
Discrete Sets of Many-Body Sturmians

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ABSTRACT: In this work, we present a method to obtain two-particle Coulomb Sturmians Functions (CSF) with an expansion in a set of L^2 basis functions. In the two-body case, we recover the exact (discrete) spectrum of the CSFs for negative energies and a discretized approximation for positive ones. Besides, we make use of this method to analyze the two-independent electron problem as a Generalized Sturmian problem. We propose a discretized version of the wave function in terms of the CSF states, and show that the problem reduces to find numerical coincidences between energy-dependent eigencharges of the mutually independent one-electron systems. This expansion methodology includes the continuum information which is lost in the sets used previously in the literature, and is complete when the size of the basis goes to infinity. © 2008 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 125–134, 2009

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1. Introduction

The configuration interaction (CI) method has been widely used to deal with two-electron atomic bound states. Roughly, it is based on the

expansion of the wave function in a set of eigenstates of the total angular momentum operator L^2 , where the positions of the electrons are determined by the spherical coordinates which locate the electrons relative to the nucleus. By means of such expansion, one arrives to a two-dimensional equation in the radial electronic coordinates, whose solution is approximated as a superposition of two-electron configurations. Other methods in which the basis expands the behavior of the wave function in all the interparticle distances are more rapidly convergent (see [1, 2] and references therein), but generally the calculation is very time consuming, and the algebra is too much complicated to be extended from two to many-electron atoms, compared to the case of the CI scheme.

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In principle, it seemed that the most adequate two-electron configurations to be applied in the CI calculations were the discrete set of products of Hydrogenic atomic orbitals (HAO), one for each radial coordinate. They remove the kinetic energy and the central potential terms in the three-body Schrödinger equation, and also become the exact configurations when the electronic interaction is neglected. However, since the Hydrogenic continuum information is not included, the discrete two-electron basis is not complete, and convergence to the exact physical state cannot be reached.

Shull and Löwdin introduced an alternative Laguerre-type basis in order to achieve completeness of the radial solution [3]. As the Hydrogenic atomic orbitals these functions also remove the kinetic term from the three-body Schrödinger equation and have a free parameter, which can be related to the energy and optimized to accelerate convergence. The basis functions have the analytical form of the Hydrogenic orbitals, consisting of an associated Laguerre polynomial multiplied by the exponential decaying factor, the only difference being that their functional argument is independent of the index which enumerates the basis. This basis set is complete because the parameter appearing in the basis functions is not defined in terms of the energy. The Coulomb Sturmian functions (CSF) have been also used as an alternative basis set within the CI method. These functions originate from a two-body Coulomb problem taking the charge as eigenvalue and where the energy is considered as a parameter. For negative energies, the complete eigenvalue, spectrum and eigenvectors are the discrete set of charges $Z = n\sqrt{-2mE}$, $n = 1, 2, \dots$, which adopt that fixed energy as a bound state, and the Laguerre-type functions associated to this spectrum. These functions are known as the CSF because of their connection with the Sturm-Liouville theory. For positive energies, the same definition for the charge in terms of the energy appears in the definition of the CSF, but in this case because of the continuous spectrum of the energy a continuous spectrum for the charge results [4, 5]. The discrete index n is replaced by a continuous one. When dealing with two-body problems the CSF form a complete basis set both for positive and negative energies [4, 5].

In an attempt to generalize the CSF basis to many electron systems, Avery, Aquilanti, and coworkers proposed a N -electron basis set analogue to the one-electron CSF, which removes the total and kinetic energy terms from the many-body Schrödinger equation. The generalized Sturmians basis (GS),

which has been extensively discussed in a series of recent publications (See [6–10] and references therein), is constructed as the product of N negative energy one-electron CSFs, and corresponds to the solution of the Schrödinger equation of an independent electron system, where the total energy is a parameter and the (common) nuclear charge is the eigenvalue [6, 7]. The method presented has proven to be useful in solving different kind of atomic and molecular systems as can be seen from the large list of papers and books published by authors such as, Avery and Aquilanti among others. However, that GS basis is not complete, as shown by Szmytkowski recently [11]. He found that the N -electron eigencharge problem also contains a continuum spectrum, where one of the CSF is related with a positive one-electron energy, being the total energy still negative (there is also a part of the charge spectrum where both electrons have positive energies and the eigencharge has a continuum spectrum). Thus the complete eigencharge solution resulting for negative total energy contains a double discrete spectrum, composed by products of two bound CSF (the usual GS set), and discrete-continuous parts, composed by a product of bound and continuum CSF. The discrete GS methodology implemented by Avery does not include all the eigenvalues and eigenfunctions of the basis set, but only those corresponding to the double discrete energy subspace. Because the complete basis has a continuum spectrum for all energies, the atomic systems can only be solved in an approximated way if the continuous part of the charge spectrum is now included. The introduction of that part of the spectrum within the methodology proposed by Avery cannot be done with standard matrix (algebraic) techniques, reducing in this way the capabilities and utility of the method itself. The main aim of this article is to propose a way to avoid these problems. In this report, we introduce an alternative to the GS method, which allows the introduction of positive energy Sturmians functions within the framework of matrix algebra. Our method is based on the quadrature expansion of the solution of the CSF, that leads to a discretization of the complete spectrum of eigencharges. We show that within our approach, the addition of continuum states to the basis is straightforward, and the drawback of previous methods are overcome in an easy and usable way.

