A General Method to Obtain Sturmian Functions for Continuum and Bound State Problems With Coulomb Interactions

A. L. FRAPICCINI,[1,2] J. M. RANDAZZO,[1,2] G. GASANEO,[3]
F. D. COLAVECCHIA[1,2]

[1]*Division Colisiones Atómicas, Centro Atómico Bariloche, 8400 S. C. de Bariloche, Río Negro, Argentina*
[2]*Consejo Nacional de Investigaciones Cientificas y Técnicas, CONICET, Argentina*
[3]*Departamento de Física, Universidad Nacional del Sur, 8000 Bahía Blanca, Buenos Aires, Argentina*

Received 30 October 2008; accepted 2 December 2008

DOI 10.1002/qua.22029

ABSTRACT: In this article, we investigate discretization schemes to represent Sturmian functions for both positive and negative energies in the presence of a long range Coulomb potential. We explore two methods to obtain Sturmian functions for positive energy. The first one involves the expansion of the radial wave function in a L^2 finite basis set, whereas the second one introduces the discretization of the radial coordinate domain of the Hamiltonian or, alternatively, the Green function. We apply them to find the bound states and scattering phase shift for $\mathcal{N}$-electron atoms close to the critical charge. Both methods are able to describe bound states near threshold, as well as continuum states with very good convergence properties. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 110: 963–974, 2010

Key words: Sturmian function; scattering; phase shift; critical charge

Correspondence to: A. L. Frapiccini; e-mail: afrapic@uns.edu.ar

Contract grant sponsor: ANPCYT (Argentina).
Contract grant numbers: PICTR 2003/0437 and PICT 04/20548.
Contract grant sponsor: Universidad Nacional del Sur (Argentina).
Contract grant number: PGI 24/F038.
Contract grant sponsor: CONICET (Argentina).
Contract grant number: P1P5595.

1. Introduction

In the standard way of studying quantum mechanical problems, the time independent Schrödinger equation is considered as an eigenproblem for the energy and the wave function of the particle. However, from a mathematical point of view, there are other parameters in the equation and some of them can be used as eigenvalues. The solutions of these problems are called Sturmian functions because they are known to be solutions of a Sturm–Liouville equation [1, 2]. They have been widely used as a basis set in atomic physics calculations, e.g., to expand the Coulomb Green function [3] or to determine atomic energy levels [4–6] with excellent accuracy. These functions are defined to be the solutions of the time independent Schrödinger equation for *fixed* energy plus some boundary conditions according to the physical features of the problem to be solved. In addition, in this approach, it is the strength of the potential that acts as the eigenvalue. The main advantage of using these Sturmian functions as a basis set is that they make this interaction potential diagonal, thus providing a rapidly convergent expansion of the solution even in complex atomic problems [7].

To define a Sturm–Liouville problem completely, a two point boundary condition must be given. For example, one can ask for regularity at the origin and the correct asymptotic behavior for large distances according to the energy domain: for negative energies, the solutions should decrease exponentially like bound-states and form a complete, discrete set of square integrable functions. The case of positive energy Sturmians is slightly different, because they might be defined to satisfy outgoing, incoming, or standing wave boundary conditions. The spectrum of eigenvalues thus depends on the choice of the asymptotic behavior of the eigenfunction.

A discrete set of Sturmian eigenvalues and eigenfunctions with purely outgoing wave condition for the two-body Coulomb problem has been used, see e.g. [8]. However, for positive energies these functions became unbounded as the distance r between the particles increases. Rawitscher [9] was able to define a set of Sturmians functions with outgoing wave condition making use of the Coulomb or free particle Green's function. He showed that, even in the case where a long range potential was present, they constitute a discrete basis set with discrete, complex eigenvalues.

Following his approach, we propose here two systematic methods to obtain Sturmian functions for both negative and positive energies. In the first scheme, we expand the solution of the radial part of the Schrödinger equation in a L^2 Laguerre type basis set, whereas in the second one, we discretize the equation in a radial grid.

The outline of this work is as follows. In Section 2, we present a brief review of the Sturm–Liouville problem, where we consider the different types of asymptotic behavior according to the energy domain. In Section 3, we introduce two different methods to find the Sturmian functions whose eigenvalues form a discrete set given any boundary condition, and we plotted some of the results for a modified attractive Coulomb potential with a short range interaction. Finally, in Section 4, we show some applications of both the negative as well as positive energy Sturmians as basis set to solve the $\mathcal{N}$-electron atom with a one-active electron model [10]. We show that this basis set is therefore suitable to construct the wave function of a given bound or scattering problem for both long range Coulomb potentials or short range ones.

Atomic units are used unless otherwise stated.

2. Theory: Review of the Sturm–Liouville Problem

To precisely state our theoretical framework, we start with the two-body time independent Schrödinger equation,

$$\left[-\frac{1}{2\mu}\nabla^2 + V_0 + \beta\overline{V} - E\right]\Phi(\mathbf{r}) = 0. \qquad (1)$$

It is convenient for our purposes to split the interaction in two terms, V_0 and $\beta\overline{V}$. The first term V_0, includes the long range Coulomb tail of the potential. The second one, $\beta\overline{V}$, describes the behavior of the interaction at short distances, and the coefficient β controls the strength of $\overline{V}$. The explicit form of this potential is not relevant.

As usual, $E = k^2/2\mu$ is the energy, k is the relative momentum between the particles, and μ is the reduced mass. Many of the applications in atomic physics involve spherically symmetric potentials, which allows one to solve Eq. (1) by separation of variables. Writing Eq. (1) in spherical coordinates and assuming that the wave function is the product of an angular spherical harmonic Y_l^m "and" a radial part S_l/r, we have

$$\Phi(r,\theta,\phi) = \frac{1}{r} S_l(r) Y_l^m(\theta,\phi), \tag{2}$$

and the following radial equation results for $S_l(r)$:

$$[H_0 + \beta\overline{V} - E]\, S_l(r) = 0. \tag{3}$$

The radial Hamiltonian H_0 is given by

$$H_0 = -\frac{1}{2\mu}\frac{d^2}{dr^2} + \frac{l(l+1)}{2\mu r^2} + V_0, \tag{4}$$

where as usual $l(l+1)$ represents the eigenvalue of the squared angular momentum $\mathbf{L}^2$ [11].

