Generating optimal Sturmian basis functions for atomic problems

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(Received 8 January 2010; revised manuscript received 16 March 2010; published 27 April 2010)

In this paper we discuss the optimization of Sturmian basis functions by studying bound atomic systems within the configuration interaction method. Our investigation clearly shows how the fulfillment of correct physical boundary conditions at short and large distances from the nucleus improves the convergence rate of the method. This is illustrated first through a one-electron atom, and then with the two-electron systems. For the ground state of the helium atom, and with 35 Sturmian functions per electron and angular momenta, we obtain an energy of −2.903 712 820 a.u., outperforming previous similar calculations [Bromley and Mitroy, Int. J. Quantum Chem. **107**, 1150 (2007)].

DOI: 10.1103/PhysRevA.81.042520 PACS number(s): 31.15.A−

I. INTRODUCTION

Several methods have been developed to approximately solve the Schrödinger equation for two-electron atoms. Probably the simplest is the configuration interaction (CI) method in which the two-electron wave functions are expanded in spherical harmonics (or biharmonics) and a complete basis set for each radial coordinate [1,2]. Although the rate of convergence with the CI approach is not as fast as that obtained with other methods which use all interparticle coordinates (see, e.g., [3–5]), its extension to deal with n-electron atomic systems is straightforward; uncorrelated basis functions remain therefore a very useful tool. The convergence rate of CI expansions is strongly related to the properties of the chosen radial configurations. In this contribution we address this issue by proposing an optimized way of defining the basis functions. Applications first to a one-electron atomic model, and then to two-electron systems, will illustrate the efficiency of the method. Improved energy convergence rates are particularly significant if large or complex systems were to be studied.

The main characteristics of atomic wave functions can be exemplified by a one-electron system Schrödinger equation in the s-wave ($l = 0$) model:

$$\left[-\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + U(r) - E\right]\Phi(r) = 0, \tag{1}$$

where the first term in the brackets is the kinetic energy, $U(r)$ is a central potential, $E < 0$ is the energy (only bound states will be considered here), and $\Phi(r)$ is the radial wave function. Atomic potentials associated with Coulomb-like interactions can be written as $U(r) = U_{\rm aux}(r) + \tilde{U}(r)$, where the auxiliary potential $U_{\rm aux}(r)$ is assumed to have well-defined Coulomb-like behaviors associated with the charges $Z_{\rm in}$ and $Z_{\rm as}$, respectively, in the limits $r \to 0$ and $r \to \infty$; $\tilde{U}(r)$ models a short-range perturbation, without Coulomb-like singularities. The physical boundary conditions imposed to the wave function $\Phi(r)$ are integrability and regularity in the range $r \in [0,\infty)$. In addition, the Coulomb character of the potential $U_{\rm aux}(r)$ provides well-defined behaviors,

$$\lim_{r\to 0}\frac{d\Phi(r)}{dr} = -Z_{\rm in}\Phi(r) \tag{2a}$$

$$\lim_{r\to\infty}\Phi(r) \propto \varphi_{\rm as}(r) = e^{-\kappa r - \frac{Z_{\rm as}}{\kappa}\ln(2\kappa r)}, \tag{2b}$$

where $\kappa = \sqrt{-2E} > 0$. Relation (2a) corresponds to Kato cusp condition for two-body coalescence [6].

One kind of radial basis functions which has been widely used in CI calculations is the set of Coulomb Sturmian Functions (CSF) [1,2,7]. They are solutions of a two-body Coulomb Schrödinger equation, where the charge of the Coulomb potential is considered as the eigenvalue, and the (negative) energy is taken as an externally fixed parameter, the same for all CSF. This makes the basis elements having the same damped asymptotic behavior [i.e., the same κ value in Eq. (2b)]. A two-point boundary condition (regularity at the origin and the exponential behavior at infinity) problem can be set and is of the form of the Sturm-Liouville theory. This is why the CSF were named Sturmians (see, e.g., Ref. [8,9]).

Different CI approaches have been implemented using Sturmian functions, based on adequate choices of the energy parameters. In this way, the damped behavior of the basis is adjusted to reproduce the truly bound state behavior, and then the convergence rate of the expansions increased. However, none of these basis sets fulfills the correct physical conditions that the wave function should have, that is, the cusp conditions at the Coulomb singularities and appropriate logarithmic factors in the asymptotic behavior given for the one-electron case, by relations (2a) and (2b), respectively. Instead of the fixed values $Z_{\rm as}$ and $Z_{\rm in}$, the eigenvalue appears in those equations for the CSF case. As a consequence an unnecessary large number of CSF will be required to represent the proper behavior in both regions.

In this report we continue with the study initiated in our previous publication [10,11], concerning the optimization of the Sturmian Functions (SF) basis. We explicitly show how adjusting the basis functions to have the proper behavior both at the origin and at large distances increases the convergence rate of the CI approach. To do so, we apply the method introduced in Ref. [10] to generate different types of SF basis satisfying: i) condition (2a) but not (2b); ii) condition (2b) but not (2a); and iii) both conditions (2a) and (2b). For comparison, we also generate CSF which do not satisfy either (2a) or (2b). All these basis functions are first applied to the study of a simple two-particle atomic model (Sec. II), in order to illustrate how

each of these properties affect the convergence of the energy calculation. The application to two-electron systems is then considered (Sec. III). We first study the Temkin-Poet (TP) model to put in evidence that, with an optimized choice of the parameters, substantially smaller matrices are needed to obtain a similar level of energy accuracy. Then, we perform highly accurate calculations of the partial-wave series of the ground state of the helium atom. Our energy values are compared with those obtained with the high-precision CSF variational calculations of Bromley and Mitroy [1], and with ours published in [10]. Concluding remarks are given in Sec. IV.