The article is arranged as follows. In Section 2.1 a review of the theory of Sturmian functions is presented. We first discuss the general theory in Section 2.1. In Section 2.2 and 2.3 we review the quadrature and finite differences scheme used to obtain

a discrete charge spectrum for any (negative or positive) energy [12]. The extension to the problem of two-electron atoms is discussed in Section 3. A complete description of the full charge spectrum is presented in Section 3.1. Orthogonality and completeness is also discussed in this section. In Section 4, the quadrature representation for the two-electron Sturmian functions is presented and its properties are discussed. In Section 5 some conclusion are drawn. We employ atomic units ($m = \hbar = e = 1$) throughout.

2. Two-Body Sturmians

2.1. GENERAL THEORY

The Sturmian functions for a particle in a physical potential V are defined as the solutions of the Schrödinger equation

$$\left[-\frac{1}{2\mu} \nabla_r^2 - E \right] \Psi_v(\mathbf{r}) = -\beta_v V \Psi_v(\mathbf{r}), \quad (1)$$

with physical boundary conditions:

$$\lim_{r \rightarrow 0} r \Psi_v(r) = 0 \quad \text{and} \quad \lim_{r \rightarrow \infty} r \Psi_v(r) < \infty,$$

where E is the energy, which is considered as a fixed parameter, and β_v is the eigenvalue to be determined. The complete set of functions obtained from the eigenproblem forms a basis whose spectrum depends on the value of the energy in Eq. (1). If the energy is negative, then $\beta_v V$ must be attractive. The eigenvalues adjust the depth of the potential so that there exist a bound state of energy E . Then the eigenproblem leads to an infinite discrete spectrum of eigenvalues β_v with $v = \{n, l, m\}$ ($n = 1, 2, \dots$, $l = 0, 1, \dots$, and $m = -l, l$) [13–15], whose associated eigenfunctions are exponentially decreasing with r .

It is an easy task to show that the eigenfunctions satisfy potential weighted orthonormality conditions of the form

$$\langle \Psi_{v'} | V | \Psi_v \rangle = \int d\mathbf{r} \Psi_{v'}(\mathbf{r}) V(\mathbf{r}) \Psi_v(\mathbf{r}) = \delta_{n',n} \delta_{l',l} \delta_{m',m}, \quad (2)$$

so that the closure relation is

$$\sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{n=1}^{\infty} \Psi_{n,l,m}(\mathbf{r}') \Psi_{n,l,m}(\mathbf{r}) V(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'). \quad (3)$$

In the case of dealing with positive energies, there is always a continuum state for any depth of the

atomic potential. In those cases, the spectrum of β_v is continuous and covers the whole real axis: $n = \gamma$, $-\infty < \gamma < \infty$. Examples of functions satisfying these boundary conditions have been discussed by Szmytkowski [4] and by Gasaneo and Colavecchia [5] for the two-body Coulomb problem. According to the boundary condition (2.1), the eigenfunctions have standing-wave boundary conditions at large distances. They satisfy orthogonality and closure relations of the form

$$\langle \Psi_{v'} | V | \Psi_v \rangle = \int d\mathbf{r} \Psi_{v'}(\mathbf{r}) V(\mathbf{r}) \Psi_v(\mathbf{r}) = \delta(\gamma' - \gamma) \delta_{l',l} \delta_{m',m}, \quad (4)$$

$$\sum_{l=0}^{\infty} \sum_{m=-l}^l \int_{-\infty}^{\infty} d\gamma \Psi_{\gamma,l,m}(\mathbf{r}') \Psi_{\gamma,l,m}(\mathbf{r}) V(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'). \quad (5)$$

From the Eqs. (3) and (5), it can be seen that each set of Sturmian functions forms a complete and orthogonal basis set in the domain $0 \leq r < \infty$ [5, 16] independently of the sign of the energy. There is no mixed spectrum like in the energy eigenvalue case.

2.2. A QUADRATURE SCHEME

When $V = \frac{Z}{r}$, the Eq. (1) can be solved analytically. However, it is our interest to obtain discrete solutions for negative as well as positive energies. One way is to obtain quadrature solutions as in Ref. [12]. Approximate solutions can be written as:

$$\Psi_v^N(\mathbf{r}) = \frac{1}{r} B_v^N \sum_{k=0}^{N-1} a_k^v \varphi_{k,l}(\lambda, r) Y_l^m(\theta, \phi) \quad (6)$$

where $Y_l^m(\theta, \phi)$ is the Spherical Harmonic function defined in Ref. [17] and

$$\varphi_{k,l}(\lambda, r) = (2\lambda r)^{l+1} e^{-\lambda r} L_k^{2l+1}(2\lambda r). \quad (7)$$

$L_k^\alpha(x)$ are the generalized Laguerre polynomials [18]. λ is a free parameter which can vary for each l in order to optimize partial wave expansions for many-electrons atoms [19]. When V in Eq. (1) is the Coulomb potential, the coefficients a_k^v have an analytical expression:

$$a_k^v = \frac{k! P_k^{l+1}(\tilde{\gamma}_v; \phi)}{\Gamma(2l + 2 + k)}, \quad k = 0, 1, \dots, N-1, \quad (8)$$

