|S_{v,l}\rangle$ correctly up to the required region.

3. Coulomb Potential

The method presented in the preceding section applies to any physical, well-behaved potential. In this section, we restrict ourselves to the Coulomb potential $V(r) = Z/r$. Since we have chosen a basis set that resembles the features of the Coulomb problems, the matrix elements $V_{m,n}^C$ are found to be diagonal:

$$V_{m,n}^C = -Z \left\langle \varphi_{l,m} \left| \frac{1}{r} \right| \varphi_{l,n} \right\rangle = -Z \delta_{m,n} \frac{\Gamma(2l + 2 + n)}{n!}. \tag{21}$$

Numerical evaluation of the roots of $\det(\mathbf{M} - \beta_v \mathbf{V}^C)$ gives a set of eigenvalues β_v , $v = 1, 2, \dots, N$, and the solutions of the eigensystem of Eq. (17) allows us to find the coefficient expansions $a_{n,l}^v$ and the normalization constants $B_{v,l}^N$.

However, analytical results can also be obtained for the Coulomb potential by exploiting the tridiagonal structure of the matrix $\mathbf{M} - \beta_v \mathbf{V}^C$. Using the definition of $V_{m,n}^C$ given by Eq. (21), we can reduce Eq. (16) to a three-term recurrence relation

$$(n + 1)P_{n+1}^{l+1}(\gamma_v, \phi) - 2[\gamma_v \sin \phi + (n + l + 1) \cos \phi]P_n^{l+1}(\gamma_v, \phi) + (n + 2l + 1)P_{n-1}^{l+1}(\gamma_v, \phi) = 0, \tag{22}$$

where we have introduced $P_n^{l+1}(\gamma_v, \phi)$, $\cos \phi$ and γ_v as given by

$$P_n^{l+1}(\gamma_v, \phi) = \frac{\Gamma(2l + 2 + n)}{n!} a_{l,n}^v, \tag{23}$$

$$x = \cos \phi = \frac{E - \frac{\lambda^2}{2\mu}}{E + \frac{\lambda^2}{2\mu}}, \quad \gamma_v = -\frac{\beta_v Z \mu}{\sqrt{2\mu E}}, \tag{24}$$

with $n = 0, 1, \dots, N - 1$. This recurrence relation can be solved in terms of special functions, provided

that $P_{-1}^{l+1} = 0$ and $P_0^{l+1} = 1$ [19–21]. The solution $P_n^{l+1}(\gamma, \phi)$ of the recurrence relation with these initial conditions has the following hypergeometric representation:

$$P_n^{l+1}(\gamma; \phi) = \frac{\Gamma(n + 2l + 2)}{n! \Gamma(2l + 2)} e^{in\phi} \times {}_2F_1[-n, l + 1 - i\gamma, 2l + 2; 1 - e^{-2i\phi}], \tag{25}$$

where ${}_2F_1[0, b, c, z]$ represents the Gauss function [18]. From Eq. (24), we see that $\cos \phi \in [-1, 1]$ if and only if $E \geq 0$. At negative energies, $\cos \phi$ lies outside this interval, and the analytic continuation [18]

$$\cos^{-1} x = \frac{\pi}{2} + i \ln \left[ix + \sqrt{1 - x^2} \right] \tag{26}$$

for the inverse trigonometric function must be used.

The eigenvalues β_v for any energy are determined by requiring

$$P_N^{l+1}(\gamma_v, \phi) = 0. \tag{27}$$

The functions $P_n^{l+1}(\gamma; \phi)$ as defined by Eq. (25) are the Pollaczek polynomials when they are considered as a function of $\cos \phi$, and the charge and the angular momentum are fixed parameters in Eq. (22). However, in our case, we take $P_n^{l+1}(\gamma; \phi)$ as a function of β_v which is included only in second parameters of the Gauss function, and the energy and the angular momentum are fixed parameters. The polynomials that we obtain through the condition of Eq. (27), which we shall call charge polynomials, differ from those studied by Yamani and Reinhardt [22] and Broad [23–25]. The charge polynomials are similar to the Laguerre polynomials and its properties while the properties of the Pollaczek polynomials are similar to the Gegenbauer ones. Figure 1 plots the charge polynomials as a function of the charge for negative [Fig. 1(a)] and positive energies [Fig. 1(b)], and compare its behavior with the Pollaczek polynomials as a

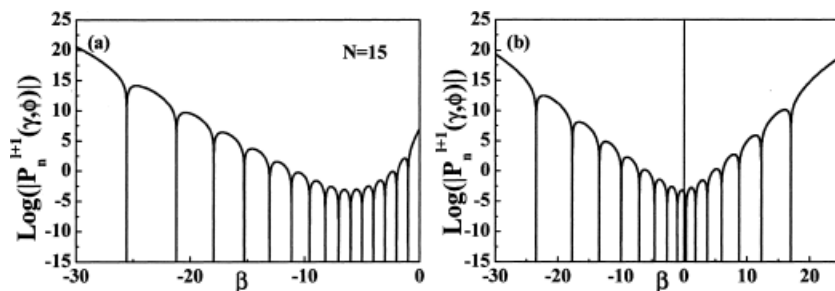


FIGURE 1. Charge polynomials of the Coulomb Sturmian problem for (a) negative, and (b) positive energy.