The radial Schrödinger equation (3) is usually considered as an eigenvalue problem where $S_l(r)$ and E (or the momentum k) are defined as the eigenfunction and eigenvalue, respectively. However, we consider here the situation where the coefficient β is assumed to be the eigenvalue and the energy is a fixed parameter in the equation [12]. We can completely define the Sturm–Liouville problem with two boundary conditions for the Eq. (3) that can be written as [13]:

$$\left.\frac{dS_l(r)}{dr}\right|_{r=a} + \alpha_a S_l(a) = 0 \tag{5}$$

$$\left.\frac{dS_l(r)}{dr}\right|_{r=b} + \alpha_b S_l(b) = 0 \tag{6}$$

for the domain $r \in [a,b]$. In our case, r is defined from 0 to ∞, thus we can take $a = 0$ and $b = R$, with $R \longrightarrow \infty$. Our function $S_l(r)$ must be regular at the origin,

$$S_l(r) = 0, \quad r = 0 \tag{7}$$

We require this condition for both negative and positive energies. The boundary condition at large distances depends on the value of the energy. On one hand, for negative energies we ask for

$$S_l(R) \longrightarrow 0, \quad R \longrightarrow \infty. \tag{8}$$

On the other hand, for positive energy we have different choices: standing, outgoing or incoming waves boundary conditions. The standing wave Sturmian function is obtained with

$$S_l(R) = 0 \quad \text{when } R \to \infty. \tag{9}$$

The outgoing (+) and incoming (−) waves can be cast in the form (6) as:

$$\left.\frac{dS_l(r)}{dr}\right|_{r=R} \pm ikS_l(R) = 0, \quad R \longrightarrow \infty \tag{10}$$

for short range potentials, and

$$\left[\frac{dS_l(r)}{dr} \pm i\left(k + \frac{Z}{kr}\right) S_l(r)\right]_{r=R} = 0, \quad R \longrightarrow \infty \tag{11}$$

for Coulomb ones, where we assumed that V_0 goes as Z/r for large distances, and that $\overline{V}$ is a short range potential. Alternatively, one can write these conditions as

$$S_l(R) \longrightarrow H_l^{(\pm)}(R), \quad R \longrightarrow \infty \tag{12}$$

where $H_l^{(\pm)}(r)$ represent the exact solutions of Eq. (3) irregular at the origin and having incoming (−) or outgoing (+) waves.

The solution of Eq. (3) with boundary conditions at $r = 0$ and $r = R$ leads to the discretization of β. For all the cases considered, a finite set of eigenvalues β_ν with $\nu = 1, 2, \ldots$ and eigenfunctions $S_{\nu,l}(r)$ results from the Sturm–Liouville problem for large but finite values of R. The solutions and eigenvalues for negative as well as positive energy with standing-wave boundary condition are real valued. However, complex eigenvalues and eigenfunctions result for positive energy and incoming or outgoing boundary conditions.

For all those cases, the Sturm–Liouville theory establishes that closure property and orthogonality condition

$$\sum_\nu S_{\nu,l}(r')S_{\nu,l}(r)\overline{V}(r) = \delta(r' - r) \tag{13}$$

$$\langle S_{\nu',l}|\overline{V}(r)|S_{\nu,l}\rangle = \int_0^R dr\, S_{\nu',l}(r)\overline{V}(r)S_{\nu,l}(r) = \delta_{\nu',\nu} \tag{14}$$

must be fulfilled by the eigenfunctions.

A formal solution can be obtained for positive energies, which can also be extended to negative energies. The Eq. (3) can be rewritten as follows

$$[E - H_0]S_l(r) = \beta\overline{V}(r)S_l(r). \tag{15}$$

The Green's function associated with the left hand side is defined by the equation

$$[E - H_0]G_0^{(\mathrm{st},\pm)}(r,r') = \delta(r - r') \tag{16}$$

where st represents standing and + (−) are outgoing (incoming) boundary conditions. Multiplying Eq. (15) by left with $G_0^{(\mathrm{st},\pm)}$ and integrating over the domain $r \in [0,\infty]$ we obtain the following integral equation

$$S_l(r) = \beta \int_0^\infty dr' G_0^{(\mathrm{st},\pm)}(r,r')\overline{V}(r')S_l(r'). \tag{17}$$

3. Evaluation of the Sturmian Functions

In this section, we present two different ways to obtain the Sturmian basis for a given short range $\overline{V}$ and asymptotic potential V_0. The first one uses a finite L^2 basis set of N elements and reduces the problem to a $N \times N$ eigensystem. The second method introduces a discretization of either the radial Sturmians equation Eq. (3) or the integral equation Eq. (17).

3.1. L^2 BASIS SET REPRESENTATION

In a previous article [14] we studied the L^2 discretization of Coulomb and Coulomb-like potentials using a Laguerre-*type* basis set with a free, real parameter λ

$$\varphi_{n,l}(\lambda, r) = (2\lambda r)^{l+1} e^{-\lambda r} L_n^{2l+1}(2\lambda r), \tag{18}$$

$L_n^{\alpha}(x)$ is a generalized Laguerre polynomials [15]. This basis set is orthogonal with respect to the weight function $1/r$

$$\left\langle \varphi_{n',l} \left| \frac{1}{r} \right| \varphi_{n,l} \right\rangle = \frac{\Gamma(2l+2+n)}{n!} \delta_{n',n} \tag{19}$$

where Γ is the Gamma function as usual. We expanded the Sturmian function in a finite basis set

$$S_l^N(r) = \sum_{n=0}^{N-1} a_n \varphi_{n,l}(\lambda, r), \tag{20}$$

and replacing this in Eq. (15), we obtained a $N \times N$ matrix system. The boundary conditions satisfied by these Sturmian functions are regularity at origin (7) and asymptotic condition given by Eq. (8) for negative energy. For positive energy, we only ask $S_l(R)$ to be bounded for $R \to \infty$. These conditions do not lead to a discretization of the eigenvalue β and then, positive energy Sturmians have a continuous spectrum that spans over all real values of β. An example of functions satisfying these boundary conditions have been discussed by Szmytkowski [16] and Gasaneo and Colavecchia [17] for the two-body Coulomb problem. The eigenvalues given by solving Eq. (15) with this standing wave condition are real and represent a discretization of the continuum eigenvalues of the exact solution.

Now we want to define other asymptotic conditions for positive energy, such as outgoing or incoming waves. To this end, we introduce the finite Laguerre expansion (20) into Eq. (17), and project onto the basis elements $\langle \varphi_{m,l} | \frac{1}{r}$,

$$a_m \frac{\Gamma(2l+2+m)}{m!} = \beta \sum_{n=0}^{N-1} a_n \int_0^{\infty} \int_0^{\infty} dr dr' \varphi_{m,l}(\lambda, r) \frac{1}{r} G_0^{(st,\pm)}(r, r') \overline{V}(r') \varphi_{n,l}(\lambda, r'). \tag{21}$$

To obtain these matrix elements we open with the Laguerre representation of the Green's function [18]

$$G_0^{(st,\pm)}(r, r') = \sum_{j=0}^{\infty} \sum_{j'=0}^{\infty} \varphi_{j',l}(\lambda, r') g_{j,j'}^{(st,\pm)} \varphi_{j,l}(\lambda, r). \tag{22}$$

As pointed out in the previous section, the Sturmian function S_l has a boundary condition at large distances satisfying Eq. (8), Eq. (10), or Eq. (11) according to the energy domain, which are defined by the asymptotic behavior of the Green's function. In the positive energy case, the matrix elements of the outgoing Green's function were defined in [18] as

$$g_{j,j'}^{\pm} = \frac{-\lambda p_{j_<}^{l}(x;\lambda) q_{j_>}^{\pm l}(E;\lambda)}{(E+\lambda^2/2)(j+1)_{2l+1}(j'+1)_{2l+1}} \tag{23}$$

with $j_<$ and $j_>$ are the lesser and greater of j and j', $x = (E - \lambda^2/2)/(E + \lambda^2/2)$, $(n)_l$ is the Pochhammer symbol and p_j^l and $q_j^{\pm l}$ are Pollaczek polynomials [19].