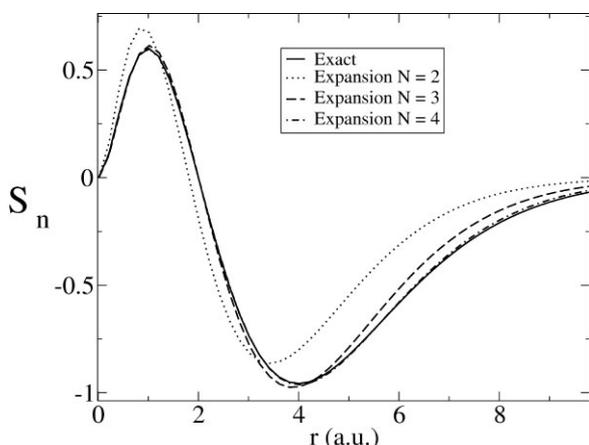


FIGURE 1. Expansion of the two particle CSF for $E = -0.5$ (a. u.), $l = 1$ and $n = 2$, with the Laguerre basis of Eq. (7).

where $P_k^{l+1}(\gamma; \phi)$ are charge polynomials similar to the Pollaczek polynomials:

$$P_k^{l+1}(\gamma; \phi) = \frac{\Gamma(k + 2l + 2)}{k! \Gamma(2l + 2)} e^{ik\phi} {}_2F_1[-k, l + 1 - i\gamma, 2l + 2; 1 - e^{-2i\phi}], \quad (9)$$

where $\tilde{\gamma}_v = \frac{Z\beta_v\mu}{\lambda}$, $\cos \phi = \left(E - \frac{\lambda^2}{2\mu}\right) / \left(E + \frac{\lambda^2}{2\mu}\right)$ and ${}_2F_1[a, b, c; z]$ is the Gauss function [18]. The expansion of the eigenfunctions of Eq. (6) in a L^2 subspace force the spectrum to be discrete: $v = \{n, l\}$, $n = 0, 1, \dots, N$. The normalization factor B_v^N is defined in order to satisfy normalization Eq. (2):

$$B_v^N = \sqrt{\frac{\Gamma(N + 2l + 1) 2 \sin \phi}{N!}} \times \left[\frac{dP_N^{l+1}}{d\gamma} \Big|_{\gamma=\gamma_v} P_{N-1}^{l+1}(\gamma_v, \phi) \right]^{-1/2}. \quad (10)$$

It has been shown that the coefficients (9) are polynomials in β_v , and these eigenvalues are the N solutions of [12]

$$P_N^{l+1}(\gamma; \phi) = 0. \quad (11)$$

For $E < 0$, the expansion (6) rapidly converges to the exact negative energy CSF as N increases, as shown in Figure 1. For $E > 0$, better approximations to the exact continuum stationary CSF are obtained for larger values of N until the fall of exponent of

the Laguerre basis Eq. (7) dominates. A complete discussion of this topics can be found in Ref. [12].

2.3. A FINITE DIFFERENCES SCHEME

Here, we discuss how to numerically solve the radial Sturmians equation within a finite differences scheme. If V is a spherically symmetric potential we can write:

$$\Psi_v(\mathbf{r}) = \frac{1}{r} S_{n,l}(r) Y_{l,m}(\theta, \varphi) \quad (12)$$

and we only have to solve for $S_{n,l}(r)$ the following radial equation:

$$\left[-\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)}{2\mu r^2} - E \right] S_{n,l}(r) = -\beta_v V(r) S_{n,l}(r). \quad (13)$$

We propose a discretization of the wave function $S_{v,l}(r)$ in an equally spaced radial grid:

$$S_{n,l}(r_i) \cong S_i, \quad i = 0, 1, \dots, N-1 \quad (14)$$

where $r_i = i \times \Delta r$ and where we have suppressed the quantum number l and v for clarity. The second order derivative of $S_{v,l}(r)$ can be approximated by

$$\frac{d^2 S_{n,l}(r)}{dr^2} = \frac{1}{\Delta r^2} [S_{i+1} - 2S_i + S_{i-1}]. \quad (15)$$

Then Eq. (13) transforms into a set of linear equations:

$$-\frac{1}{2\mu} \frac{1}{\Delta r^2} S_{i+1} - \frac{1}{2\mu} \frac{1}{\Delta r^2} S_{i-1} + [h_i - E] S_i = -\beta_v V(r_i) S_i, \quad (16)$$

($i = 0, 1, \dots, N-1$) and we have defined:

$$h_i = \left[\frac{1}{\mu} \frac{1}{\Delta r^2} + \frac{l(l+1)}{2\mu r_i^2} \right] \quad (17)$$

This leads to a generalized eigenvalue problem for the vector $\mathbf{s} = \{S_0, S_1, \dots, S_{N-1}\}$:

$$[\mathbf{H} - E\mathbf{I}]\mathbf{s} = -\beta\mathbf{V}\mathbf{s}$$

with the diagonal matrices $[\mathbf{I}]_{ij} = \delta_{ij}$ and $[\mathbf{V}]_{ij} = V(r_i)\delta_{ij}$; and we defined the tridiagonal matrix $[\mathbf{H}]_{ij} = \delta_{ij} h_i - \frac{1}{2\mu} \frac{1}{\Delta r^2} (\delta_{i,j-1} + \delta_{i,j+1})$.