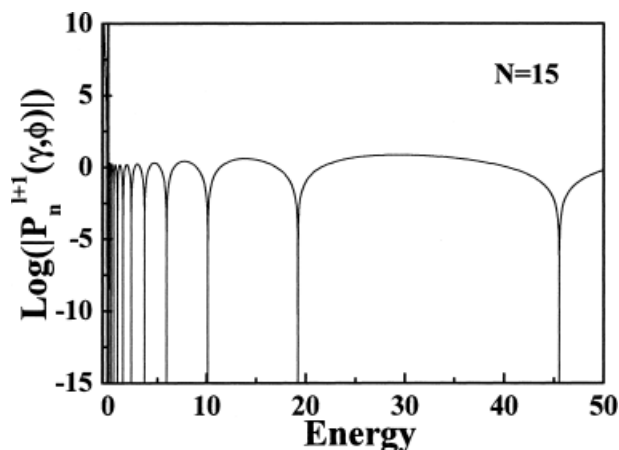


FIGURE 2. Pollaczek polynomials as a function of energy.

function of the energy for fixed charge (see Fig. 2). All the plots are done in logarithmic scale because of the fast growing magnitude of the functions. For negative energy, the charge polynomials cross the β axis for negative values, with $N - 1$ nodes, and grows fast after each node. The same trend is observed for positive energies, but the $N - 1$ nodes can take positive or negative charge values. In contrast, the Pollaczek polynomials grow smoothly with $N - 1$ nodes as a function of the energy, and can take positive as well as negative values.

The normalization constant $B_{v,l}^N$ for the Coulomb potential is obtained replacing the expansion given by Eq. (15) with the coefficients written in terms of the charge polynomials into the orthogonality relation of Eq. (19) for $v = v'$, giving

$$B_{v,l}^N = \sqrt{\frac{\Gamma(N + 2l + 1)2 \sin \phi}{N!}} \times \left[\frac{dP_N^{l+1}}{d\gamma} \Big|_{\gamma=\gamma_v} P_{N-1}^{l+1}(\gamma_v, \phi) \right]^{-1/2}. \quad (28)$$

To obtain this result, we have derived and used the Christoffel–Darboux relation for the coefficients γ_v :

$$\sum_{n=0}^{N-1} \frac{n!}{\Gamma(2l + 2 + n)} P_n^{l+1}(\gamma_v, \phi) P_n^{l+1}(\gamma_{v'}, \phi) = \frac{N!}{\Gamma(2l + 1 + N)} \times \frac{P_N^{l+1}(\gamma_v, \phi) P_{N-1}^{l+1}(\gamma_{v'}, \phi) - P_{N-1}^{l+1}(\gamma_v, \phi) P_N^{l+1}(\gamma_{v'}, \phi)}{2 \sin \phi (\gamma_v - \gamma_{v'})} \quad (29)$$

which is obtained from the recurrence relation, Eq. (22).

Finally, in terms of the charge polynomials of Eq. (25), the expansion for the CSF for negative energies reads

$$|S_{v,l}^N\rangle = B_{v,l}^N \sum_{n=0}^{N-1} \frac{n!}{\Gamma(2l + 2 + n)} P_n^{l+1}(\gamma_v; \phi) |\varphi_{n,l}\rangle, \quad (30)$$

with the normalization $B_{v,l}^N$ given by the expression of Eq. (28).

In the next two sections, we discuss several aspects of the Sturmian functions for the Coulomb potential with $Z = -1$, $\mu = 1$, and restrict ourselves to s states, i.e., $l = 0$. States with nonzero angular momentum have similar properties.

3.1. NEGATIVE ENERGIES CSF

Equation (4) for the Coulomb potential with the boundary conditions of Eqs. (6) and (7) is satisfied for negative energies by the Sturmian function

$$\langle r | S_{v,l} \rangle = S_{n,l}(E, r) = \sqrt{\frac{(n - l - 1)!}{\Gamma(n + l + 1)}} (2kr)^{l+1} e^{-kr} L_{n-l-1}^{2l+1}(2kr), \quad (31)$$

where $k = \sqrt{-2\mu E}$, and the eigenvalues β_n are given by the relation

$$\beta_n = \frac{n\sqrt{-2\mu E}}{Z\mu}, \quad (32)$$

with $n = 1, 2, \dots$. In the finite subspace $\{\varphi_{n,l}\}_{n=0}^{N-1}$, however, we found N eigenvalues for a given negative energy. As we increase the number of basis elements, we recover the discrete spectrum of the exact solution of Eq. (32).