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

II. STURMIAN BASIS FUNCTIONS FOR ONE-ELECTRON SYSTEMS

The Sturm-Liouville (SL) eigenvalue problem [9] is based on the following equation, defined in the closed interval $[a,b]$:

$$-\frac{d}{dr}\left(p(r)\frac{dy_n(r)}{dr}\right)+q(r)y_n(r)=\beta_n\omega(r)y_n(r), \tag{3}$$

together with the boundary conditions:

$$\left[a_1\frac{dy_n(r)}{dr}+a_2y_n(r)\right]_{r=a}=0 \tag{4a}$$

$$\left[b_1\frac{dy_n(r)}{dr}+b_2y_n(r)\right]_{r=b}=0, \tag{4b}$$

where a_i,b_i $(i=1,2)$ are constants independent of the eigenvalue β_n. Provided $p(r)$, $q(r)$, and the weight function $\omega(r)$ are continuous on $[a,b]$, Eqs. (3), (4a), and (4b) define a complete and discrete ($n\in\mathbb{N}$) set of solutions $y_n(r)$ in the interval, with well–known properties including orthogonality and closure relations:

$$\int_a^b y_{n'}(r)\omega(r)y_n(r)dr=\delta_{n',n} \tag{5a}$$

$$\sum_{n=1}^{\infty}y_n(r)\omega(r)y_n(r')=\delta(r-r'). \tag{5b}$$

We recall that our aim is to investigate how to optimize Sturmian basis functions to solve the physical problem given by Eq. (1) together with conditions (2a) and (2b). We shall restrict the discussion to s-wave ($l=0$) models, the generalization to higher angular momenta being straightforward. Atomic-like basis functions $\Phi_n(r)$, adequate for CI expansions, can be obtained by comparing Eqs. (3) with (1) and setting $p(r)=r^2/2$, $q(r)=r^2[U_{\rm SL}(r)-E]$, $\omega(r)=r^2V(r)$, and $y_n(r)=\Phi_n(r)$; $U_{\rm SL}(r)$ and $V(r)$ are atomic potentials whose singularities at $r=0$ are not worse than r^{-1}. Besides the regularity and integrability conditions, the physical restrictions (2a) and (2b) can be converted into SL boundary conditions (4a) and (4b) with the choice $a_1=1$ and $a_2=Z_{\rm in}$ at the point $r=a=0$, and $b_1=1$ and $b_2=\kappa+\frac{Z_{\rm as}}{\kappa r}$ for $r=b\to\infty$.

Special care must be taken when cusp conditions are imposed through Eq. (4a), since a regularity condition was already assumed at $r=0$. If $V(r)$ had a Coulomb singularity, the charge $Z_{\rm in}$ associated to a cusp condition of a regular function would be dependent of the eigenvalue β_n since it is multiplying $\omega(r)$ in Eq. (3). When $V(r)$ has no Coulomb (or worse) divergence at $r=0$, the only Coulomb divergence is associated with the externally fixed potential $U_{\rm SL}(r)$: In this case a unique (physical) cusp condition can be imposed. We can therefore fulfill both conditions (the cusp and regularity ones) at the small price of restricting the action of the potential $V(r)$ close to $r=0$.

We must also be prudent when imposing the fall-off condition, since it is not a point boundary condition, but an asymptotic one. Again, in order that the condition (4b) takes the form of Eq. (2b) for $r\to\infty$ with $Z_{\rm as}$ independent of the eigenvalue, $V(r)$ must be a short-range potential, and the charge $Z_{\rm as}$ must belong uniquely to the potential $U_{\rm SL}(r)$ ($U_{\rm SL}\to Z_{\rm as}/r$ for $r\to\infty$).

These properties imply inner and asymptotic behaviors which are eigenvalue independent [11]. As a result, the whole set of Sturmians functions conform a discrete and complete set which have: i) the same asymptotic behavior, corresponding to a particle of energy E moving in the outer region of a Coulomb potential with charge $Z_{\rm as}$; and ii) the same cusp condition, associated with the charge $Z_{\rm in}$. In intermediate regions, each of the basis functions represents a particle moving in a potential with different magnitude β_n; $V(r)$ plays an important role in the method and is referenced as the generating potential.

The best value of the energy E in the Sturmian equation (which appears also in the asymptotic behavior through κ) seems to be the energy of the state they are intended to represent; the latter is, of course, not known until a first simple (low-order) diagonalization is performed. However, one can always estimate it with alternative methods such as independent electron models in the case of two- and many-electron atoms.