If we multiply from the left by the inverse of the diagonal potential matrix and solve the resulting eigenvalue problem, we will obtain real standing

waves with homogeneous boundary conditions at r_0 and at $r_{max} + \Delta r$. The resulting matrix is also tridiagonal, and can be solved up to very large sizes. By means of iterative algorithms [20], the computational effort can be concentrated in obtaining only a selected number of eigenvalues. Once they have been obtained, the corresponding eigenvectors are calculated through inverse or direct iteration.

3. The Two-Electron Sturmian Functions

Following the GS method [7, 11], we solve the separable three-body eigenvalue problem

$$\left[-\frac{1}{2\mu} \nabla_{\mathbf{r}_1}^2 - \frac{1}{2\mu} \nabla_{\mathbf{r}_2}^2 - E \right] \Phi_\nu(\mathbf{r}_1, \mathbf{r}_2) = -\beta_\nu (V_1(r_1) + V_2(r_2)) \Phi_\nu(\mathbf{r}_1, \mathbf{r}_2) \quad (18)$$

using spherical coordinates $(r_i, \theta_i, \varphi_i, i = 1, 2)$ for each electron, and the nucleus is assumed at rest in the center of coordinates. The appropriate boundary conditions for this problem are

$$\lim_{r_i \rightarrow 0} r_i \Phi_\nu(\mathbf{r}_i, \mathbf{r}_j) = 0 \quad \text{and} \quad \left| \lim_{r_i \rightarrow \infty, r_j \text{small}} r_i \Phi_\nu(\mathbf{r}_i, \mathbf{r}_j) \right| < \infty \quad (i, j = 1, 2) \quad (19)$$

where the energy E is a fixed parameter, β_ν is the eigenvalue, and ν stands for all quantum numbers. For simplicity we will concentrate our attention in the case where the interactions are Coulomb ones, $V_i = \frac{Z}{r_i}$. Since Eq. (18) is separable in the coordinates \mathbf{r}_1 and \mathbf{r}_2 , we propose a solution of the form:

$$\Phi_\nu(\mathbf{r}_1, \mathbf{r}_2) = C_\nu \Psi_{\nu_1}(\mathbf{r}_1) \Psi_{\nu_2}(\mathbf{r}_2) \quad (20)$$

where in this case we denote $\nu = \{\nu_1, \nu_2\}$, $\nu_i = \{n_i, l_i, m_i\}$ l_i and m_i are the angular momentum and its projection along the z axis, respectively, n_i (γ_i when dealing with positive energies) is the radial quantum number and C_ν is a normalization factor. Then replacing Eq. (20) in Eq. (18) and separating the subsystems we have:

$$\left[-\frac{1}{2\mu} \nabla_{\mathbf{r}_i}^2 - E_i \right] \Psi_{\nu_i}(\mathbf{r}_i) = -\beta_\nu^{(i)} \frac{Z}{r_i} \Psi_{\nu_i}(\mathbf{r}_i) \quad (i = 1, 2) \quad (21)$$

where E_1 is the separability constant ($E_2 = E - E_1$). Since the eigenvalue generally depends on the

energy, we must choose only those values of the separation constant E_1 which gives the same value of β_ν for each subsystem. We will show below how Eq. (18) can be analytically solved when V_i is the Coulomb potential, and how to use the complete quadrature methodology that can also be applied when V_i is an arbitrary potential.

3.1. EXACT GENERALIZED CSF

As was already mentioned, if we take the functions $|\Psi\rangle$ as the exact solutions of Eq. (1) with $V = \frac{Z}{r}$, we will have an exact solution of Eqs. (18) and (19), for those values of the separation constant such that $\beta^{(1)} = \beta^{(2)}$. The complete spectrum of Eq. (18) for $E < 0$ is discussed in [11]. We will review it and show what happens in the case $E > 0$. We can distinguish between two cases:

Case $E < 0$

In this case, the separation constant E_1^ν can satisfy one of the three conditions:

(i) $E_1^\nu < 0$, $E - E_1^\nu < 0$. In this case both energies are negative, and the energies are related to the eigenvalues through the discrete (Coulombian) relation:

$$E_1^\nu = -\frac{(\beta_\nu Z \mu)^2}{2n_1^2}, \quad E_2^\nu = E - E_1^\nu = -\frac{(\beta_\nu Z \mu)^2}{2n_2^2}, \quad n_1, n_2 \in \mathbb{N}. \quad (22)$$

The eigenvalues are given by

$$\beta_\nu = -\frac{n_1 n_2}{Z \mu} \sqrt{\frac{-2E}{n_1^2 + n_2^2}}. \quad (23)$$

Substituting back Eq. (23) into (22) we obtain the energies:

$$E_1^\nu = \frac{n_2^2}{n_1^2 + n_2^2} E, \quad E_2^\nu = \frac{n_1^2}{n_1^2 + n_2^2} E. \quad (24)$$

It is important to note that in this case of double negative energy the solutions are products of functions of the form (7), where the λ parameter must be replaced by the n -dependent quantity: $n_1 n_2 \sqrt{-2E/x n_1^2 + n_2^2}$. Although a product of Laguerre-type functions of the form of Eq. (7) with fixed parameter λ (which can be different for each electron) represents a suitable basis to expand discrete as well as continuum

states, the set with eigenvalue given in Eq. (23) and n -dependent argument does not. This is the explanation of why the discrete negative-energy GS are sometimes confused with the complete Laguerre-type products.