First we study how the discrete spectrum is recovered as N increase, plotting our results for the β_v against the exact law as a function of the energy (Fig. 3). The free parameter was chosen to be $\lambda = 2$, and the number of element basis were $N = 5, 15$ and 25 (for convenience, we show only the first five eigenvalues). As expected, as the number of element basis is increased, the relation between the β_v and the energy tends to the exact law given by Eq. (32), and convergence of the eigenvalues is achieved very rapidly.

The approximate Coulomb Sturmians are plotted for the first four eigenvalues as a function of the

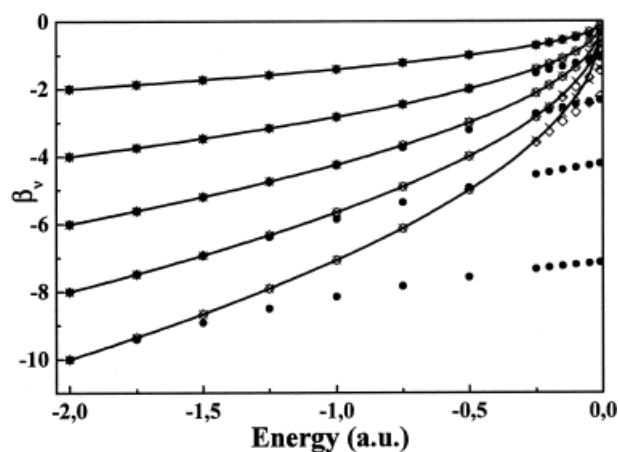


FIGURE 3. Charge eigenvalues of the Coulomb Sturmian problem as a function of the negative energy for different number of element basis with \bullet , $N = 5$; \diamond , $N = 15$; \times , $N = 25$; and unbroken curve, $\beta_v = -n\sqrt{-2E}$.

radius and comparison with the exact CSF of Eq. (31) for a fixed negative energy and a different number of basis elements are shown in Figure 4. We observe for the approximate Sturmian functions the same trend

noticed for the eigenvalues: those which correspond to lower values of n [as in Fig. 4(a) and (b)] need fewer terms to converge to the exact CSF, and as n increases, more element basis are required for the expansion to correctly reproduce the features of the exact CSF at large radius. However, convergence is achieved very rapidly through a range of different negative energies and eigenvalues, with an accuracy of 10^{-5} for $N = 15$, with an appropriate value of the free parameter λ .

Another test that we can perform is the evaluation of the Coulomb Green's function. Its representation in terms of the exact Sturmians functions, given by Eq. (31), is [3,27]:

$$G_l(E, r, r) = \sum_{n=0}^{\infty} \frac{S_{n,l}(E, r)S_{n,l}(E, r)}{1 - n\sqrt{-2\mu E}}.$$

Here we can define $G_l^N(E, r, r)$ which is the representation for $G_l(E, r, r)$ in the N -dimensional subspace generated by the functions $S_{n,l}^N(E, r)$

$$G_l^N(E, r, r) = \sum_{n=0}^N \frac{S_{n,l}^N(E, r)S_{n,l}^N(E, r)}{1 - \beta_n^N}$$

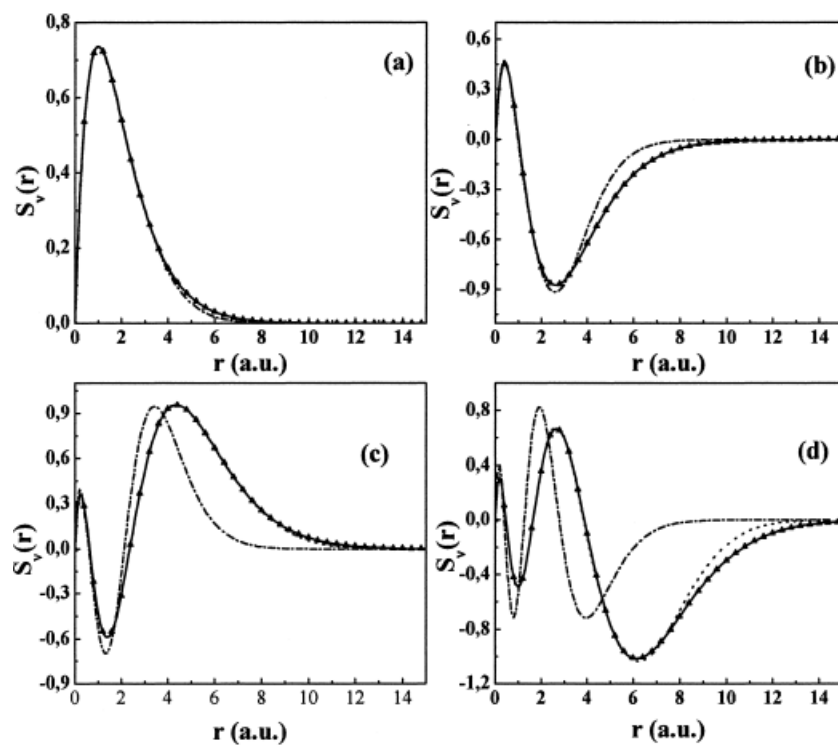


FIGURE 4. CSF as a function of r for negative energies for (a) first, (b) second, (c) third, and (d) fourth charge eigenvalue; dash-dot-dash curve, $N = 5$; dotted curve, $N = 10$; unbroken curve, $N = 15$; and \blacktriangle , exact CSF.

