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Sturmian functions in a L^2 basis: Critical nuclear charge for *N*-electron atoms

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Abstract

Two particle Sturmian functions [M. Rotenberg, Ann. Phys., NY 19 (1962) 262; S.V. Khristenko, Theor. Math. Fiz. 22 (1975) 31 (Engl. Transl. Theor. Math. Phys. 22, 21)] for a short range potentials are obtained by expanding the solution of the Schrödinger equation in a finite L^2Laguerre-*type* basis. These functions are chosen to satisfy certain boundary conditions, such as regularity at the origin and the correct asymptotic behavior according to the energy domain: exponential decay for negative energy and outgoing (incoming or standing wave) for positive energy. The set of eigenvalues obtained is discrete for both positive and negative energies. This Sturmian basis is used to solve the Schrödinger equation for a one-particle model potential [A.V. Sergeev, S. Kais, J. Quant. Chem. 75 (1999) 533] to describe the motion of a loosely bound electron in a multielectron atom. Values of the two parameters of the potential are computed to represent the Helium isoelectronic series and the critical nuclear charge Z_c is found, in good agreement with previous calculations.

Keywords: Sturmian functions; Critical nuclear charge; *N*-electron atoms

1. Introduction

The Sturmian functions [1,2] for a two-body system are of particular interest in atomic physics. These functions are solutions of the two-body Schrödinger equation for some physical potential, where the energy is fixed and the strength of the potential is the eigenvalue. Besides, they satisfy a set of boundary conditions of the physical problem to be solved. Negative energy Sturmians that decay exponentially at large distances make a discrete basis for negative energies, and have been widely used in atomic physics to determine atomic energy levels [4–6], or to expand the Coulomb Green function (see [7] and references therein).

Meanwhile, at positive energies, Sturmian functions might be defined to satisfy outgoing, incoming or standing wave boundary conditions. The spectrum of eigenvalues thus depend on the choice of the asymptotic behavior of the eigenfunction. Ovchinnikov and Macek [8] obtained a discrete set of eigenvalues for purely outgoing wave Sturmians, however this functions became unbounded as r increased. Rawitscher [9] was able to define a set of Sturmians with outgoing wave condition even in the case where a long range potential was present, showing that they constitute a discrete basis set with discrete eigenvalues.

Following this approach, we propose a systematic method to obtain Sturmian functions for both negative and positive energies, expanding the solution of the radial part of the Schrödinger equation in a L^2 Laguerre-*type* basis set. The use of the Green's function ensures the asymptotic behavior in the entire energy domain. This basis set is therefore suitable for constructing the wave function of a given scattering problem for both long range Coulomb potentials or short range potentials.

In Section 1 of this paper we present a brief review of the Sturmian theory and an analysis of the different asymptotic behavior according to the energy domain. In Section 2 we outline the general method to expand the two-particle Sturmian functions in terms of Laguerre-*type* basis, and obtain orthogonality and closure relations restricted to a finite subspace. Numerical results for a Coulomb well potential are shown for both negative and positive energies. In Section 3 we use the

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negative energy Sturmian theory to study the bound states of a potential proposed by Kais and Sergeev [3], which represents the one active electron model for an N-electron atom. We also find the value of the critical charge, that is, the minimum charge necessary to bind the electrons, for the He-isoelectronic series. Finally, in Section 4 we present the summary of our work, draw some conclusions and suggest some applications. Atomic units are used unless otherwise stated.

2. Theory of Sturmian functions

The Sturmian functions for a two-particle system interacting through a general short range potential $V(\bar{r})$ satisfy the equation [9]

$$\left[-\frac{1}{2\mu}\nabla_r^2 + V_0 - E\right]\Phi(\bar{r}) = -\beta_\nu V(\bar{r})\Phi(\bar{r}) \tag{1}$$

subject to appropriate physical boundary conditions. The first term in the left hand side of Eq. (1) represents the kinetic energy of the system, V_0 is either a long range potential (such as a Coulomb potential) or zero (free particle), E the energy, considered a fixed parameter and β_ν, the strength of the potential, is the eigenvalue to determine. For a spherically symmetric potential, separation of variables can be performed, which leads to the radial Schrödinger equation

$$[H_0 - E]y_l^\nu(r) = -\beta_\nu V(r)y_l^\nu(r) \tag{2}$$

where the H_0 is given by

$$H_0 = -\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2\mu r^2} + V_0 \tag{3}$$

To complete the formulation of this Sturm–Liouville problem, it is necessary to add two boundary conditions, which will be defined according to the energy domain.