(ii) $E_1^v > 0, E - E_1 < 0$. If only one of the energies is positive, there is a continuous relation between the charge and that energy, and a discrete one for the other subsystem. For the continuum spectrum we use the relation $\beta_\gamma = -\gamma\sqrt{2E}/Z\mu, \gamma \in \mathfrak{R}$, so that

$$E_1^v = \frac{(\beta_v Z\mu)^2}{2\gamma_1^2}, \quad E_2^v = E - E_1^v = -\frac{(\beta_v Z\mu)^2}{2n_2^2},$$

$$\gamma_1 \in (n_2, \infty), n_2 \in \mathbb{N}, \quad (25)$$

and the eigenvalues are given by

$$\beta_v = -\frac{\gamma_1 n_2}{Z\mu} \sqrt{\frac{-2E}{\gamma_1^2 - n_2^2}} \quad (26)$$

and

$$E_1^v = -\frac{n_2^2}{\gamma_1^2 - n_2^2} E, \quad E_2^v = \frac{\gamma_1^2}{\gamma_1^2 - n_2^2} E. \quad (27)$$

(iii) $E_1^v < 0, E - E_1^v > 0$. This case is similar to (ii):

$$E_1^v = -\frac{(\beta_v Z\mu)^2}{2n_1^2}, \quad E_2^v = E - E_1^v = \frac{(\beta_v Z\mu)^2}{2\gamma_2^2},$$

$$\gamma_2 \in (n_1, \infty), n_1 \in \mathbb{N} \quad (28)$$

and

$$\beta_v = -\frac{\gamma_2 n_1}{Z\mu} \sqrt{\frac{-2E}{\gamma_2^2 - n_1^2}}. \quad (29)$$

The separability constants are given by

$$E_1^v = \frac{\gamma_2^2}{\gamma_2^2 - n_1^2} E, \quad E_2^v = -\frac{n_1^2}{\gamma_2^2 - n_1^2} E. \quad (30)$$

The corresponding wave functions are products of positive and negative energies Coulomb eigenfunctions, according of the signs of E_1^v and E_2^v . Since one of the energies E_1^v or E_2^v are always negative, the product $\beta_v Z$ must be negative. The restrictions $\gamma_i \in (n_j, \infty), i, j = 1, 2, i \neq j$ in Eq. (26) and (29) are imposed to satisfy $E < 0$.

Case $E > 0$

Here, the energy distribution can take the sub cases (ii) and (iii) given above, with the replacements $\gamma_i \in (n_j, \infty) \rightarrow \gamma_i \in (0, n_j), i, j = 1, 2, i \neq j$. In all these cases the eigenvalue is negative, according to the fact that the central potential support negative energy one-electron states. We also have another option:

(iv) $E_1^v > 0, E - E_1^v > 0$. In this last case we have

$$E_1^v = \frac{(\beta_v Z\mu)^2}{2(\gamma_1^\pm)^2}, \quad E_2^v = E - E_1^v = \frac{(\beta_v Z\mu)^2}{2(\gamma_2^\pm)^2},$$

$$\gamma_i^\pm \in \mathfrak{R}^\pm, i, j = 1, 2 \quad (31)$$

so that $\gamma_i^\pm, i, j = 1, 2$ are both positive or negative. The continuum spectrum of eigenvalues is

$$\beta_v = \pm \frac{\gamma_1^\pm \gamma_2^\pm}{Z\mu} \sqrt{\frac{2E}{(\gamma_1^\pm)^2 + (\gamma_2^\pm)^2}}. \quad (32)$$

Substituting back into Eq. (31) we have

$$E_1^v = \frac{(\gamma_2^\pm)^2}{(\gamma_1^\pm)^2 + (\gamma_2^\pm)^2} E, \quad E_2^v = \frac{(\gamma_1^\pm)^2}{(\gamma_1^\pm)^2 + (\gamma_2^\pm)^2} E. \quad (33)$$

In summary, for $E < 0$ the eigencharges have a double discrete spectrum, corresponding to the case in which both E_1 and E_2 are negative, and a discrete spectrum embedded in the continuum, corresponding to the case where E_1 and E_2 have different sign. On the other hand, when $E > 0$, there is again a mixed spectrum when E_1 and E_2 have different sign, and a double continuum one, corresponding to the case in which both energies are positive. We see that whatever the sign of the energy, the basis set includes continuum functions. Thus the GS procedure implemented previously by different authors does not contain a complete set of function [7–10].