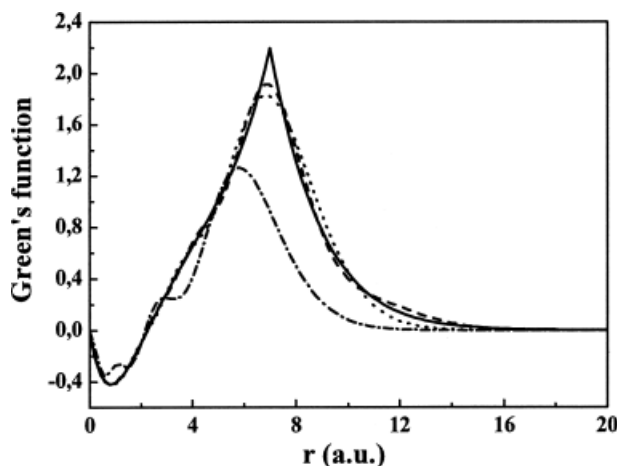


FIGURE 5. Expansion of the Coulomb Green Function for a negative energy for a fixed r' with dash-dot-dash curve, $N = 8$; dotted curve, $N = 10$; dashed $N = 15$; and unbroken curve, exact Coulomb Green function.

In Figure 5 we see how the convergence is achieved increasing N for negative energy and a fixed value of r' .

We also compared convergence of the representation $G_l^N(E, r, r')$ within the subspace with the representation expanded in terms of the exact Sturmian functions. This can be seen in Figure 6, where we plotted the Coulomb Green's function for negative energy and fixed r' . We note that the approximate Green's function G_l^N converges as rapidly as the exact Sturmian expansion for the same number of terms.

3.2. POSITIVE ENERGY CSF

The eigenfunctions $S_{v,l}(r)$ that correspond to positive energies regular at the origin and satisfying the boundary condition given by Eq. (11) at infinity also have an exact solution [14, 15]:

$$S_{v,l}(r) = \frac{|\Gamma(l+1+i\eta)|}{i^{l+1}\sqrt{2\pi}\Gamma(2l+2)} e^{\frac{\pi}{2}\eta} (2i\sqrt{2\mu E})^{l+1} \times e^{-i\sqrt{2\mu E}r} {}_1F_1[l+1+i\eta; 2l+2; 2i\sqrt{2\mu E}r] \quad (33)$$

where $\beta_\eta = \eta\sqrt{-2\mu E}/Z\mu$ is continuous and runs over the whole real axis. The restriction of the expansion to an N -dimensional subspace results in a discretization of the charge continuum, which becomes increasingly dense as the number of basis elements

tends to infinity. The discrete representation of $|S_{v,l}\rangle$ within this subspace is

$$|S_{v,l}^N\rangle = B_{v,l}^N \sum_{n=0}^{N-1} \frac{n!}{\Gamma(2l+2+n)} P_n^{l+1}(\gamma_v; \phi) |\varphi_{n,l}\rangle. \quad (34)$$

The functions $|S_{v,l}^N\rangle$ satisfy the orthogonality and closure relation

$$\begin{aligned} \langle S_{v',l}^N | V | S_{v,l}^N \rangle &= Z B_{v',l}^N B_{v,l}^N \sum_{n=0}^{N-1} \frac{n!}{\Gamma(2l+2+n)} P_n^{l+1}(\gamma_{v'}; \phi) P_n^{l+1}(\gamma_v; \phi) \\ &= \delta_{v',v} \end{aligned} \quad (35)$$

$$\sum_{v=1}^N |S_{v,l}^N\rangle \langle S_{v,l}^N| V = \delta^N(r-r'), \quad (36)$$