The first boundary condition requires that the Sturmians functions should be regular at the origin for both negative and positive energies,

$$y_l^\nu(r) = 0, \quad \text{when } r = 0. \tag{4}$$

The second boundary condition defines the asymptotic behavior of the functions, depending on the energy E of the system. At negative energies, Sturmians must behave as bound states and decrease exponentially,

$$y_l^\nu(R) \to 0, \quad \text{for } R \to \infty. \tag{5}$$

Besides, there are different choices for positive energies: outgoing, incoming or standing wave asymptotic condition. The first two options can be summarized by writing the boundary condition as

$$y_l^\nu(R) = H_l^\pm(R), \quad \text{for } R \to \infty, \tag{6}$$

where $H_l^\pm$ is the usual outgoing (incoming) Coulomb or free wave function depending on the form of V_0. The separation of the entire potential in long (V_0) and short (V) range effects has the advantage of including the correct asymptotic behavior in the resulting function. The standing wave Sturmian is

$$y_l^\nu(R) = 0, \quad \text{when } R \to \infty. \tag{7}$$

For large but finite values of R, Eq. (2) together with boundary conditions at $r = 0$ and R, define a Sturm–Liouville problem which leads to a discrete set of eigenvalues β_ν and eigenfunctions y_l^ν with $\nu = 1, 2, \ldots$ For negative energy and positive energy standing wave Sturmians, the spectrum of eigenvalues is real, while for outgoing or incoming positive energy Sturmians the spectrum is complex. Thus, these Sturmian functions define a complete discrete basis with orthogonality and closure properties

$$\langle y_l^{\nu'}|V|y_l^\nu\rangle = \int_0^\infty \mathrm{d}r\, y_l^{\nu'}(r)V(r)y_l^\nu(r) = \delta_{\nu',\nu} \tag{8}$$

$$\sum_\nu y_l^\nu(r')V(r)y_l^\nu(r) = \delta(r' - r) \tag{9}$$

Using the definition of the Green's function

$$[E - H_0]G_0(r, r') = \delta(r' - r), \tag{10}$$

Eq. (2) is transformed into an integral equation of the form

$$y_l^\nu = \beta_\nu G_0 V y_l^\nu \tag{11}$$

The use of the Green's functions ensures the correct asymptotic behavior of the resulting Sturmian function y_l^ν, provided that the long range effects of the Coulomb potentials are included in G_0.

3. Sturmians in a L^2 Laguerre-*type* basis set

To solve the integral equation defined in Eq. (11), we consider a finite, Laguerre-*type* basis set with a free, real parameter λ

$$\varphi_{n,l}(r) = \mathrm{e}^{-\lambda r}(2\lambda r)^{l+1}L_n^{2l+1}(2\lambda r), \tag{12}$$

where L_n^α are the generalized Laguerre polynomials [10]. We expand the Sturmian function, solution of Eq. (2) as

$$|y_l^\nu\rangle = A_{l,\nu}\sum_{n=0}^\infty a_{n,l}^\nu|\varphi_{n,l}\rangle. \tag{13}$$

The Laguerre basis is orthogonal with weight function $w(r) = 1/r$:

$$\left\langle \varphi_{m,l}\left|\frac{1}{r}\right|\varphi_{n,l}\right\rangle = \delta_{m,n}\frac{\Gamma(2l+2+n)}{n!}. \tag{14}$$

We replace the Laguerre representation of $|y_l^\nu\rangle$ in Eq. (11) and project onto $\langle y_l^{\nu'}|1/r$, to obtain a set of equations given by

$$a_{m,l}^\nu = \beta_\nu\sum_{n=0}^{N-1} a_{n,l}^\nu T_{m,n} \tag{15}$$

where the matrix elements $(\mathbf{T})_{m,n} = T_{m,n}$ are

$$T_{m,n} = \frac{m!}{\Gamma(2l+2+m)}\left\langle \varphi_{m,l}\left|\frac{1}{r}G_0V\right|\varphi_{n,l}\right\rangle \tag{16}$$