With the expansion of the Green's function in terms of the basis set, we obtain the matrix system

$$a_m = \beta \sum_{n=0}^{N-1} a_n \left\{ \sum_{j'=0}^{\infty} g_{m,j'} \left[\int_0^{\infty} dr' \varphi_{j',l}(\lambda, r') \overline{V}(r') \varphi_{n,l}(\lambda, r') \right] \right\} \tag{24}$$

The terms inside the brackets define the matrix elements

$$T_{m,n} = \sum_{j'=0}^{\infty} g_{m,j'}^{+} \langle \varphi_{j',l} | \overline{V} | \varphi_{n,l} \rangle \tag{25}$$

and the integral equation in (17) is then transformed into a standard eigenvalues problem

$$\mathbf{T}\overline{a} = \frac{1}{\beta} \overline{a} \tag{26}$$

T is a $N \times N$ matrix, whose eigenvalues are found by solving Eq. (26), and leads to a discrete set of eigenvalues β_ν and eigenfunctions $S^N_{\nu,l}(r)$ with $\nu = 1,2,\ldots,N$. As stated in the previous section, in the case of outgoing or incoming wave condition for the Green's function, the N eigenvalues are complex, and tend to the exact ones as N increases. Having a convergent expression for the Green's function within the Laguerre-type basis set, the problem is thus reduced to find the matrix elements of the potential $\overline{V}$ in this basis and to find the eigenvalues β_ν and the eigenvectors a^ν_n.

The Sturmian functions obtained satisfy orthonormality

$$\langle S'^N_{\nu,l}|\overline{V}|S^N_{\nu,l}\rangle = \delta_{\nu',\nu}, \tag{27}$$

and closure relation

$$\sum_{\nu=1}^{N} S^N_{\nu,l}(r')S^N_{\nu,l}(r)\overline{V}(r) = \delta^N(r'-r) \tag{28}$$

with $\delta^N(r'-r) \longrightarrow \delta(r'-r)$ as the number of elements basis N increases.

3.2. DISCRETIZATION OF THE HAMILTONIAN AND RADIAL INTEGRAL

Here we discuss how to numerically solve the radial Sturmians Eq. (15) or Eq. (17) within the framework of the finite difference method [20]. Application of this method leads to a generalized eigenvalue problem where box boundary conditions $S_l(r=0) = S_l(r=r_{\max}) = 0$ are naturally fulfilled. As we will see later, it can be modified to accommodate arbitrary conditions at $r_{\max}$ of the form (5).

Let us start with a discretization of the wave function $S_{\nu,l}(r)$

$$S_{\nu,l}(r_i) \cong S_i, \quad i = 1,2,\ldots,N \tag{29}$$

in a uniform radial grid $r_i = i \times \Delta r$ (we have suppressed the indexes ν, l for the sake of simplicity). We also assume that the functions $S_{\nu,l}(r)$ are defined up to a given radius $r_{\max} = (N-1)\Delta r$, such that $\overline{V}(r) \cong 0$ for $r \geq r_{\max}$. The second order derivative in Eq. (15) can be approximated up to $O(\Delta r^2)$ on the grid by

$$\frac{d^2S_{\nu,l}(r)}{dr^2} \cong \frac{1}{\Delta r^2}[S_{i+1} - 2S_i + S_{i-1}]. \tag{30}$$

Then, Eq. (15) is

$$-\frac{1}{2\mu}\frac{1}{\Delta r^2}S_{i+1} - \frac{1}{2\mu}\frac{1}{\Delta r^2}S_{i-1} + h_iS_i = -\beta_\nu\overline{V}(r_i)S_i \tag{31}$$

where

$$h_i = \frac{1}{\mu}\frac{1}{\Delta r^2} + \frac{l(l+1)}{2\mu r_i^2} + \frac{Z}{r_i} - \frac{k^2}{2}, \quad i = 1,\ldots,N \tag{32}$$

As we are solving the eigenvalue problem only within the box of radius $r_{\max}$, this recurrence relation takes the matrix form:

$$\begin{pmatrix} h_1 & -\frac{1}{2\mu}\frac{1}{\Delta r^2} & \cdots & 0 \\ -\frac{1}{2\mu}\frac{1}{\Delta r^2} & h_2 & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ 0 & \cdots & -\frac{1}{2\mu}\frac{1}{\Delta r^2} & h_N \end{pmatrix}\begin{pmatrix} S_1 \\ S_2 \\ \vdots \\ S_N \end{pmatrix} = -\beta_\nu \begin{pmatrix} \overline{V}(r_1) & 0 & \cdots & 0 \\ 0 & \overline{V}(r_2) & 0 & \vdots \\ 0 & \cdots & \ddots & \cdots \\ 0 & 0 & \cdots & \overline{V}(r_N) \end{pmatrix}\begin{pmatrix} S_1 \\ S_2 \\ \vdots \\ S_N \end{pmatrix}. \tag{33}$$

Note that the three term recurrence relation is truncated at the borders. As a consequence, the solutions of the generalized eigenvalue problem of Eq. (33) exactly satisfy the condition $S_0 = 0$; that is, the right behavior at the origin. Besides, the system includes implicitly the condition $S_{N+1} = 0$, which describes only the standing wave condition at the exterior border of the grid. Let us assume that the behavior at the border of the grid is given by an arbitrary, non- zero function $F_{\text{as}}(r)$ [Eq. (11), for example]. Then, we have to include the relation

$$\frac{S_{N+1}}{S_N} = \frac{F_{\text{as}}(N\Delta r)}{F_{\text{as}}((N-1)\Delta r)} \tag{34}$$

to set exactly the right boundary condition at $r = r_{\max}$, which can be written as:

$$S_{N+1} = S_N \times \frac{F_{\text{as}}(N\Delta r)}{F_{\text{as}}((N-1)\Delta r)}. \tag{35}$$

Then, the contribution from the exterior boundary condition in the recurrence relation can be introduced through the substitution

$$h_N \longrightarrow h_N - \frac{1}{2\mu}\frac{1}{\Delta r^2}\left[\frac{F_{\text{as}}(N\Delta r)}{F_{\text{as}}((N-1)\Delta r)}\right]. \tag{36}$$

Eq. (11) can be exactly satisfied at $r_{\max}$ if we set $F_{\text{as}}(r) = H^{(\pm)}(r)$. For bound states, we can use box boundary conditions, or their asymptotic form

$$F_{\text{as}}(r) = e^{-\sqrt{2\mu|E|}r + \frac{Z}{\sqrt{2\mu|E|}}\ln\left(2\sqrt{2\mu|E|}r\right)}. \tag{37}$$

which is valid for Coulomb ($Z \neq 0$) as well as for short range potentials ($Z = 0$).