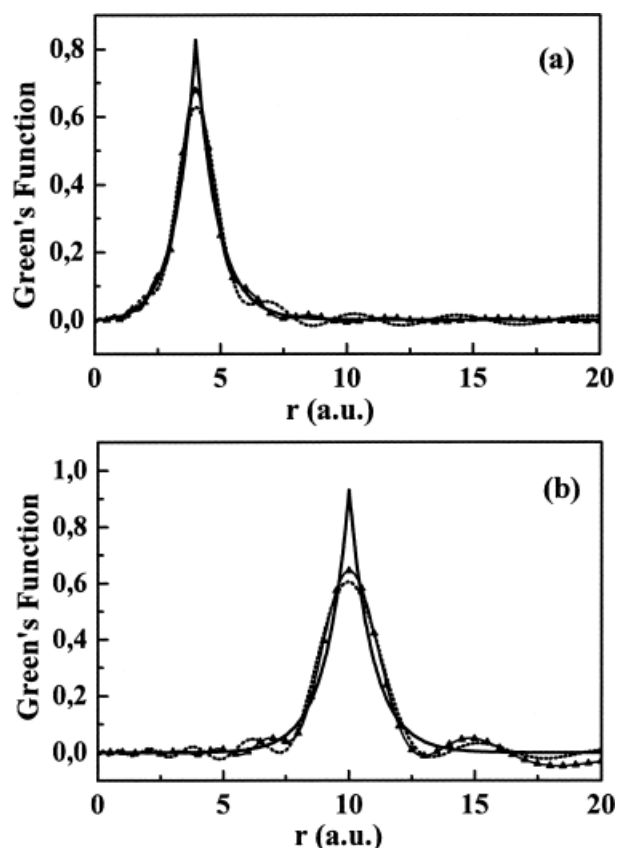


FIGURE 6. Comparison of expansions of the Coulomb Green function for a negative energy: dotted curve, in terms of exact Sturmian functions; —▲— in terms of the approximate Sturmians; unbroken curve, exact Coulomb Green function and (a) $r' = 4$; (b) $r' = 10$.

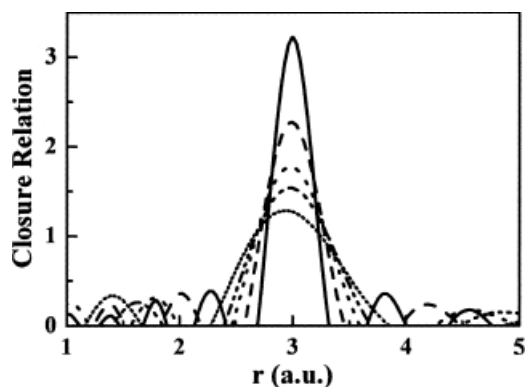


FIGURE 7. Construction of the closure relation of the Coulomb Sturmian set for dotted curve, $N = 15$; dash-dotted curve, $N = 20$; dotted curve, $N = 25$; dashed curve, $N = 40$ and unbroken curve, $N = 80$. The closure relation tends to the Dirac's delta as the basis size increases.

and the normalization $B_{\nu,l}^N$ is given by Eq. (28). Thus, the continuum is replaced by a discrete set of normalizable states that becomes complete as $N \rightarrow \infty$. As the number of element basis increases, the orthogonality relation tends to that defined for the continuum given by Eq. (12), thus, as $N \rightarrow \infty$, $\langle S_{\nu',l}^N | V | S_{\nu,l}^N \rangle \rightarrow \delta(\nu' - \nu)$. A similar result was found by other investigators when the energy was used as eigenvalue instead of the charge [28, 29]. Figure 7 presents the results for the closure relation, and here we can see how the Dirac delta on the coordinate is reproduced and completeness of the subspace is achieved with increasing N . The charge states should resemble the true continuum states as the whole real axis becomes populated when the number of basis elements N increases. Using a discretization of

the continuum energy states through this Laguerre-type basis, Yamani and Reinhardt [22] recognized the zeros of $P_N^{l+1}(\gamma, \phi)$ on the energy as the quadrature abscissas of a Gauss-Pollaczek quadrature representation for the Coulomb Green's function. The role of choice of charge discretization for positive energies in the quadrature generated by the basis deserves further investigation.

The results of the CSF for $E = 1$ a.u. as a function of r are shown in Figure 8. We compare these results with the exact expression of Eq. (33) for $N = 40$. The approximation reproduces the true continuum states until the exponential fall-off dominates.

4. Coulomb Screened Potentials

We can now extend our analysis to the so-called Coulomb screened potential with a Herman and Skillman-type expression [30]:

$$V^{CS}(r) = \frac{Z_1}{r} + \left(Z_2 + \frac{Z_3}{r} \right) e^{-ar}. \quad (37)$$

At large distances, the potential $V^{CS}(r)$ of Eq. (37) behaves as Z_1/r , while at the origin like $(Z_1 + Z_3)/r$. This is the typical behavior showed by the effective potential obtained with the Hartree-Fock equations for many-electron atoms. Potentials like $V(r)$ can be used to represent the electron-nucleus interaction of an active electron on a many-electron atom.

The matrix elements $V_{m,n}^{CS}$ of $V^{CS}(r)$ are much more complex than those corresponding to the Coulomb potential; nevertheless, they can be determined in closed form, giving

$$\begin{aligned} V_{m,n}^{CS} = & -Z_1 \delta_{m,n} \frac{\Gamma(2l+2+n)}{n!} \\ & - \frac{Z_2}{2\lambda} \left[2(n+l+1) \frac{\Gamma(n+m+2l+2)}{n!m!} \frac{\gamma^{2l+2}}{(\gamma+1)^{n+m+2l+2}} {}_2F_1[-m, -n; -n-m-2l-1; 1-\gamma^2] \right. \\ & - (n+1) \frac{\Gamma(n+m+2l+3)}{(n+1)!m!} \frac{\gamma^{2l+2}}{(\gamma+1)^{n+m+2l+3}} {}_2F_1[-m, -n-1; -m-n-2l-2; 1-\gamma^2] \\ & \left. - (n+2l+1) \frac{\Gamma(n+m+2l+1)}{(n-1)!m!} \frac{\gamma^{2l+2}}{(\gamma+1)^{n+m+2l+1}} {}_2F_1[-m, -n+1; -n-m-2l; 1-\gamma^2] \right] \\ & - Z_3 \frac{\Gamma(n+m+2l+2)}{n!m!} \frac{\gamma^{2l+2}}{(\gamma+1)^{n+m+2l+2}} {}_2F_1[-m, -n; -n-m-2l-1; 1-\gamma^2], \end{aligned} \quad (38)$$