3.2. ORTHOGONALITY AND CLOSURE RELATION

It is an easy task to show that the two-electron L^2 Sturmians satisfy potential-weighted orthonormality conditions [7]. To see that we multiply Eq. (18) to the left by $\Phi_{\nu'}^*$, and by Φ_ν , the conjugate of the

equation satisfied by $\Phi_{\nu'}$. Taking the difference we arrive at:

$$\begin{aligned} & \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \left[-\frac{1}{2\mu} \nabla_{\mathbf{r}_1}^2 - \frac{1}{2\mu} \nabla_{\mathbf{r}_2}^2 - E \right] \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) \\ & - \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) \left[-\frac{1}{2\mu} \nabla_{\mathbf{r}_1}^2 - \frac{1}{2\mu} \nabla_{\mathbf{r}_2}^2 - E \right] \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \\ & = -\beta_{\nu} \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) \\ & + \beta_{\nu'}^* \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \\ & = -(\beta_{\nu} - \beta_{\nu'}^*) \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) \end{aligned}$$

Then, integrating over the whole space, and using the hermiticity of the kinetic energy operator:

$$(\beta_{\nu} - \beta_{\nu'}) \int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) = 0 \quad (34)$$

where we used the fact that $\text{Im}\{\beta_{\nu}\} = 0 \forall \nu$ for the boundary conditions imposed here. Then, choosing the appropriate normalization factor C_{ν} , we have:

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_{\nu'}^*(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) = \tilde{\delta}_{\nu, \nu'} \quad (35)$$

where $\tilde{\delta}_{\nu, \nu'}$ represent a Kronecker or Dirac delta according to the spectrum being considered for ν' and ν (discrete or continuous, respectively). Expression (35) implies that we can now express the closure relation in terms of the basis obtained in solving Eq. (18):

$$\begin{aligned} \mathbf{1} &= \sum_{\nu} \int d\nu \Phi_{\nu}^*(\mathbf{r}'_1, \mathbf{r}'_2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Phi_{\nu}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \delta(\mathbf{r}'_1 - \mathbf{r}_1) \delta(\mathbf{r}'_2 - \mathbf{r}_2). \quad (36) \end{aligned}$$

As it can be seen from Eq. (27), (33), and (30), the charge spectrum of the GS contains a continuum spectrum. Therefore, matrix standard techniques for the diagonalization of the eigensystem cannot be implemented, and it is necessary to develop a discretization method to overcome this difficulty.

4. Quadrature Solution For The Two-Electron Coulomb Problem

We have seen that whatever the expansion of a function with exact negative-energy GS basis, their

final expression will contain integrals over the continuum part of the charge spectrum [see Eq. (36)]. To avoid this drawback, we propose a set of approximate Sturmians GS basis to be constructed from the expansions of Eq. (6) for each electron, so that the spectrum is discrete for all separability constants E_1 and E_2 . To make a complete association one has to use those products of two-body CSF which have the same eigenvalue. To find the discretized eigenvalues and one-electron energies we proceed as follows. Using the Sturmian expansions of Eq. (6) for each electron's coordinate as ansatz for the solution of Eq. (18), we have

$$\begin{aligned} & -\Psi_{\nu_2}^{N_2}(\mathbf{r}_2) \left[\frac{\beta_{\nu_1}^{N_1} - \beta_{\nu}}{r_1} \right] \Psi_{\nu_1}^{N_1}(\mathbf{r}_1) \\ & = \Psi_{\nu_1}^{N_1}(\mathbf{r}_1) \left[\frac{\beta_{\nu_2}^{N_2} - \beta_{\nu}}{r_2} \right] \Psi_{\nu_2}^{N_2}(\mathbf{r}_2) \quad (37) \end{aligned}$$

where $\beta_{\nu_i}^{N_i}$ are the eigenvalues obtained by discretization. Since the eigenvalues of the subsystems 1 and 2 depends parametrically on the separation between E_1 and E_2 , respectively, we will obtain a L^2 solution of Eq. (37) only for those values of E_1^{ν} such that

$$\begin{aligned} \beta_{\nu_1}^{N_1}(E_1^{\nu}) &= \beta_{\nu_2}^{N_2}(E - E_1^{\nu}) = \beta_{\nu}, \quad \nu_1 = 1, \dots, N_1, \\ & \nu_2 = 1, \dots, N_2. \quad (38) \end{aligned}$$

For each fixed external energy E , this last equation discretizes the values of E_1^{ν} , E_2^{ν} , and β_{ν} , whose values will be dependent on the discretization procedure, but have to show converge to the exact ones in the limit $N \rightarrow \infty$. The advantages of the discretization procedure presented here is that the problem can always be solved by matrix methods. Besides, in the case of dealing with Coulomb potentials and Laguerre-type expansions, it involves tridiagonal matrices. Aside from the numerical simplicity that it represents, there is a polynomial equation for the eigenvalues. In addition, the eigenvalues are always strictly increasing functions of the energy as shown in Figure 2. These last facts imply that the function

$$f(E_1) = \beta_{\nu_1}^{N_1}(E_1^{\nu}) - \beta_{\nu_2}^{N_2}(E - E_1^{\nu}) \quad (39)$$

has always one and only one zero as a function of E_1^{ν} , and each of the last $N_1 \times N_2$ Eqs. (38) has only one solution β_{ν} ($\nu = 1, 2, \dots, N_1 \times N_2$).