Furthermore, Eq. (15) can be simplified using the expansion of the Green's function in the Laguerre basis

$$G_0 = \sum_{j,j'=0}^{\infty} |\varphi_{j',l}\rangle g_{j,j'} \langle\varphi_{j,l}|. \tag{17}$$

The asymptotic behavior of G_0 is now included in the matrix elements $g_{j,j'}$. For positive energies the outgoing Green's function is given by [11]

$$g^{+}_{j,j'} = \frac{-\lambda p^{l}_{j_<}(E;\lambda) q^{+l}_{j_>}(E;\lambda)}{(E+\lambda^2/2)(j+1)_{2l+1}(j'+1)_{2l+1}} \tag{18}$$

where $j_<$ and $j_>$ are the lesser and greater of (j, j'), $(n)_l$ the Pochhammer symbol and p^l_j and q^{+l}_j are the regular and irregular Pollaczek polynomials [11]. The extension of the Green's function G^+_0 to negative energies gives the correct asymptotic behavior for this energy domain. Using expression (17) in (15) the elements $T_{m,n}$ can be written as

$$T_{m,n} = \sum_{j=0}^{\infty} g_{j,m} \langle\varphi_{j,l}|V|\varphi_{n,l}\rangle. \tag{19}$$

The matrix $\mathbf{T}$ of size $N \times N$, has complex elements in the outgoing, positive energy case and real for negative energies.

For example, we calculate the Sturmian functions corresponding to a Coulomb well auxiliary potential

$$V(r) = \begin{cases} -\dfrac{1}{r}, & \text{if } r < \rho \\ 0, & \text{if } r > \rho \end{cases} \tag{20}$$

and a Coulomb potential $V_0 = -1/r$. We use this potential to test our method, since this problem has a well-known analytical solution. We solve the Schrödinger Eq. (2) for each region defined by the range of V. We match both solutions at $r = \rho$, with appropriate boundary conditions for the inner (regular at the origin) and outer (exponential decay for negative energy and outgoing wave for positive energy) regions.

First we compare the eigenvalues obtained numerically with the exact ones for a negative energy in Table 1 and positive energy in Table 2, and study its convergence as the number N of element basis increases. We use $\lambda = 2.1$ in all the calculations.

At negative energies we see fast convergence of the first six eigenvalues, which are real and positive; and convergence is uniform for increasing N. For positive energies, the requirement of outgoing wave asymptotic condition gives complex eigenvalues,

Table 1
First six eigenvalues for the model potential (20) compared to the exact ones for $E = -1.1$ a.u., $\rho = 20$ and $l = 0$

$N = 10$	$N = 20$	$N = 50$	Exact β_v
0.483	0.483	0.483	0.483
1.967	1.967	1.967	1.967
3.477	3.476	3.476	3.476
5.156	5.152	5.151	5.151
7.236	7.217	7.216	7.215
9.834	9.775	9.772	9.770

Table 2
Absolute value of the first six eigenvalues for the Coulomb well potential with $E = 1.1$ a.u., $\rho = 20$ and $l = 0$

$N = 80$	$N = 100$	$N = 120$	Exact $\lvert\beta_v\rvert$
0.907	0.889	0.876	0.882
0.970	0.964	0.953	0.946
1.607	1.586	1.577	1.594
1.640	1.645	1.639	1.624
2.661	2.670	2.665	2.647
2.805	2.779	2.774	2.798

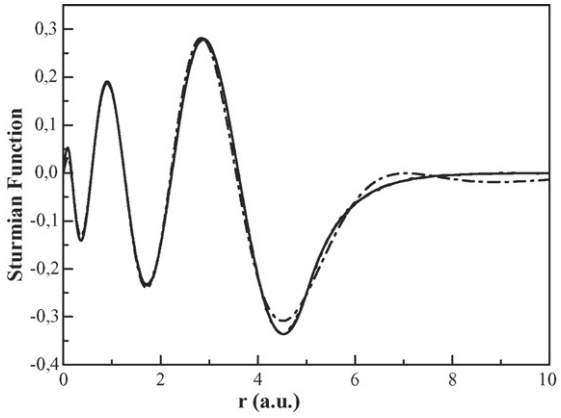

Fig. 1. Sturmian function for the Coulomb well potential with $\rho = 5$ and $E = -1.1$ a.u. for $\beta_v = 9.770$. The full line is the exact solution and the dashed-dotted line the Sturmian for $N = 10$.

with negative imaginary part, and the absolute value is given in Table 2. Convergence is achieved increasing the number of element basis, and it does not appear to be a uniform rule as in the negative energy case. The Sturmian functions for a given eigenvalue are shown in Fig. 1 (negative energy) and Fig. 2 (positive energy), where in both cases we observe good convergence as N increases.