Once the proper matrix elements in the boundary are included, we solve the generalized eigenvalue problem and obtain the spectrum of the resulting functions, which is discrete and complex in case of outgoing or incoming waves.

The disadvantage of finding solutions through Eq. (17) is that the evaluation of the kernel of the integral involves multiple evaluations of the Coulomb Green's function. However, it is instructive to solve it to compare with the matrix method discussed earlier. The discretized form of Eq. (17) is:

$$S_i = \beta \sum_{j=1}^{N} \Delta r G_0^{\mathrm{st},\pm}(i\Delta r, j\Delta r)\overline{V}(j\Delta r) S_j \qquad (38)$$

Multiplying each side of Eq. (38) by $(\overline{V}(i\Delta r))^{-1/2}$ we have

$$y_i = \beta \Delta r \sum_{j=1}^{N} \overline{V}(i\Delta r)^{1/2} G_0^{(\mathrm{st},\pm)}(i\Delta r, j\Delta r)\overline{V}(j\Delta r)^{1/2} y_j \qquad (39)$$

were we have made the substitution $\overline{V}(i\Delta r)^{1/2} S_i \to y_i$, such that the matrix of the discretized integral equation becomes symmetric. Then we have to solve the eigenvalue problem:

$$\mathbf{M}\mathbf{y} = \lambda \mathbf{y} \qquad (40)$$

where $\lambda = 1/\beta$ and

$$[\mathbf{M}]_{i,j} = \Delta r \overline{V}(i\Delta r)^{1/2} G_0^{(\mathrm{st},\pm)}(i\Delta r, j\Delta r)\overline{V}(j\Delta r)^{1/2}. \qquad (41)$$

As stated before, the Green's function imposes the correct outgoing (incoming) boundary conditions to the solution, so the set $S_i = (\overline{V}(i\Delta r)^{1/2})^{-1/2} y_i$ resulting from the system (39) are the functions we were looking for.

3.3. COMPARISON OF NUMERICAL METHODS

We show here some numerical results of the calculation of Sturmian functions with the three different methods of the preceding paragraphs. Different boundary conditions can be chosen for positive energy states. First, we show some results for the standing wave Sturmians. In the frame of the L^2 Laguerre expansion, the eigenvalues obtained by solving Eq. (15) represent a discretization of the continuum real axis. In Figure 1 we show the first eigenvalue obtained by setting $V_0 = -1/r$, $l = 0$, and a Yukawa short range potential $\overline{V} = e^{-\alpha r}/r$ with $\alpha = 0.01$, for a fixed free parameter λ, varying the number of basis elements N. The eigenvalue does not seem to converge to a specific value, but it merely represents a discretization of the continuum, which becomes more dense as the number of basis elements increases.

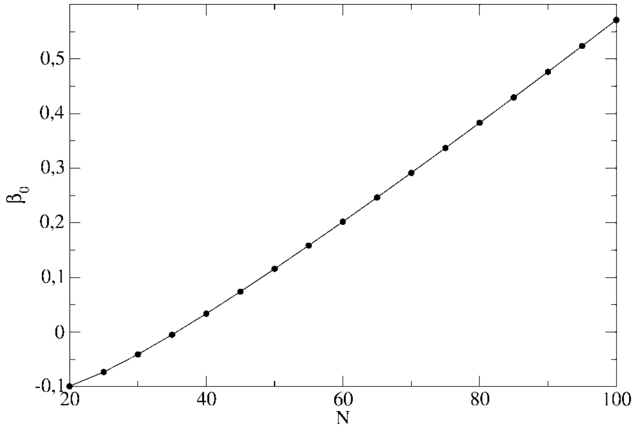

FIGURE 1. First eigenvalue of the Laguerre expansion for the Sturmians with standing wave condition as a function of the size of the basis set. We set $E = 2$, $V_0 = -1/r$, $l = 0$ and the short range potential was chosen to be the $\overline{V} = e^{-0.01r}/r$.

Within the radial discretization method proposed in the previous section, the boundary condition (9) can be solved exactly. In Figure 2, we show an example of the convergence of the numerical (box-based) positive energy Sturmians. We make use of the same potential as before, and took $r_{\max} = 30$, as the boundary of the radial grid.

For outgoing wave boundary condition, we analyze the convergence of the methods with their intrinsic parameters: the scale factor λ in the Laguerre scheme or the box radius $r_{\max}$ in the Hamiltonian discretization method. We chose a short range potential of an exponential type $\overline{V} = -e^{-\alpha r}$, which has exact solution for $l = 0$.

In Figure 3, we see that the Laguerre expansion exhibits a rather independent behavior of the λ value for the range considered: both real and imaginary part oscillate around the exact value, and the amplitude diminishes as the number of basis elements increases.

In Figure 4, we see a different behavior than in the previous case for the Hamiltonian discretization: here the solution approaches to the exact value

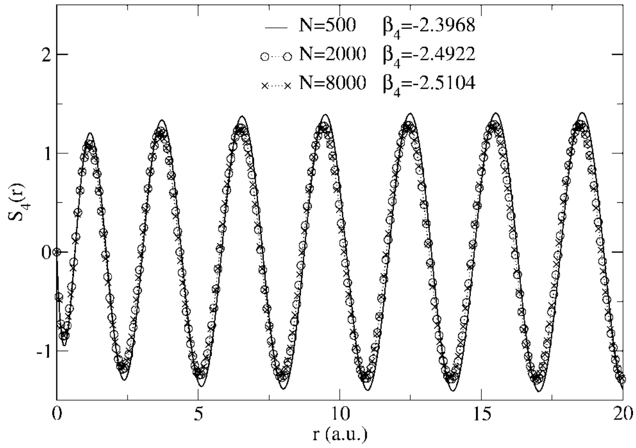

FIGURE 2. Sturmian function of order four (increasing in the absolute value of the eigenvalue) versus the radial coordinate, for various sizes of the discretized Hamiltonian matrix. Here we set $E = 2$, $V_0 = -1/r$, $r_{\max} = 30$(a.u.), $l = 0$ and $\overline{V} = e^{-0.01r}/r$. The functions where normalized to unity at $r = 3.4$.

oscillating and decreasing in amplitude as the $r_{\max}$ increases. Note that, if a "bad" cut radius is chosen, the eigenvalue will not be corrected by increasing the size of the grid (diminish dx). In contrast, in Figure 3, we see that the Laguerre eigenvalues, even with a small number of element basis, only give an error in the second significant decimal digit. The eigenvalues found by the Green's integral discretization as in Eq. (38) show the same trend as the Hamiltonian discretization and are not shown here. Similar results were obtained for different smooth potentials. Also, we note that high order eigenvalues show the same behavior, although they converge with different percentage relative error to the exact values.