The numerical procedure employed to evaluate the Sturmian functions and eigenvalues for arbitrary potentials has been described in an earlier publication [10] and will not be presented here. We only need to mention that the numerical relative precision of the expansion is of the order of 10^{-8}–10^{-9}, small enough for the present purposes.

By setting $U_{\rm SL}(r)=0$ and $V(r)=-\frac{1}{r}$ in our evaluation algorithms, we are able to generate also CSF as a particular case. They correspond to Coulomb potentials of different magnitudes so that they cannot satisfy the proper, unique, Kato cusp condition (2a), or indeed have the proper asymptotic behavior (2b). Both $Z_{\rm in}$ and $Z_{\rm as}$ are eigenvalue dependent and vary with n. Thus, an expansion in terms of CSF will require a large number of basis functions to represent appropriately the behaviors at the cusp and in the asymptotic region. As this implies an unnecessary large number of basis functions, the CSF basis set is not ideal—in this sense—to represent an atomic system.

From now on, for simplicity, we will use in the expansions the functions $S_n(r)=r\Phi_n(r)$ rather than $\Phi_n(r)$. Among the main properties of the functions $S_n(r)$ we can mention the nondegeneracy of the eigenvalues β_n, and the orthonormality and closure relations [see Eqs. (5a) and (5b)]:

$$\int_0^{\infty}dr\,S_{n'}(r)V(r)S_n(r)=\delta_{n',n}, \tag{6a}$$

$$\sum_{n=1}^{\infty}S_n(r')S_n(r)V(r)=\delta(r-r'). \tag{6b}$$

Let us study the ground state of the two-particle system described by the radial Schrödinger equation (1) with the potential $U(r) = U_{\rm aux}(r) + \tilde{U}(r)$, where

$$U_{\rm aux}(r) = -\frac{Z_{\rm as}}{r} + \frac{(-Z_{\rm in} + Z_{\rm as})e^{-\alpha r}}{r}, \tag{7}$$

and $\tilde{U}(r)$ is a perturbation which does not modify the Coulombic behavior of $U_{\rm aux}(r)$ neither at $r \to 0$ nor for $r \to \infty$. For the illustration, we choose $\tilde{U}(r)$ as

$$\tilde{U}(r) = \tilde{U}_0 e^{-\sigma(r-r_0)^2}, \tag{8}$$

(α,σ, and r_0 are positive parameters).

By choosing $U_{\rm SL}(r) = U_{\rm aux}(r)$ in the Sturm-Liouville equation (3), all eigenfunctions will have the same Coulomb properties as the state we want to represent through the CI expansion. The solution $\Phi(r)$ of Eq. (1) with condition (2a) is approximated by

$$\Psi(r) = \sum_{n=1}^{N_{1e}} a_n \frac{S_n(r)}{r}, \tag{9}$$

where N_{1e} is the size of the radial basis.

We take as generating potential,

$$V(r) = -\frac{e^{-\lambda r}}{r}\left[r^{\delta} e^{-\gamma r^2} + \left(1 - e^{-\gamma r^2}\right)\right], \tag{10}$$

with $\delta > 0$ and $\gamma > 0$ so that no further Coulomb singularities are added. The exact ground-state wave function can be obtained with a very precise numerical algorithm [12]. For illustration purposes, we diagonalize the radial Eq. (1) using $N_{1e} = 7$ SF, with the following parameters: $Z_{\rm in} = -1$, $Z_{\rm as} = -1/4$, $\alpha = 0.9$, $\tilde{U}_0 = -1/2$, $r_0 = 5/2$, and $\sigma = 5$. The eigenenergies E and the expansion coefficients a_n are obtained through the Galerkin method [10]. Figure 1 shows the exact ground-state wave function and the seven SF (top panel) and CSF (bottom panel). It is evident that the SF span a smaller region of the space, where the bound state develops. In the region $r > 5$ a.u., the SF have an exponentially damped behavior (in agreement with the physical state), while the $n = 6$ and $n = 7$ CSF still have a local maximum.

The differences in behavior between the CSF and SF sets, with respect to conditions (2a) and (2b), can be seen from Figs. 2 and 3 where we plot the ratios $\frac{1}{\Phi_n(r)}\frac{d\Phi_n(r)}{dr}$ and $S_n(r)/\varphi_{as}(r)$, respectively. In Fig. 3 a unique ratio $(-Z_{\rm in})$ is found through the SF construction, but not for CSF. In Fig. 2 we clearly observe that the asymptotic behavior is eigenvalue dependent for CSF but not for SF.

In order to investigate the role of the fulfillment by the basis of proper boundary conditions, the energy parameter was set equal to the value obtained with Ref. [12] with an accuracy of 10^{-14}, which for brevity we will call "exact" value. In this way, we concentrate only on the effects of the Coulomb potentials. For that purpose we performed four different variational calculations (Sturmian expansions) with different parameters λ, δ, and γ. In the first one we choose $\lambda = 0$, $\delta = 0$, and $\gamma = 0$ for the generating potential, that is, $V(r) = -1/r$; this expansion does not preserve the conditions (2a) and (2b), and