4. One electron model

In this section we study the Sturmian functions for a one active electron model potential of the form [3]

$$V(r) = -\frac{1}{r} + \frac{\gamma}{r}(1 - \mathrm{e}^{-\delta r}) \tag{21}$$

in the negative energy range. This potential is used to approximate the interaction between a loosely bound electron and the atomic core in a multielectron atom. For a N-electron atom with nuclear charge Z, this effective potential must tend to $-Z/r$ at small distances and to $(-Z + N - 1)/r$ as r increases. After the scaling transformation $r = Zr'$, the potential tends to $-1/r$ at small r and $(-1 + (N-1)/Z)/r$ for large r. Then, defining the free parameter γ in Eq. (21) as $\gamma = (N-1)/Z$, gives the correct limiting behavior of the effective potential.

If we split the potential in Eq. (21) as $V_0 = -1/r$ and $V = (1 - \mathrm{e}^{-\delta r})/r$, we will see that the free parameter γ can be considered as the eigenvalue of the problem as in Eq. (2). Thus now we fix a negative energy and study the behavior of the "charge" $\gamma = \beta_v$. As a first step we study the eigenvalues as

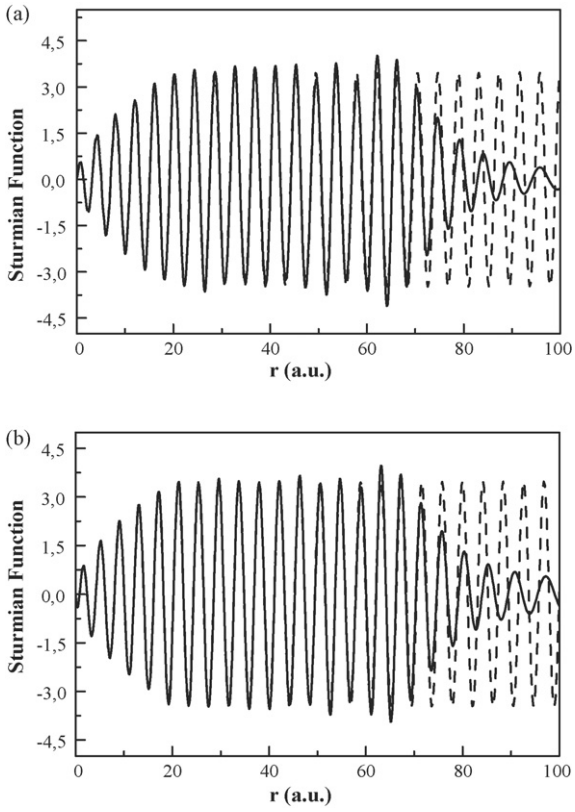

Fig. 2. Real (a) and Imaginary part (b) of the Sturmian function for the Coulomb well potential with $\rho = 20$ and $E = 1.1$ a.u. for $\beta_\nu = 0.270744 - i0.838841$. The full line is the solution for $N = 120$ and the dashed line is the exact Sturmian.