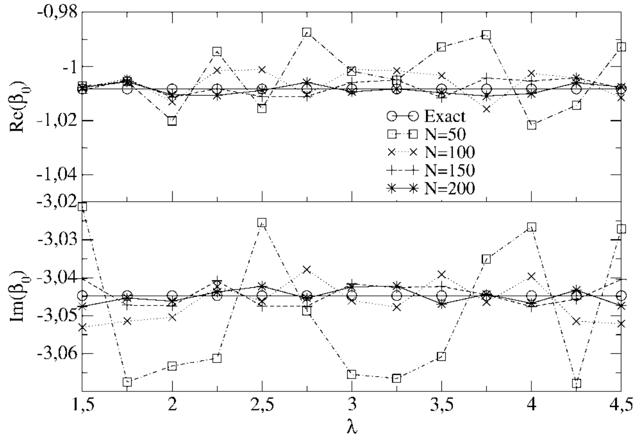

FIGURE 3. Convergence of the first eigenvalue of an exponential potential with $\alpha = 1$ for the Laguerre expansion. Top: real part and bottom: imaginary part. The energy is $E = 1.7$ a.u.

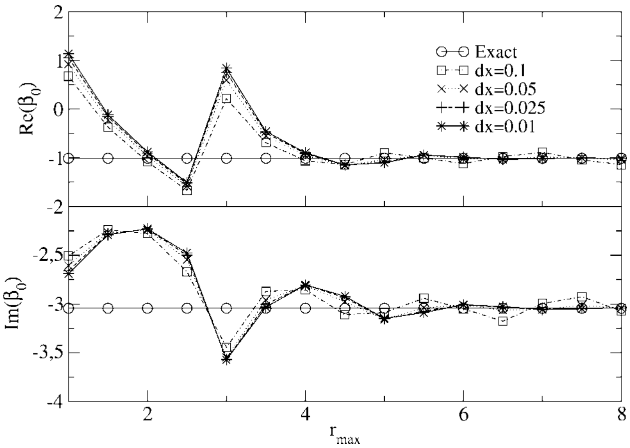

FIGURE 4. Same as Figure 3 for the Hamiltonian radial discretization.

For completeness, we show calculations for the eigenfunctions of $V_0 = -1/r$ and a short range Yukawa potential $\overline{V} = -e^{-\alpha r}/r$ with $\alpha = 1$ in Figure 5. Both eigenvalues and eigenfunctions converge with the three different methods. However, the eigenvalues for each method do not converge in the same way, as seen before, and also the Coulomb potential somehow adds a background noise. In Figure 6, we show the Sturmian functions for a Coulomb box potential (defined as a Coulomb potential up to a radius $r = r_0$ and zero for $r > r_0$) taking $V_0 = 0$, and see that convergence is achieved more rapidly than in the previous case. Further studies on this matter will be addressed in a future work.

4. Application: $\mathcal{N}$-Electron Atoms with a Model Potential

4.1. BOUND STATES AND CRITICAL NUCLEAR CHARGE

In the precedent section, we have shown that either the Laguerre expansion or the Hamiltonian discretization can describe the solutions of a variety of two-body potentials. Hence, they are suitable to expand any solution of a Schrödinger equation for a given system. Let us consider the radial wave equation for an atomic bound state described with a

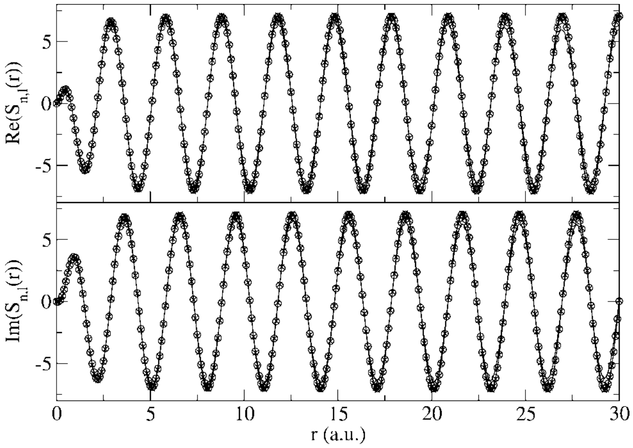

FIGURE 5. Top: real part and bottom: imaginary part of the Sturmian function for the Yukawa potential with $\alpha = 1$, $l = 1$, and $E = 2.1$ a.u. for the first eigenvalue. Solid line: Laguerre expansion with $N = 100$ and $\beta_1 = 2.571 - \imath 4.870$; circle: Green function discretization with $r_{\max} = 10$ a.u. and $\beta_1 = 2.571 - \imath 4.871$; cross: Hamiltonian discretization with $r_{\max} = 10$ a.u. and $\beta_1 = 2.570 - \imath 4.878$. Both discretization schemes give the same functions for all practical purposes.

potential of the form $V_0 + V$

$$[H_0 + V]f_{n,l}(r) = E_{n,l}f_{n,l}(r), \tag{42}$$

where H_0 is given by Eq. (4) and V contains the short range part of the total potential. We can expand the solution using the negative energy Sturmian basis set with the same H_0 as in Eq. (42) and a short range potential $\overline{V}$ of the same range as V. We have

$$f^M_{n,l}(r) = N_{n,l}\sum_{\nu=1}^{M} b_{\nu,l}\widetilde{S}_{\nu,l}(r) \tag{43}$$

with $N_{n,l}$ some normalization constant and $\widetilde{S}_{\nu,l}$ the Sturmian found with either one of the methods described before. Replacing this on Eq. (42) an projecting again onto the basis set we obtain the equation

$$\sum_{\nu=1}^{M} b_{\nu,l}[EO_{\nu',\nu} + M_{\nu',\nu}] = E_{n,l}\sum_{\nu=1}^{M} b_{\nu,l}O_{\nu',\nu}, \tag{44}$$

where we have defined the overlap matrix $O_{\nu',\nu} = \langle \widetilde{S}_{\nu',l}|\widetilde{S}_{\nu,l}\rangle$, and $M_{\nu',\nu} = -\beta_{\nu,l}\langle \widetilde{S}_{\nu',l}|\overline{V}|\widetilde{S}_{\nu,l}\rangle + \langle \widetilde{S}_{\nu',l}|V|\widetilde{S}_{\nu,l}\rangle$. To find the energy eigenvalues, we search for the energy of the basis set such that $\det(\mathbf{M}) = 0$, and therefore $E_{n,l} = E$.