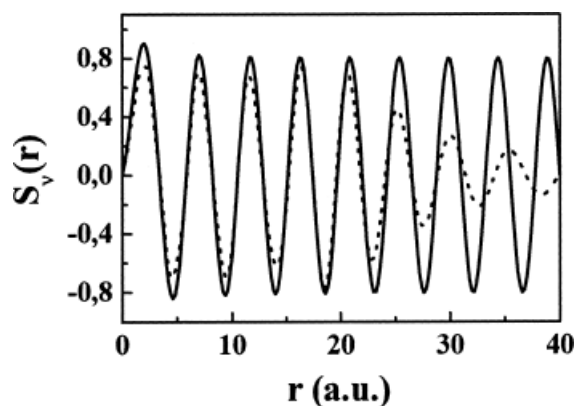


FIGURE 8. CSF as a function of r for positive energy for a given eigenvalue for dotted curve, $N = 40$, and unbroken curve, exact solution.

where we defined $\gamma = 2\lambda/\alpha$. Note that choosing $\lambda = \alpha/2$, all the hypergeometric functions reduces to 1 in the last expression. We noted here that, in addition to the diagonal part of the matrix, the exponential term of the potential gives rise to a full $N \times N$ matrix, which obviously reduces to the preceding results for the Coulomb potential for $Z_2 = Z_3 = 0$. Now, we can numerically evaluate the roots of the determinant to find the N set of eigenvalues β_v and the coefficient expansion $a_{n,l}^v$ as well as the normalization constant $B_{v,l}^N$.

The determinant of the $N \times N$ matrix $\mathbf{M} - \beta_v \mathbf{V}^{CS}$ gives a polynomial of degree N in β . This is analogous to the polynomials obtained for the pure Coulomb potential, in the sense that solving the determinant was equivalent to find the roots of charge polynomials of Eq. (25) of degree N . For the Coulomb screened potential, however, we do not have an analytical expression for the polynomials, and they are obtained by solving the determinant.

4.1. NEGATIVE AND POSITIVE ENERGY STURMIANS FOR HELIUM-LIKE SYSTEMS

Within the frame of the independent electron model, the potential for each electron in a helium-like atom can be expressed approximately by Eq. (37) with charges $Z_1 = Z_3 = -1$, $Z_2 = -2$, and $\alpha = 4$ [30]. We plot the eigenvalues obtained from the roots of $\det(\mathbf{M} - \beta_v \mathbf{V}^{SC})$ as a function of the energy and compare them with the relation given by Eq. (32) for the pure Coulomb potential for negative energies and $l = 0$ in Figure 9. We can see from the figure that the first "charge" eigenvalues follows a law similar to the $\sqrt{-2\mu E}$ corresponding to the pure Coulomb potential with $Z = -2$. In Figure 9, we can also see

the convergence of the eigenvalues as the number of basis elements N increases.

The Sturmian functions for the screened potential are plotted in Figure 10 as a function of the radius for a different number of basis elements, and we compared them with the exact Sturmians, which were found solving equation (4) for the potential (37) numerically. We show the Sturmian functions for the first four eigenvalues, and observe good rate of convergence.

For the positive energy case, the continuum Sturmians are replaced, as in the pure Coulomb potential case, by a set of normalizable states of the form

$$S_{v,l}^N(r) = B_{v,l}^N \sum_{n=0}^{N-1} a_{n,l}^v \varphi_{n,l}(\lambda r), \quad (39)$$

where the $a_{n,l}^v$ are the eigenvectors resulting from Eq. (17) for the Coulomb screened potential. According with Eqs. (19) and (20), the orthogonality and closure relations are given by

$$\langle S_{v',l}^N | V | S_{v,l}^N \rangle = B_{v',l}^N B_{v,l}^N \sum_{n=0}^{N-1} \sum_{m=0}^{N-1} a_{n,l}^v a_{m,l}^{v'} V_{m,n}^{CS} = \delta_{v',v} \quad (40)$$

$$\sum_{v=1}^N |S_{v,l}^N\rangle \langle S_{v,l}^N| V = \delta^N(r - r'), \quad (41)$$

where $B_{v,l}^N$ is the normalization constant, and $V_{m,n}^{CS}$ are the matrix elements given by Eq. (38). It can be verified that as the number of element basis increases, the orthogonality relation tends to that