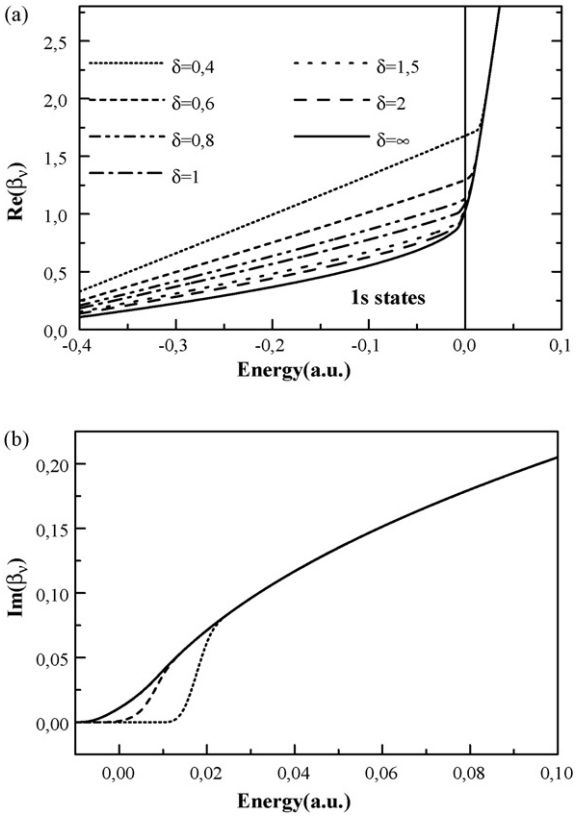

Fig. 3. (a) Real part and (b) imaginary part of the eigenvalues for potential of Eq. (21) as a function of the energy for different values of δ for 1s states.

a function of the energy for different parameters δ. To this end, we define a critical screening parameter δ_c, such that the largest bound-state energy level is exactly zero. It has been determined that $\delta_c = 1.1906$ for 1s states and $\delta_c = 0.2202$ for 2p states [12].

The results for 1s and 2p charge states are shown in Figs. 3 and 4. In the energy region where $\beta_\nu \approx 1$, $V(r)$ behaves like a pure Yukawa potential. Then, the eigenvalues $\beta_\nu(E)$ depend strongly on the value of δ. If $\delta < \delta_c$, then we may find another bound state for $\beta_\nu > 1$. However, if $\delta > \delta_c$ when $\beta_\nu \approx 1$, the potential can not support another negative energy state. In this case, the eigenvalue tends to the Coulomb form $\beta_\nu = 1 - n\sqrt{-2E}$, as δ increases, where n here stands for the energy level quantum number. Meanwhile, we can see that for the positive energies, the charges become complex with positive imaginary part, meaning that the effective potential is now a complex and emitting one.

The model potential (21) may be used to map any isoelectronic series for an N-electron atom, since when $\gamma = \beta_\nu = (N-1)/Z$, the eigenvalue represents the scaled charge of an atomic system. The free parameter δ is then fixed such that for the corresponding scaled ionization energy of the outer electron, the scaled charge of this atom is an eigenvalue. In Fig. 5 we show the parameter δ as a function of the scaled ionization energy [13,14] for the *He*-isoelectronic series in its ground state. The numerical results for the series were fitted with a function obtained by the study of the eigenvalues as a function of the energy and the

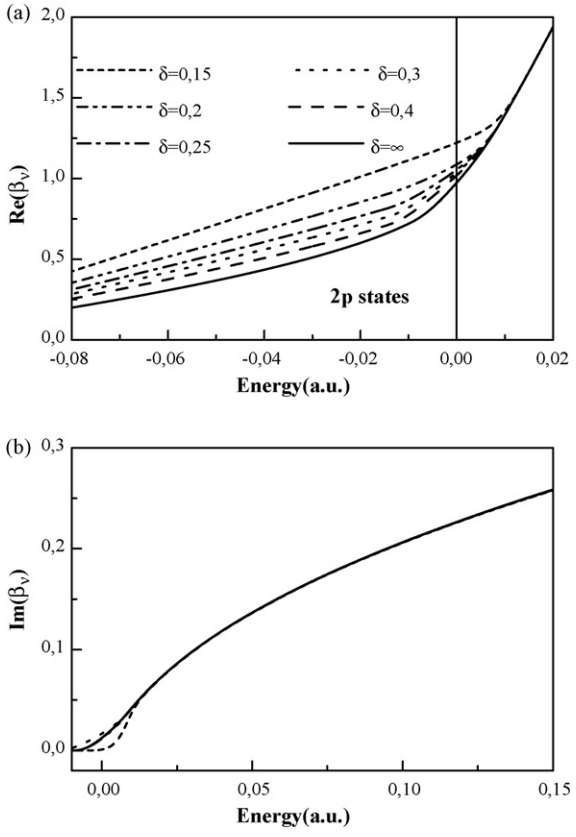

Fig. 4. (a) Real part and (b) imaginary part of the eigenvalues for potential of Eq. (21) as a function of the energy for different values of δ for 2p states.