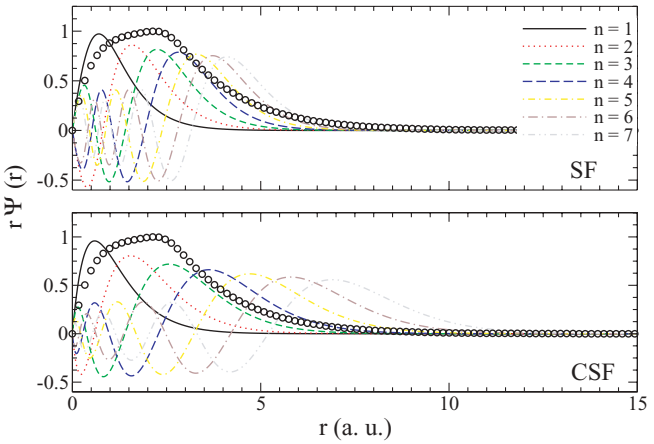

FIG. 1. (Color online) $r\Psi(r)$ (open circles) and seven asymptotically optimized SF (lines, top) and CSF (lines, bottom).

is similar to a CSF expansion (it differs only through the central potential $U_{\rm SL}(r)$, which is not the purely Coulomb one as in the CSF case). In a second calculation ($\delta = \gamma = 0$), we vary the parameters δ and γ, in order to impose to the expansion only condition (2a), without taking care of the asymptotic behavior. In the third calculation, we gradually change the asymptotic behavior of the basis set from having different Coulomb factors (associated to each eigenvalue) to having only one corresponding to $Z_{\rm as}$; in this case, however, we do not preserve the Kato condition at the origin. Finally, we impose both conditions (2a) and (2b), by varying all three parameters. In Table I, we compare the exact energy value $E_{\rm exact}$ [12] with the results obtained with these different SF expansions of size $N_{1e} = 5$ (the CSF result is also included). We can clearly see by looking at the relative errors ΔE that the imposition of the correct physical boundary conditions on the basis improves the energy value of the diagonalizations. Besides, it appears also that imposing the correct asymptotic behavior has more relevance for the convergence than the cusp condition. These results show that with the same number of basis functions better energies are obtained when the physics of the state to be represented is incorporated in the basis functions.

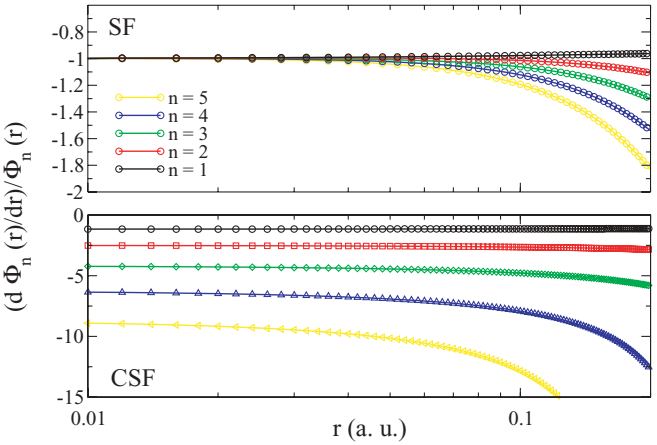

FIG. 2. (Color online) $\frac{1}{\Phi_n(r)}\frac{d\Phi_n(r)}{dr}$ as a function of r for the first five SF (top) and CSF (bottom).

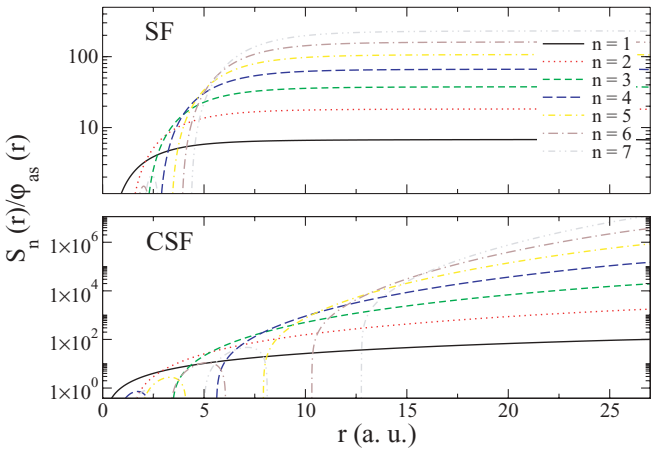

FIG. 3. (Color online) $S_n(r)/\varphi_{as}(r)$, with $\varphi_{as}(r)$ defined by (2b), as a function of r, for the first five SF (top) and CSF (bottom).

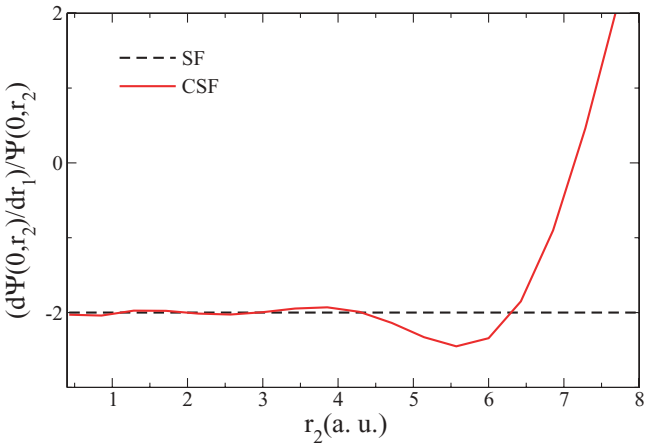

FIG. 4. (Color online) $R(r_1,r_2)=\frac{1}{\Psi(r_1,r_2)}\frac{d\Psi(r_1,r_2)}{dr_1}$ evaluated at $r_1=0$, as a function of r_2. The two-electron wave function was evaluated by means of the SF with condition (2a) (dashed line) and the CSF (solid line).