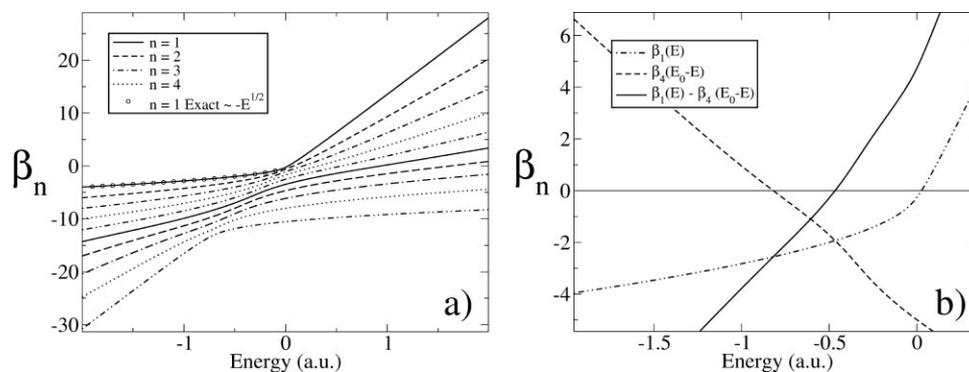


FIGURE 2. Eigenvalues of the Eq. (1) as a function of the energy. All the eigencharges are strictly increasing functions of the energy, and the coincidences as a function of E_1^v are always reached.

This is shown in Figure 2(a) where the charge eigenvalues are plotted versus the separation constant E_1 . We also show [Fig. (2b)] the behavior of one particular eigenvalue of each subsystems as a function of the separability constant. It can be seen that the eigenvalue corresponding to the system 1 is a monotonically increasing function of the energy. On the contrary, that one corresponding to the system 2 is a monotonically decreasing function of E_1 . Their difference is zero at a only one particular value E_1^v . The associated eigenfunctions correspond to a product of two-body Coulomb functions of charge $Z\beta_v^N$ with generally distinct pairs of energies E_1^v and $E_2^v = E - E_1^v$, which are not restricted to be negative. For total energy $E < 0$, at least one of E_1 or E_2 is negative. Since a negative value of the energy in equation Eq. (18) gives always negative eigencharges, the charges satisfying Eq. (38) must be negative. For $E > 0$, this is not the case, and the charges can be positive or negative.

Once we find the eigenvalues β_v , we construct an antisymmetrized basis set:

$$\begin{aligned} \Phi_v^N(\mathbf{r}_1, \mathbf{r}_2) = & \frac{1}{\sqrt{2}} (\Psi_{\nu_1}^{(N_1)}(\mathbf{r}_1) \Psi_{\nu_2}^{(N_2)}(\mathbf{r}_1) \\ & \pm \Psi_{\nu_1}^{(N_1)}(\mathbf{r}_2) \Psi_{\nu_2}^{(N_2)}(\mathbf{r}_2)) \chi^\pm, \\ & \nu = 1, \dots, N_1 \times N_2 \quad (40) \end{aligned}$$

where χ^+ (χ^-) is the singlet (triplet) total spin wave function of the two electron function. The basis set (40) is also an approximate solution of Eq. (18). Since the radial functions of Eq. (6) tend to the exact ones when $N_i \rightarrow \infty$, the function Φ_v^N converges to the exact solution of the eigenvalue problem Eqs. (18) and (19) in that limit. The quadrature solutions

satisfy a orthogonality relation analog to that of Eq. (35):

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_{\nu'}^{*N}(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Phi_\nu^N(\mathbf{r}_1, \mathbf{r}_2) = \tilde{\delta}_{\nu, \nu'}. \quad (41)$$

where $\tilde{\delta}_{\nu, \nu'}$ represents always a Kronecker delta the symbol, since the Φ_v^{*N} belongs to an L^2 subspace. The closure relation in that subspace can be written in as

$$\begin{aligned} \mathbf{1}^N = \sum_{\nu=1}^{N_1 \times N_2} \Phi_\nu^{*N}(\mathbf{r}'_1, \mathbf{r}'_2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Phi_\nu^N(\mathbf{r}_1, \mathbf{r}_2) \approx & \delta(\mathbf{r}'_1 - \mathbf{r}_1) \\ & \times \delta(\mathbf{r}'_2 - \mathbf{r}_2) \quad (42) \end{aligned}$$

where the Φ_v^N are the quadrature of Eq. (6) for positive or negative energy.

In Figures 3(a) and (b), we show two basis elements for an energy parameter of -2.903 a.u. (almost the energy of the ground state of the Helium atom) and in Figures 3(c) and (d) those for an energy of -1 a.u. (which is the energy of the first double excited state of *He* in the independent electron approximation), as a function of the radial coordinates of the electrons. Cases *a* and *c* represent pure discrete states obtained from the eigenvalue Eq. (18), and correspond to the choice $n_1 = n_2 = 1$ and $n_1 = n_2 = 2$ in Eq. (22), respectively. The state shown in Figure 3(a) is equivalent to the bound state of an independent electron system with an effective charge of -1.7 a.u. Figure 3(b) represents the same system with a bounded behavior for one electron and a L^2 approximation of a continuum wave function for the other, where the nuclear charge eigenvalue is -2.78 a.u. Figure 3(c) shows the state representing a double-excited state in the independent electron model, for a nuclear charge of -2 a.u., and Figure 3(d) one