We consider now a potential that describes a $\mathcal{N}$-electron system in the one electron model as [10]

$$V_{\mathrm{mod}}(r) = -\frac{1}{r} + \frac{\gamma}{r}(1 - e^{-\delta r}) \tag{45}$$

with $\gamma = (\mathcal{N} - 1)/Z$, and Z the nuclear charge. This effective potential must tend to $-Z/r$ at small distances and to $(-Z + \mathcal{N} - 1)/r$ as r increases. After the scaling transformation $r = Zr'$, the potential tends to $-1/r$ at small r and $(-1 + (\mathcal{N} - 1)/Z)/r$ for large r, giving the correct limiting behavior for an effective potential of an $\mathcal{N}$-electron atom. In a previous work [21], we analyzed Eq. (45) solving the Sturmian equation [Eq. (15) or Eq. (17)] taking $\gamma = \beta$, $V_0 = -1/r$ and $\overline{V} = \frac{1}{r}(1 - e^{-\delta r})$.

In the methods presented earlier, one can take the potentials V_0 and V freely, depending on the problem under scrutiny. For this system, it is convenient to choose the potentials as $V_0 = (\gamma - 1)/r$ and $V = -\gamma e^{-\delta r}/r$ to construct the Sturmian basis set. In this way, V_0 contains all the long range (Coulomb) interactions. Then, we solve the wave equation (44) in the Sturmian basis. This means that now both the Sturmian basis set and the bound state function $f^M_{n,l}$ will have the correct asymptotic behavior.

As a first test, we mapped the He and Li-isoelectronic series by determining the parameter δ such that for $\gamma = (\mathcal{N} - 1)/Z$, the scaled ionization energy $E = -Ip/Z^2$ is an eigenvalue of (42). The results are shown in Table I. These values can be

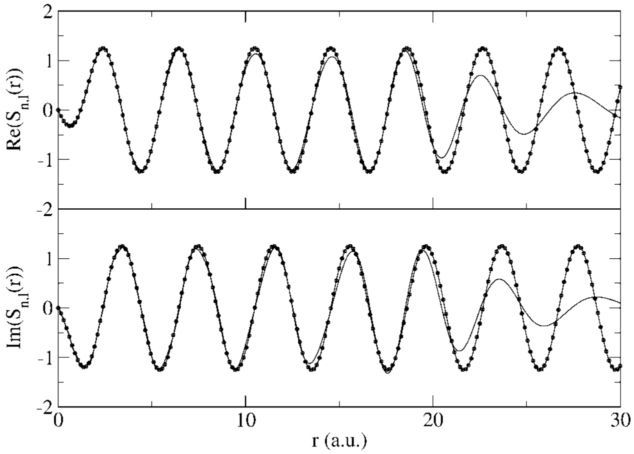

FIGURE 6. Idem 5 for the Coulomb box potential with $l = 0$ and $E = 1.2$ (a. u.) for the first eigenvalue. Laguerre: $N = 40$ and $\beta_1 = -0.295 - \imath 0.778$, Green discretization: $r_{\max} = 2.0$ a.u. and $\beta_1 = -0.292 - \imath 0.775$, Hamiltonian discretization: $r_{\max} = 2.0$ a.u. and $\beta_1 = -0.292 - \imath 0.775$.

TABLE I
Value of the parameter δ in (45) for the He and Li-isoelectronic series.

Z	1	2	3	4	5	6	7
δ_{He}	0.9091	1.0662	1.1307	1.1637	1.1837	1.1973	1.2068
δ_{Li}	—	—	0.7015	0.7459	0.7724	0.7895	0.8027

obtained with either the Laguerre expansion or the radial discretization with the same potentials V_0 and $\overline{V}$ for the Sturmians, setting adequate values for λ and $r_{\max}$ for each method. We choose tho achieve four significant figures $N = 40$ for the Laguerre expansion and $dx = 3.3 \times 10^{-4}$ a.u. in the numerical grid method.

Then, we can extrapolate γ such that for $E = 0$, $\gamma_c = (N-1)/Z_c$ to obtain the critical charge Z_c. The corresponding δ value is obtained by linear extrapolation from the neutral atom and the negative ion of the series. In Figure 7 we plot the energy as a function of γ. It is clear from this figure that the energy is a nonlinear function of the charge in the vicinity of $E = 0$. We obtained a critical charge $Z_c = 0.92$ for the He and $Z_c = 2.07$ for the Li, in good agreement with other authors [10].

We explore the bound state waves as a function of the nuclear charge, for $Z \to Z_c$ in Figure 8. It is clear how the function becomes unbounded as it gets closer to the critical charge, and they slowly change their character to continuum functions, spreading out to large distances.

4.2. STURMIAN FUNCTION OF THE SCATTERING PROBLEM

Let us consider now the radial Schrödinger equation for a potential of the form $V_0 + V$, Eq. (42) for a scattering problem

$$[H_0 - E]f(r) = -Vf(r) \tag{46}$$

where H_0 is given again by Eq. (4) and V is a short range potential whose effect is to change the scattering solution of

$$[H_0 - E]f_0(r) = 0 \tag{47}$$

by adding a function which is regular at the origin and purely outgoing at large distances [9]. If the solution of Eq. (47) is known, then the additional function can be expanded in the outgoing Sturmian functions for an auxiliary potential $\overline{V}$ with range similar to that defined by V. We expand

$$f_M(r) = f_0(r) + \sum_{\nu=1}^{M} b_{\nu,l}\widetilde{S}_{\nu,l}(r). \tag{48}$$

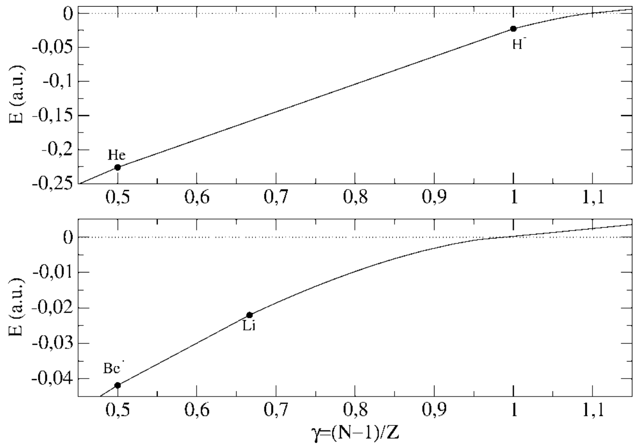

FIGURE 7. Energy as a function of $\gamma = (N-1)/Z$ for the He (top) and Li (bottom) isoelectronic series.