III. STURMIAN BASIS FUNCTIONS FOR TWO-ELECTRON SYSTEMS

Consider now the Schrödinger equation for two-electron systems of nuclear charge Z ($Z=2$ for helium):

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_1}-\frac{1}{2}\nabla^2_{\mathbf{r}_2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}-E\right]\Psi(\mathbf{r}_1,\mathbf{r}_2)=0. \quad (11)$$

As is usual in uncorrelated CI calculations, we use a partial-wave expansion of the electron-electron potential,

$$\frac{1}{r_{12}}=\sum_{l=0}^{\infty}\frac{r_<^l}{r_>^{l+1}}\frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_l^m(\hat{\mathbf{r}}_1)Y_l^{m*}(\hat{\mathbf{r}}_2). \quad (12)$$

We propose an expansion of the wave function of the form:

$$\Psi_S^{L,M}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\nu}^{N_{2e}}a_\nu^{L,M,S}\Phi_{\nu,S}^{L,M}(\mathbf{r}_1,\mathbf{r}_2), \quad (13)$$

where

$$\Phi_{\nu,S}^{L,M}(\mathbf{r}_1,\mathbf{r}_2)=\mathcal{A}_S\frac{S_{n_1,l_1}(r_1)}{r_1}\frac{S_{n_2,l_2}(r_2)}{r_2}\mathcal{Y}_{l_1,l_2}^{L,M}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2), \quad (14)$$

($\nu=\{l_1,l_2,n_1,n_2\}$), and the operator $\mathcal{A}_S$ is defined by

$$\mathcal{A}_S F(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}[F(\mathbf{r}_1,\mathbf{r}_2)+(-1)^S F(\mathbf{r}_2,\mathbf{r}_1)], \quad (15)$$

ensuring spin symmetry. The basis elements (14) are eigenstates of the total angular momentum operator and its projection along the $\hat{\mathbf{z}}$ axis, with quantum numbers L and M, respectively. Parity conservation $(-1)^L=(-1)^{l_1+l_2}$ restricts the angular quantum numbers. The radial indexes should also be restricted to avoid redundancies in the expansion. For example, for the TP model in which only the $l=0$ term is retained in (12), the number N_{2e} of two-electron configurations is given in terms of the number N_{1e} of one-electron functions (see [10] for details):

$$N_{2e}=\tfrac{1}{2}N_{1e}[(-1)^S+N_{1e}]. \quad (16)$$

Hereafter we shall consider only the $S=0$ case.

In the following illustrations we aim to show the advantages of our optimized SF over the traditional CSF. To achieve this, we start with simple TP calculations and then present results of high-precision calculations for the real helium atom. The central potential of the two-electron atomic system is purely Coulombic (charge $Z=2$). In order to model the electron-electron repulsion when one of the coordinate r_i is large, we propose to use the same potential $U_{SL}(r)$ taken in the one-electron case (Sec. II), which includes a pure Coulomb potential as a particular case [see Eq. (7)]. We then study different values of the asymptotic charges when generating the basis, in order to compare with a CSF calculation. A very simple ($N_{1e}=7$) variational calculation for the TP ground-state energy yielded the following optimal basis parameters: $\gamma=4$, $\lambda=0.25$, $\delta=0.5$, $\alpha=1.1$, $Z_{in}=2$, and $Z_{as}=1.14$. The value of Z_{as} appears as a screened charge and thus simulates the effect of the interelectronic repulsion term.

TABLE I. Energy E and relative errors $\Delta E=|(E-E_{exact})/E_{exact}|$ obtained with a CSF expansion and with three different SF expansions satisfying separately conditions (2a) or (2b), or both (2a) and (2b). The exact value was found through the use of a precise algorithm [12]. All values are in atomic units.

	E	ΔE	λ	δ	γ
Exact, E_{exact}	−0.239 06	0	–	–	–
CSF	−0.231 82	0.0303	0	0	0
SF (2a)	−0.232 71	0.0266	0	8	4
SF (2b)	−0.235 77	0.0138	0.23	0	0
SF (2a) and (2b)	−0.236 09	0.0128	0.41	9	4

TABLE II. Energy E and relative errors ΔE obtained with $N_{1e}=7$ CSF and SF for the Temkin-Poet model (the SF result corresponds to the optimal parameters: $\gamma=4$, $\lambda=0.25$, $\delta=0.5$, $\alpha=1.1$, $Z_{in}=2$, and $Z_{as}=1.14$). All values are in atomic units.

	E	ΔE
Exact [13]	−2.879 028 767	0
CSF	−2.878 933 952	$3.3\ 10^{-5}$
SF	−2.879 010 264	$6.4\ 10^{-6}$

TABLE III. Sets of parameters p_i used in generating the Sturmian basis functions for $L_i = 0$ and $L_i = 12$. The sets p_0 and p_{12} are used for the results shown in Tables IV and V, respectively. All values are in atomic units.