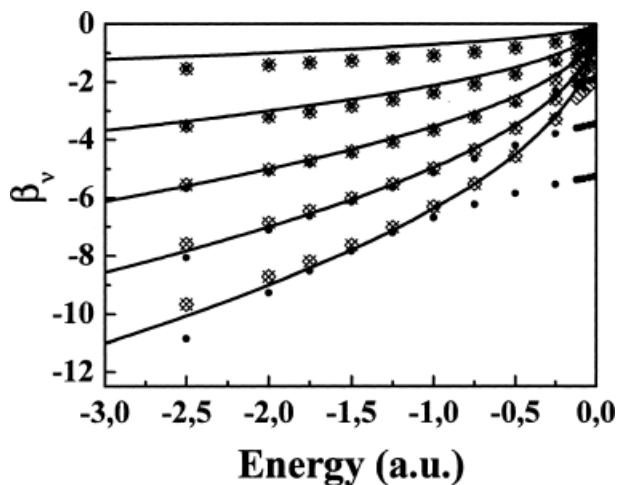


FIGURE 9. Charge eigenvalues of the Coulomb screened Sturmians as function of the negative energy for \bullet , $N = 5$; \diamond , $N = 15$; \times , $N = 25$; and unbroken curve, $\beta_v = -n\sqrt{-2E}/2$.

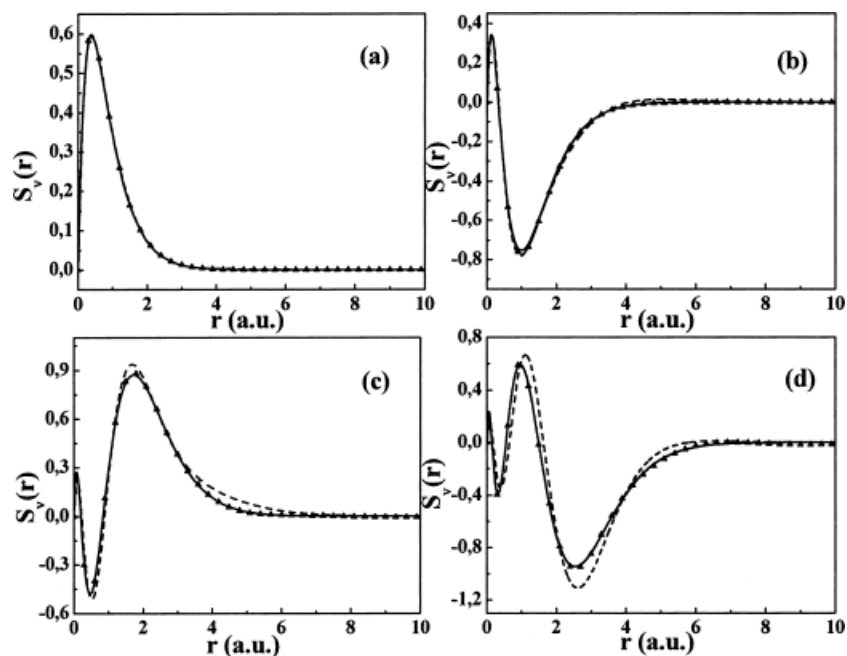


FIGURE 10. Sturmian functions for the Coulomb screened potential as a function of the radius for (a) first, (b) second, (c) third, and (d) fourth eigenvalue and dashed curve, $N = 5$; unbroken curve, $N = 10$; and $-\blacktriangle-$ exact Sturmian for the Coulomb screened potential.

defined for the continuum of Eq. (12), and the same goes for the closure relation.

The Sturmian function defined here can be used to solve the He atom as well as atoms with larger number of electrons but where only two of them are considered as active electrons. Here we consider, as a simple example, the application of the Sturmian functions to solve the Schrödinger eigenequation

$$\left[H_l + \left\{ -\frac{1}{r} - \left(2 + \frac{1}{r} \right) e^{-4r} \right\} \right] |\Psi_i\rangle = E_i |\Psi_i\rangle \quad (42)$$

for the energy eigenvalues. The potential $V^{CS}(r)$ with the parameters as defined in Eq. (42) represents the interaction of an electron with a dressed nucleus of charge 2. We used three different basis sets to expand the energy eigenfunction $|\Psi_i\rangle$: (a) Coulomb energy eigenstates corresponding to charge $Z = -2$, (b) Sturmian functions for the Coulomb potential as in Section 3 and (c) Sturmian functions for the Coulomb screened potential as in Section 4 with $Z_1 = -1$, $Z_2 = -1.9$, $Z_3 = -1$, and $\alpha = 3.9$. The $|\Psi_i\rangle$ were expanded as

$$|\Psi_i\rangle = \sum_{v=0}^{N-1} b_v |\chi_{v,l}^N\rangle \quad (43)$$

where $|\chi_{v,l}^N\rangle$ represents each of the basis sets used. Replacing $|\Psi_i\rangle$ into Eq. (42) and projecting onto the basis, we find the energy states E_i by solving a $N \times N$ matrix eigensystem. We then obtain N energy eigenvalues, which can be either positive or negative, the positive energies represent a discretization of the continuum, and the negative ones are an approximation of the true bound states of the system. The free parameter λ for the Laguerre-type basis was chosen to give the best possible value of the ground state energy. Table I presents the results obtained for the first four negative energy eigenvalues. It is seen how convergence of energy eigenvalues is achieved as the number N of element basis is increased.