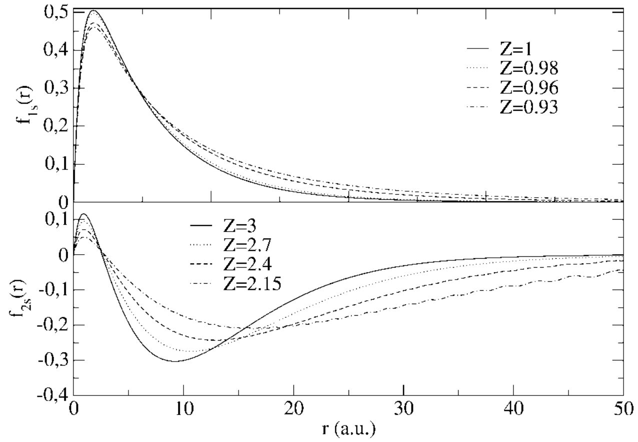

FIGURE 8. Bound state functions for the He (top) and Li (bottom) isoelectronic series for different charges.

Introducing this expression into Eq. (46) and projecting onto $\langle \widetilde{S}_{\nu',l}|$ gives

$$\sum_{\nu=1}^{M} b_{\nu,l}(\beta_\nu \delta_{\nu,\nu'} - \langle \widetilde{S}_{\nu',l}|V|\widetilde{S}_{\nu,l}\rangle) = \langle \widetilde{S}_{\nu',l}|V|f_0\rangle, \qquad (49)$$

using the normalization (27). Solving Eq. (49) for the coefficients b_ν, we find an expression for the scattering function $f_M(r)$ corresponding to the potential $V_0 + V$.

The asymptotic form of the regular solution f_0 is

$$f_0(r) \longrightarrow \sin(kr - l\pi/2 - Z/k\ln(2kr) + \sigma_l), \qquad (50)$$

where σ_l is the Coulomb phase shift. The Sturmian basis set in which we expand the scattering term is solution of the *same* Hamiltonian H_0. As the auxiliary potential $\overline{V}$ is a short range potential, the general asymptotic form of the outgoing Sturmian basis set is

$$\widetilde{S}_{\nu,l}(r) \longrightarrow \alpha_{\nu,l}H_l^+(r) \longrightarrow \alpha_{\nu,l}e^{i(kr - l\pi/2 - Z/k\ln(2kr)+\sigma_l)}, \qquad (51)$$

see Eq. (11). Inserting the asymptotic forms from Eq. (50) and Eq. (51) in Eq. (48), we obtain an expression for f_M at large distances

$$f_M \longrightarrow e^{i\Delta_l}[F_l(r)\cos\Delta_l + G_l(r)\sin\Delta_l]. \qquad (52)$$

Here Δ_l is a phase shift due to the short range distorting potential V in Eq. (46), and $F_l(r)$ and $G_l(r)$ are the regular and irregular Coulomb wave functions. The value of the phase shift Δ_l could be obtained directly using explicitly the asymptotic form (51), but the calculation of the parameters $\alpha_{\nu,l}$ showed some numerical instabilities. Instead, if $r = r_c$ is the point where the potential V goes to zero, then the phase shift Δ_l can be obtained from the numerical values of f_M and its derivative: defining $\rho = f'_M(r = r_c)/f_M(r = rc)$

$$\Delta_l = \tan^{-1}\left(\frac{\rho F_l(r_c) - F'_l(r_c)}{G'_l(r_c) - \rho G_l(r_c)}\right). \qquad (53)$$

We can split the terms in the potential (45) according to its range (V_0 containing long range part of V_{mod}) as

$$V_0 = \frac{(\gamma - 1)}{r} \qquad V = -\frac{\gamma}{r}e^{-\delta r} \qquad (54)$$

Choosing the Sturmian basis set to be solution of V_0 with an auxiliary Yukawa potential $\overline{V}$, we solve the matrix system (49) to find the coefficients b_ν and to obtain the scattering function f_M and the phase shift Δ_l.

In Figure 9, we plot the results obtained for the potential V_{mod} corresponding to a He atom with $\gamma = 0.5$ and δ given in Table I. We used two of the three different method explained in the previous section to calculate the Sturmian basis set. The results are compared with numerical solution of Eq. (46). The Green's integral discretization has been left apart because it gives the same results as the Hamiltonian discretization, but the program to solve the eigensystem takes longer. The function was renormalized to behave as a sine for large distances.

Our results give a very good representation of the scattering function summing very few Sturmians (for example, we used $N = 160$ basis set elements in the Laguerre basis set but we sum up to $N = 80$ to achieve convergence in the phase shift). The two methods converge to the exact solution up to $r = 80$ a. u.. There, the Laguerre solution fails both in phase and amplitude to give the exact solution, while the discretization methods do not accurately describe the phase of the wave. This is due to the representation of the asymptotic region in the methods: the Laguerre basis gives the correct solution until the exponential fall off dominates, while the discretization gives the exact solution of the Schrödinger equation for $r < r_{\max}$.

In Table II we show the values for the phase shift Δ_l for $E = 0.7$ a. u. and angular momentum $l = 0, 1, 2, 3$, compared against the exact value. There Δ_l^{Lag} is the phase shift calculated using the Laguerre expansion of the Sturmian basis set and Δ_l^H is the one

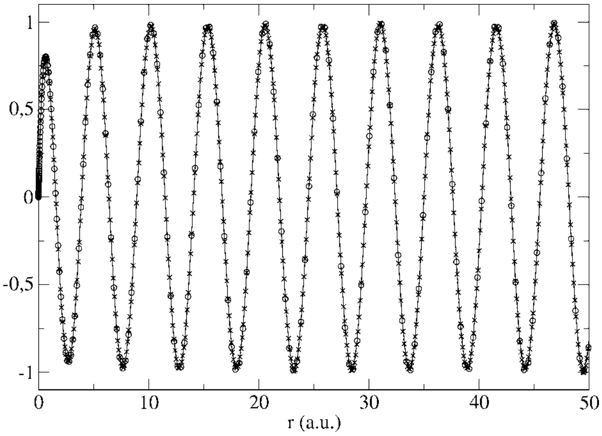

FIGURE 9. Scattering function for the potential (45) for $E = 0.7$ a.u., $l = 0$ and solid line: numerical solution, cross: Laguerre expansion, and circle: Hamiltonian discretization.

TABLE II

Phase shift Δ_l for $E = 0.7$ a. u. and angular momentum $l = 0, 1, 2, 3$ with the different methods to calculate the Sturmian basis set: Δ_l^{Lag} is the phase shift calculated using the Laguerre expansion and Δ_l^{H} the one obtained with the discretization method.

	$l = 0$	$l = 1$	$l = 2$	$l = 3$
Δ_l^{Lag}	0.4788805	0.1523833	0.0507797	0.0180913
Δ_l^{H}	0.4788805	0.1523838	0.0507805	0.0180920
Δ_l^{ex}	0.4788809	0.1523838	0.0507805	0.0180920

The exact value Δ_l^{ex} was found by solving the Schrödinger equation (46) numerically.

computed with the Hamiltonian discretization. To obtain the best result with each method, the Sturmian basis set used to solve Eq. (49) was different according to the method: for example, for the Laguerre expansion we set $\alpha = 1$ for the short range Yukawa potential (close to the δ of the potential to solve) and a parameter $\lambda = 2.1$. For the radial discretization, the exponential of the Yukawa was $\alpha = 0.6$ and the box radius was $r_{\max} = 10$ a.u. This shows that, although we can reproduce similar results with each method, they do not discretize the space in the same way.