	L_i	E_i	Z_{in}	Z_{as}	α	λ	δ	γ
p_0	0	−1.27	−2	−2	0	0.44	0.3	4
p_{12}	12	−1.05	−2	−2	0	0.93	0.3	4

The total wave function $\Psi(r_1,r_2)$ is set to satisfy the two electron-nucleus Kato cusp conditions in the limits $r_i \to 0$ ($i = 1,2$) with $-Z_{\text{in}} = -2$; this value corresponds also to a variational minimum. The effect of this condition can be appreciated in Fig. 4, where the ratio $R(r_1,r_2) = \frac{1}{\Psi(r_1,r_2)} \frac{d\Psi(r_1,r_2)}{dr_1}$, evaluated at $r_1 = 0$, is plotted as a function of r_2. We see that, as it should be for the exact wave function, the SF expansion gives the ratio $R(r_1,r_2) = -Z_{\text{in}}$ on the whole range $[0,\infty)$, while the CSF calculation shows a strong r_2 dependence.

The adequate treatment of the two-body cusp conditions and asymptotic behavior gives an improvement in the convergence rates of the two-electron expansions. This can be appreciated from observing Table II, where the energy results obtained with both the SF and CSF basis for $N_{1e} = 7$, are compared to the exact TP result [13]. Note that according to Eq. (16) the size of the two-electron basis for $N_{1e} = 7$ is $N_{2e} = 28$. To get the same order of accuracy as the SF result, $N_{1e} = 11$ CSF are needed (which correspond to $\Delta E = 8.0 \times 10^{-6}$), so that the two-electron basis size ($N_{2e} = 66$) is slightly more than the double of the SF case. With this number of SF an even better energy result would be obtained. This improvement in the convergence is in agreement with the results presented in an earlier publication [10], where only the asymptotic behavior of the basis was optimized through the generating potential for the complete helium calculations; SF yielded better results than other CSF calculations.

Let us now consider the real helium atom and larger calculations varying L_i, the maximum number of angular momenta per electron. To be able to compare directly with the work of Bromley and Mitroy [1], we choose L_i from 0 to 12, and use $N_{1e} = 20$ or $N_{1e} = 35$ radial SF for the angular momentum quantum number l_i associated with each electron. In Ref. [1], the authors performed a variational calculation, for each l_i, over the Laguerre parameter, noted here λ_{BM}, which is related to the CSF energy through $E_i^{(\text{BM})} = \frac{\lambda_{\text{BM}}^2}{2}$; this implied 13 variational parameters for their largest calculation. In our previous work [10], we made use of $N_{1e} = 20$ only, and obtained better energies than Bromley and Mitroy for the $L_i = 0$ (TP) and $L_i = 12$ cases. We should also emphasize that, in that paper, we varied only the λ parameter of the generating Yukawa potential (we also varied E_i to obtain the $L_i = 12$ result); the electron-nucleus cusp conditions were not fulfilled since we used $\delta = 0$ in Eq. (10). Using the λ parameter obtained for the $L_i = 0$ case, we computed the $L_i = 1,..,12$ cases, and obtained better results than in Ref. [1], but only for $L_i = 1$.

In the present study we introduce more parameters to control the features of the generating potential, besides the energy (E_i) and the range of the Yukawa factor λ. We first noted that no screening effects were necessary when the number of basis elements per electron N_{1e} is big enough, so we chose $Z_{\text{as}} = 2$. Also, we fixed the Coulomb behavior at the origin, setting $Z_{\text{in}} = 2$. Since the calculations with a pure Yukawa generating potential gave very accurate results, we chose $\gamma = 4$. This prevents the modification of the potential in the intermediate or asymptotic region, but allows the fulfillment of the electron-nucleus cusp conditions.

These considerations left us with only three variational parameters: E_i, λ, and δ. We chose to perform sequential optimizations for these parameters, for $L_i = 0$ and $L_i = 12$. This means to variationally select δ first, while λ and E_i are held fixed. Then, the best energy E_i is found with the new value of δ fixed, and so on. The starting point of this iteration scheme were the best parameters of our previous work [10], (i.e., $E_i = -1.483\,85$, $\lambda = 0.375$, and $\delta = 0$ for $L_i = 0$, and $E_i = -1.05$, $\lambda = 0.795$, and $\delta = 0$ for $L_i = 12$). This simple iterative mechanism converges after two iterations to optimal sets of parameters, noted p_i, which are recorded in Table III, for the two angular momenta L_i considered.

In Tables IV and V we show the results of our calculations of the helium ground-state energy evaluated with $N_{1e} = 20$, and compare them with our previous results [10], with those of Bromley and Mitroy [1], and the reference values of [13,14]. From Table IV (set of parameters p_0), it is clear that the present results are better than our previous ones for $L_i = 0,1,2,3,4$; they are also better than those of Ref. [1] but only for $L_i =$

TABLE IV. Partial-wave analysis of the helium ground state. L_i ($i = 1,2$) is the maximum angular momentum considered for each electron. Our present results, obtained with parameter set p_0 given in Table III, are compared with those published in Refs. [1] and [10], evaluated with $N_{1e} = 20$ one-electron basis functions for each radial coordinate and partial wave L_i. The values of the variational energy parameters E_i^{BM} are also indicated. Reference (noted Exact) values are from Refs. [13,14]. All values are in atomic units.