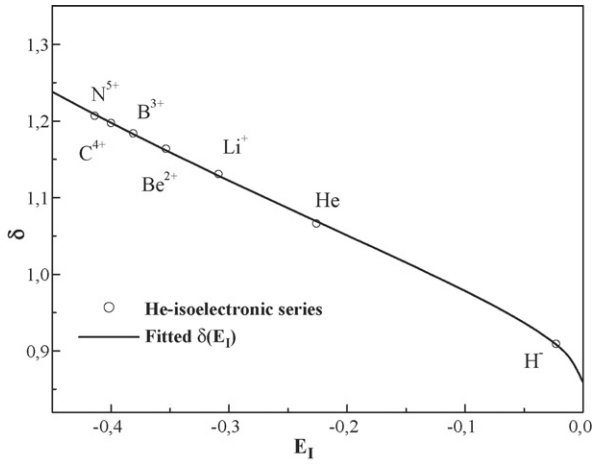

Fig. 5. Free parameter δ as a function of the ionization energy for the *He*-isoelectronic series from [13,14].

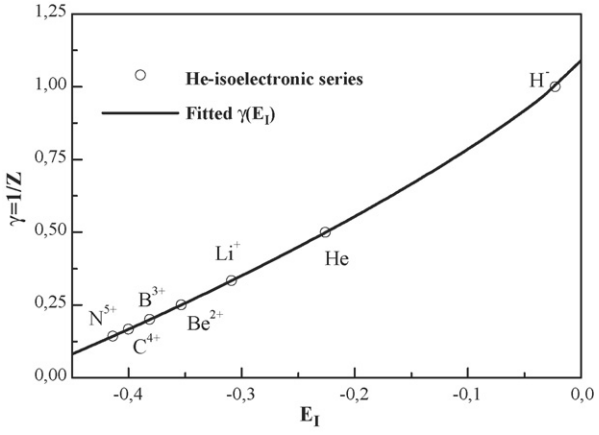

Fig. 6. Charge eigenvalue as a function of the ionization energy for the *He*-isoelectronic series.

parameter δ. The plot shows a strong non-linearity in the vicinity of $E_I = 0$, where the system passes to the continuum.

Using $\delta(E)$ to map the series, we can extrapolate the value of the critical charge Z_c, the minimum charge necessary to bind the electrons. According to this one electron scaled model, the critical charges are found from $\gamma_c = (N-1)/Z_c$, the extrapolated eigenvalue for which $E_I = 0$. Fig. 6 shows the plot of the eigenvalues as a function of the energy for the *He*-isoelectronic series, and the extrapolated critical charge is

$$Z_c = 0.917 \tag{22}$$

which agrees very well with the values obtained by Kais and Sergeev [3] and Hogreve[15] of $Z_c = 0.912$.

5. Conclusions

We presented a method to find Sturmian functions with a given asymptotic condition for both negative (exponential decay) and positive (outgoing, incoming or stationary) energies expanding the solution in a L^2 Laguerre-*type* basis set. The example presented here showed that our numerical results converge to the exact negative and positive energy (with outgoing wave condition) solution for a Coulomb well potential. The advantage of this method is that it provides a systematic way to find the Sturmian functions for almost any auxiliary potential, and provides the correct asymptotic behavior in the entire energy domain.

The model potential for an N-electron atomic system in the frame of one active electron model proposed by Kais and Sergeev [3], Eq. (21) was studied by fixing the energy and taking the parameter γ as the eigenvalue, obtaining the Sturmian functions for this potential. To study a given atomic system, the energy is fixed to be the ionization energy, and the free parameter δ is chosen such that $\gamma = (N-1)/Z$ is an eigenvalue. This allowed us to find a representation of an N-electron atom of nuclear charge Z using the Sturmian theory. Numerical results for the H e-isoelectronic series ($N = 2$) were found for the value of the parameter δ as a function of the energy. These results were also fitted to extrapolate the behavior of the eigenvalue as $E_I \to 0$. and used to obtain the critical charge for the *He*-isoelectronic series. This procedure suggests that one can obtain a significant physical information from the Sturmian functions, going beyond the simple use of them as a basis set to re-expand a wave function.

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