To continue the analysis on the critical charge, we calculated the s phase shift as a function of the energy as the charge approaches to the critical charge. We see in Figure 10 that it goes to π as the charge and energy decreases for the Helium model. This is due to a zero energy resonance at the critical charge, according to Levinson's theorem [22]. For the Lithium, it seems that the phase shift goes to π as the charge goes to the critical value, but the zero energy resonance appears to be at a charge value beyond the critical one. This is an indication of the different features of these systems, modeled with an effective one electron potential, and are directly related to the different behavior of the one-electron ionization cross section as a function of the critical charge for Helium or Lithium [23].

5. Concluding Remarks

In this article, we present different schemes to obtain Sturmian functions for both negative as well as positive energies. One method is based on the expansion of the Sturmian functions in Laguerre polynomials, whereas the other one involves the discretization of the radial coordinate in a uniform grid. Both methods are able to accurately describe wave functions containing long range Coulomb potentials. Moreover, the methods can accommodate different boundary conditions for the scattering regime: we consider the possibility of any asymptotic behavior, such as stationary, outgoing, or incoming wave boundary conditions at large but finite distances.

The schemes presented here show excellent agreement with exact wave functions. Furthermore, both methods are robust as our study of both procedures in terms of their parameters shows: results do not depend on the λ coefficient of Laguerre polynomials or the maximum value of the radial grid in the numerical discretization. Moreover, these parameters can be used freely to improve the calculations. The Sturmian functions for positive energy and outgoing wave condition were obtained for a Coulomb potential plus a short range, Yukawa potential, showing convergence for the eigenfunction and eigenvalues in the three different ways of calculation, in terms of the number of Laguerre polynomials, or the size of the radial grid.

A more stringent test of the procedures is the calculation of critical charges and wave functions in the energy threshold. The positive energy, outgoing Sturmian functions were used as a basis set to obtain the scattering function for a Hellmann [24] potential for a given $\mathcal{N}$-electron atom with nuclear charge Z. We also were able to calculate the phase shift Δ_l due to the short range potential in Eq. (46). The method shows a very good convergence, given that few terms are needed in the sum in Eq. (48) and the accuracy of the phase shift obtained is very good compared to other numerical results. This means

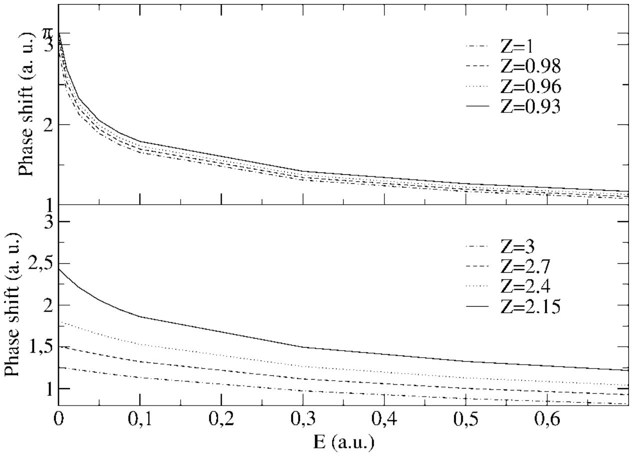

FIGURE 10. Phase shift for s-waves of the potential (45) as a function of the energy for the He (top) and Li (bottom) isoelectronic series for different charges.

that, although a large basis set is required for the scattering function to be accurate at large *r* values, we do not need to sum up all the basis elements to achieve a convergent result. Both methods have the ability to describe continuum close to the threshold, and also bound states that are spanned up to large radial distances.

We finally would like to point out that both methods rely on the separation of the interaction in two terms. This feature provides greater flexibility, since for the same problem, different separation of the potential can be used according to the specific characteristics of the physical problem one is interested to analyze.

In summary, all methods presented here are suitable to perform calculations in a wide variety of two-body problems. Work is in progress now to use them as a basis set to expand three-body continuum functions, such as those needed to describe double photoionization or electron-impact single ionization of atoms and molecules.

ACKNOWLEDGMENTS

The authors would like to thanks Dr. D. Mitnik for helpful discussions.

References

1. Rotenberg, M. Ann Phys NY 1962, 19, 262.
2. Khristenko, S. V. Teor Mat Fiz 22, 31 (Engl Transl Theor Math Phys 22, 21) (1975).
3. Maquet, A.; Veniard, V.; Marian, T. A. J Phys B 1998, 31, 3743.
4. Holøien, E. Phys Rev 1956, 104, 1301.
5. Shull, H.; Löwdin, P. O. J Chem Phys 1959, 30, 617.
6. Avery, J. Hyperspherical Harmonics and Generalized Sturmians; Kluwer: Dordrecht, 2000.
7. Ovchinnikov, S. Yu.; Macek, J. H. Phys Rev A 1997, 55, 3605.
8. Potvliege, R. M.; Shakeshaft, R. J Phys B 1988, 21, L645.
9. Rawitscher, G. Phys Rev C 1982, 25, 2196.
10. Sergeev, A. V.; Kais, S. I. J Quant Chem 1999, 75, 533.
11. Landau, L. D.; Lifshitz, E. M. Quantum Mechanics: Non-Relativistic Theory; Pergamon Press: New York, 1965.
12. Goscinski, O. Preliminary Research Report No. 217; Advances in Quantum Chemistry; Quantum Chemistry Group, Uppsala University, 1968.
13. Ince, E. L. Ordinary Differential Equations; Dover: New York, 1956; p 102ff.
14. Frapiccini, A. L.; Gonzalez, V. Y.; Randazzo, J. M.; Colavecchia, F. D.; Gasaneo, G. I. J Quant Chem 2007, 107, 832.
15. Abramowitz, M.; Stegun, I. A. Handbook of Mathematical Functions; Dover: New York, 1970.
16. Szmytkowski, R. J Phys A 1998, 31, 4963.
17. Gasaneo, G.; Colavecchia, F. D. J Phys A 2003, 36, 8443.
18. Broad, J. T. Phys Rev A 1985, 31, 1494.
19. Yamani, H. A.; Fishman, L. J Math Phys 1975, 16, 410.
20. Byron, F. W.; Fuller, R. W. Mathematics of Classical and Quantum Physics; Dover: New York, 1970.
21. Frapiccini, A. L.; Gasaneo, G.; Colavecchia, F. D.; Mitnik, D. J Elect Spect Rel Phen 2007, 161, 199.
22. Bransden, B. H. Atomic Collision Theory; Benjamin: New York, 1970.
23. Ladadwa, D.; Kais, S. I. J Quant Chem 2000, 80, 575.
24. Hellmann, H. J Chem Phys 1935, 3, 61.