		E_{L_i}: He ground-state energy (parameter set p_0, $N_{1e} = 20$ per l_i)		
L_i	N_{1e}	Present work	Previous work [10]	Ref. [1]
0	20	−2.879 028 688	−2.879 028 654	−2.879 028 507 ($E_0^{\text{BM}} = 11.520$)
1	40	−2.900 516 042	−2.900 515 957	−2.900 515 873 ($E_1^{\text{BM}} = 30.420$)
2	60	−2.902 766 487	−2.902 766 371	−2.902 766 378 ($E_2^{\text{BM}} = 51.050$)
3	80	−2.903 320 534	−2.903 320 378	−2.903 320 527 ($E_3^{\text{BM}} = 73.205$)
4	100	−2.903 517 846	−2.903 517 659	−2.903 517 973 ($E_4^{\text{BM}} = 98.000$)
Exact		−2.903 724 377 [14]		
Exact ($L_i = 0$)		−2.879 028 767 [13]		

TABLE V. Same as Table IV but using the basis parameters indicated as p_{12} (see Table III). In these calculations we also use $N_{1e} = 20$ radial functions per coordinate and for each partial wave term L_i. All values are in atomic units.

		E_{L_i}: He ground-state energy (parameter set p_{12}, $N_{1e} = 20$ per l_i)		
L_i	N_{1e}	Present work	Previous work [10]	Ref. [1]
0	20	−2.879 028 733	−2.879 028 654	−2.879 028 507 ($E_0^{\mathrm{BM}} = 11.520$)
1	40	−2.900 516 156	−2.900 515 957	−2.900 515 873 ($E_1^{\mathrm{BM}} = 30.420$)
2	60	−2.902 766 709	−2.902 766 371	−2.902 766 378 ($E_2^{\mathrm{BM}} = 51.050$)
3	80	−2.903 320 888	−2.903 320 378	−2.903 320 527 ($E_3^{\mathrm{BM}} = 73.205$)
4	100	−2.903 518 349	−2.903 517 659	−2.903 517 973 ($E_4^{\mathrm{BM}} = 98.000$)
5	120	−2.903 605 403	−2.903 604 533	−2.903 605 022 ($E_5^{\mathrm{BM}} = 120.12$)
6	140	−2.903 649 522	−2.903 648 475	−2.903 649 142 ($E_6^{\mathrm{BM}} = 146.20$)
7	160	−2.903 674 195	−2.903 672 975	−2.903 673 821 ($E_7^{\mathrm{BM}} = 174.84$)
8	180	−2.903 689 042	−2.903 687 656	−2.903 688 677 ($E_8^{\mathrm{BM}} = 202.00$)
9	200	−2.903 698 496	−2.903 696 951	−2.903 698 142 ($E_9^{\mathrm{BM}} = 231.12$)
10	220	−2.903 704 795	−2.903 703 098	−2.903 704 451 ($E_{10}^{\mathrm{BM}} = 262.20$)
11	240	−2.903 709 147	−2.903 707 307	−2.903 708 815 ($E_{11}^{\mathrm{BM}} = 292.82$)
12	260	−2.903 712 247	−2.903 710 272	−2.903 711 927 ($E_{12}^{\mathrm{BM}} = 325.12$)
Exact		−2.903 724 377 [14]		
Exact ($L_i = 0$)		−2.879 028 767 [13]		

0,1,2,3, so that no further improvement in the results would be obtained compared to [10]. On the other hand, the results obtained with the set p_{12} (Table V) are consistently better than the values given in Ref. [1], and closer to the exact value for a given L_i. The performance of each basis can be appreciated by inspecting the energy increments $\Delta E_i = E_i - E_{i-1}$. Indeed, for relatively small values of N_{1e}, one can observe that the SF basis performs better for $L_i < 6$, while for $L_i \geqslant 6$ no significant improvement is observed, the results being then quite similar to those obtained with the CSF. This is related to the fact that, for $L_i > 0$, the fulfillment of the cusp conditions has only a small effect; however, it is measurable because the basis parameter accommodates itself to minimize globally the mean energy. At the same time, for all L_i, the SF basis still performs better because of its adequate description of asymptotic conditions. Further improvements could be gained by varying the α parameter for each partial wave.

Now, one could ask whether these optimal generating Sturmian basis parameters (p_{12}) would work for even larger basis-size calculations. To answer this question, we compare our results obtained with this set with the very accurate variational values given by Bromley and Mitroy [1] with $N_{1e} = 35$ CSF and $L_i + 1$ variational parameters (i.e., 13 for $L_i = 12$). More specifically, they used $N_{1e} = 35$ orbitals for each l_i except for $l_i = 0$ and $l_i = 1$ for which they use $N_{1e} = 44$ and $N_{1e} = 36$, respectively. Here, we choose $N_{1e} = 44$ for

TABLE VI. Same as Table IV but using the basis parameters indicated as p_{12} (see Table III). In these calculations we use $N_{1e} = 35$ radial functions per coordinate and for each partial wave term L_i, except at $L_i = 0$ for which we use $N_{1e} = 44$ functions per coordinate. This is done in order to compare with calculations of Ref. [1] (see text). All values are in atomic units.