We noted that energies calculated with Sturmian basis converge faster than the Coulomb energy eigenstate for the overall range of E_i studied, and few element bases are required to find convergence.

5. Summary and Conclusions

In this work, we present a general procedure that allows us to define Sturmian functions for negative and positive energies for arbitrary, well-behaved, potentials. After a short review of the theory of Sturmian functions in Section 2, we introduce a general

TABLE I
Convergence of He energies for the problem (42) for three different basis sets.

Exact energies	Energy eigenfunctions			Coulomb Sturmians			Coulomb screened Sturmians		
	N = 10	N = 15	N = 20	N = 10	N = 15	N = 20	N = 10	N = 15	N = 20
-0.82090	-0.82070	-0.82070	-0.82070	-0.76396	-0.76393	-0.76393	-0.81065	-0.81998	-0.82083
-0.15308	-0.15306	-0.15306	-0.15306	-0.13169	-0.15209	-0.14951	-0.15289	-0.15306	-0.15307
-0.06331	-0.06059	-0.06326	-0.06330	-0.00171	-0.03152	-0.06379	-0.06433	-0.06317	-0.06331
-0.03442	—	-0.02929	-0.03392	—	—	—	—	-0.00028	-0.03398

methodology to define and obtain Sturmian functions for any given potential in an N -dimensional space generated by the Laguerre-type (L^2) basis set.

We first apply the L^2 -discretization method to the Coulomb potential, finding in this case both numerical and analytical expressions for the expansion coefficients and the normalization constant of the charge Sturmians functions. The recurrence relation obtained for the expansion coefficients is satisfied by what we have called the charge polynomials. The recurrence relation we obtain is identical to that derived by Yamani and Reinhardt [22] and Broad [23–25]. These investigators showed that the recurrence relation can be solved in terms of energy-polynomials (the Pollaczek polynomials), where the roots E_ν of the $P_N^{l+1}(\gamma, \phi_\nu) = 0$ give the eigenvalues of the problem. In our case, we solve the recurrence relation in terms of the charge. The eigenvalues are determined finding the roots β_ν of the $P_N^{l+1}(\gamma_\nu, \phi) = 0$. The differences between these polynomials are shown in Section 3. We also show that completeness is obtained by increasing the basis size. The approximate CSF for both (positive and negative) energies is compared with the exact solutions, showing good convergence for an overall range of energies. It is noted that for negative energies, few basis elements are enough to correctly reproduce the exact CSF, while for positive energies more terms are needed. This is because on discretizing the continuum, completeness of the subspace is reached only by the inclusion of a large (infinite) number of terms, for the eigenvalues obtained must resemble the continuum states.

We apply our method to the so-called Coulomb screened potential of Eq. (37) in Section 4. In this case, it was not possible to reduce the eigenvalue problem of Eq. (17) to a three-terms recurrence relation and a complete numerical solution is presented. A study of the convergence with the size of the basis is performed finding similar trends to that observed on the pure Coulomb potential case.

We show that by taking a finite number of basis functions, we can generate a set of eigenfunctions of Eq. (2), where the magnitude of the potential is the eigenvalue of the problem. We consider two different situations, depending on the value of the (parameter) energy. For negative energy, a set of functions regular at the origin and with exponential decreasing behavior at infinity are considered. The asymptotic behavior of the functions naturally leads to a set of discrete eigenvalues. When the size of the basis tends to infinity, the complete discrete spectrum corresponding to the closed form solution of the problem is recovered. For positive energies, standing-wave boundary conditions at infinity are considered. In this case, an N -dimensional discretization of the continuum spectra corresponding to the potential eigenvalues is obtained. When the size of the basis grows to infinity, the density of states grows equally, leading to the real and complete continuum spectra. The Coulomb and the Coulomb screened Sturmian functions were applied to solve the Schrödinger equation for an active electron in a helium-like atom. The rate of convergence of the energy eigenvalues is compared with that obtained when energy eigenstates are used to solve the problem. The Sturmian functions show a better rate of convergence as mentioned by, e.g., Avery [12].

The basis functions discussed in this report can be used to extend the work of Avery for many-electron atoms [12]. In a recent paper, Szmytkowski [32] showed that the basis used by Avery was not complete to solve the helium problem, and this investigator also showed that the complete basis must include positive energy Sturmians. The introduction of these states implies a continuum charge spectra [32], and then it is not possible to use matrix techniques to solve the many-electron eigenvalue problem as stated by Avery [12]. The discretization of the continuum potential eigenvalue corresponding to positive energies introduced in the present work allows the use of standard matrix techniques on

the solution of the many-electron problem. The use and application of this methodology to the helium eigenvalues will be published soon [33].

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