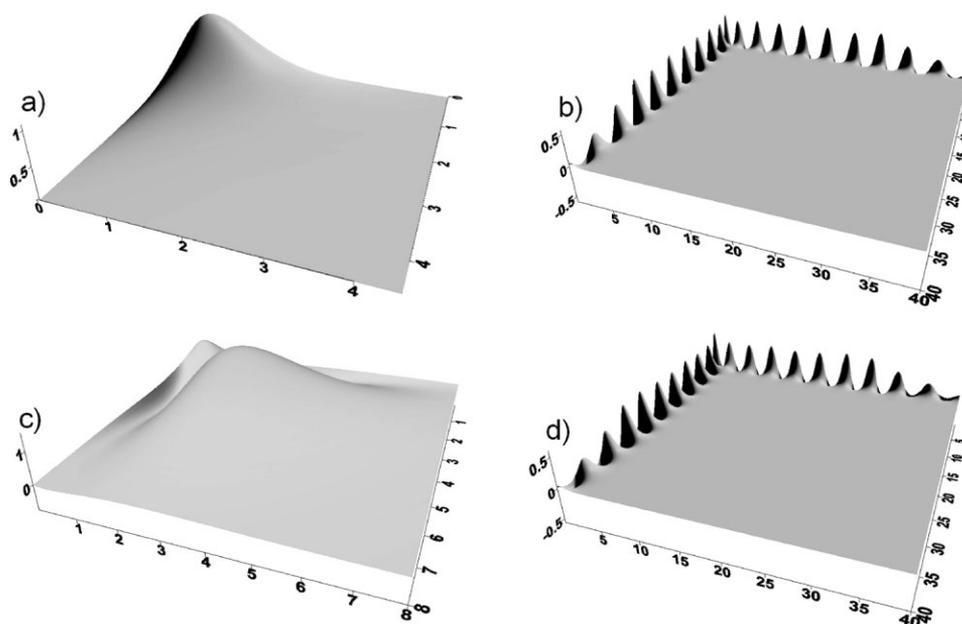


FIGURE 3. Quadrature approximations of the exact solutions of Eq. (18) as a function of r_1 and r_2 . (a): GS basis element obtained by convergence of the quadrature solution ($\Phi_v^{(N)}$) for $E = -2.903$ a.u., $n_1 = n_2 = 1$. (b): L^2 approximation to a continuum state (see text), for $E = -2.903$ a.u. (c): Same as (a) for $E = -1$ a.u., $n_1 = n_2 = 2$. (d): Same as (b) for $E = -1$ a.u.

state representing also a bound electron and a continuum one, the value of the charge eigenvalue being -2.03 a.u. Except in the case *b*, the basis states have physical boundary conditions which could be present in the real state (consider for example the mixed spectrum of the double excited state).

As we saw in Figure 1, the convergence of the Laguerre expansion to the exact negative-energy CSF is very fast. Thus, the GS method as presented by Avery [10] can be reached from our proposal by taking a sufficiently large order N_i on each of the one electron Sturmian functions and using only those states leading to total negative energy. This basis set can be done as dense as that proposed by Prof. Avery. All the results presented in the literature based on Avery's proposal can be reproduced using our proposal. A complete comparison between our quadrature and exact (Avery's) methods will be presented in a separated contribution with application to different atomic systems. The complete basis, however, is obtained for $N \rightarrow \infty$ when all the states resulting from the quadrature are used. The complete spectrum is obtained including states like Figures 3(a) and b. These states will have a very small contribution when applied to the calculation of the the ground state energy of He-like systems, because of their spatial extension. This explains why

a pure discrete GS expansion gives accurate results [7–10]. However, since the continuum charge states are basis elements obtained from the same eigenvalue problem, their presence can only improve the convergence of the GS expansion.

Figures 3(c) and (d) show the basis for an energy close to the first double excited state of Helium. When applying the basis to the calculation of these states for, e.g., He, both continuum and discrete states will have important contributions since the real spectrum is mixed at those energies. Because of their spatial extension, continuum states will also have important contributions to the highly single and double-excited states as well as to the double continuum ones.

5. Conclusions

Expanding the radial part of the solution of the two-body Coulomb Sturmian equation in a discrete set of L^2 Laguerre-type functions, we were able to obtain a discretized charge-spectrum both for positive and negative energies [12]. For negative energies we found a fast convergence to the exact CSF, while for positive ones a quadrature approximation was found.

The exact solution (and the spectra) for the Generalized Sturmians equation for negative and positive energies was reviewed. We found in agreement with Szmytkowski [11] that the charge spectrum for negative (and positives) energies contains continuous parts which were not considered by Avery [6, 7]. The inclusion of the whole charge spectrum for negative energies cannot be done using matrix techniques. This reduces the efficiency and power of the method proposed originally by Avery because it implies the use of a not complete basis set of functions. To complete the spectra, we showed that a quadrature form for the solution of the Coulomb Sturmian equations can be implemented. In this way, the spectrum is always discrete for negative and positive energies, and all the functions corresponding to negative as well as positive energies can be equally included with matrix techniques. The convergency of the quadrature Sturmians to the exact ones was shown. In the limit of N (the number of function used in the quadrature) to infinity the exact CSF are obtained both for negative as well as for positive energies. Expressions for the orthogonality and closure relations for the exact and approximated basis sets were also given. The application of the method here discussed to the study of two-electron systems will be presented in a separated contribution. A complete study of the convergency rates for two-electron atoms energies will be also presented.

The theory described in the previous sections has been designed to be useful also for the treatment of non-Coulomb potentials. We can mention the study of many-electron atoms with a certain number of active electrons in presence of a (non-Coulomb) dressed nucleus modeling the inner

electrons. Molecular systems can be equally studied, in a way similar to the scheme used in [21]. The method here discussed leads straightforwardly to the optimal basis set for those systems.

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