	E_{L_i}: He ground-state energy (parameter set p_{12}, $N_{1e} = 35$ per l_i)			
L_i	N_{1e}	Present work	N_{1e}	Ref. [1]
0	44	−2.879 028 762	44	−2.879 028 760 ($E_0^{\mathrm{BM}} = 36.98$)
1	70	−2.900 516 241	80	−2.900 516 228 ($E_1^{\mathrm{BM}} = 67.28$)
2	105	−2.902 766 843	115	−2.902 766 823 ($E_2^{\mathrm{BM}} = 103.68$)
3	140	−2.903 321 071	150	−2.903 321 045 ($E_3^{\mathrm{BM}} = 147.92$)
4	175	−2.903 518 582	185	−2.903 518 552 ($E_4^{\mathrm{BM}} = 184.32$)
5	210	−2.903 605 686	220	−2.903 605 654 ($E_5^{\mathrm{BM}} = 224.72$)
6	245	−2.903 649 854	255	−2.903 649 820 ($E_6^{\mathrm{BM}} = 259.92$)
7	280	−2.903 674 574	290	−2.903 674 539 ($E_7^{\mathrm{BM}} = 307.52$)
8	315	−2.903 689 465	325	−2.903 689 430 ($E_8^{\mathrm{BM}} = 351.12$)
9	350	−2.903 698 961	360	−2.903 698 926 ($E_9^{\mathrm{BM}} = 392.00$)
10	385	−2.903 705 298	395	−2.903 705 263 ($E_{10}^{\mathrm{BM}} = 435.12$)
11	420	−2.903 709 686	430	−2.903 709 652 ($E_{11}^{\mathrm{BM}} = 480.50$)
12	455	−2.903 712 820	465	−2.903 712 786 ($E_{12}^{\mathrm{BM}} = 528.12$)
Exact		−2.903 724 377 [14]		
Exact ($L_i = 0$)		−2.879 028 767 [13]		

$L_i = 0$, to be able to compare the TP value, and $N_{1e} = 35$ for all other angular momenta $L_i = 1, \ldots, 12$. This choice leads to a slightly smaller basis calculation than in Ref. [1]. Table VI shows that, even though optimized for a smaller basis, our results are still better than those of Bromley and Mitroy [1], for all values of the angular momenta. As far as we know, the helium ground-state energy −2.903 712 820 a.u. is the best value obtained with uncorrelated basis functions.

In Tables IV–VI, we have included, for each L_i, the $E_i^{(\mathrm{BM})}$ values which are related to the only adjustable parameter λ_{BM} of the CSF [1]. Optimization over these parameters results in energies E_i which can be about 500 times larger than our values for the largest angular momentum considered ($L_i = 12$). As these values increase considerably with L_i, the optimization is clearly not being performed over the asymptotic wave-function behavior. Instead, it is being used to avoid the spread of the basis to regions where the amplitude of the ground state is negligible. This is done in a natural way with our SF since the generating potential controls the range of the basis set (see [10] for details), and variational minima of the energies are in accordance with the true asymptotic behavior.

IV. CONCLUDING REMARKS

An overview of the CI method with Sturmian functions was presented, with an emphasis on the role of the Coulomb behavior of the auxiliary and generating potentials. Basically, we propose adequate conditions on the generating potential $V(r)$ in order that the whole set of Sturmian functions—and hence the constructed expansion representing the state—satisfy unique two-body electron-nucleus Kato cusp conditions, and has a unique Coulomb-like logarithmic asymptotic behavior. With this choice the Sturmian set concentrates in the region where the atomic wave function is mainly located. This is in contrast with the case of the CSF which, by construction, include many different behaviors in both regions.

Two illustrations were given. For one particle moving in a model central potential, the properties of the SF basis at $r \to 0$ and $r \to \infty$ exactly match those of the physical state to be represented. With this optimal choice, the CI method is highly convergent and superior to the CSF expansion. Two-electron systems are then studied. Through an adequate election of the generating potential, the two electron-nucleus Kato cusp conditions were exactly imposed on the total wave function. The convergence was also accelerated by means of an asymptotic Coulomb charge, in the auxiliary potential of the Sturmian basis, simulating the effect of the interelectronic repulsion term. For the Temkin-Poet model, the comparison between different Sturmian expansions shows that the number of two-electron CSF must be almost twice the number of optimized SF in order to obtain the same level of energy accuracy. We have then considered the partial wave series of the helium atom in its ground state, including the full electron-electron correlation. Our optimized SF basis yielded better results compared to the—already very accurate—energy values published by Bromley and Mitroy [1].

Hence, our study has illustrated how, if n-electron systems were to be studied in a similar way, the optimization of the radial basis functions may reduce considerably the computational size, and yield better energy values.

ACKNOWLEDGMENTS

The support provided by the Lorraine region for the visit of Dr. Gasaneo and Dr. Randazzo to the Laboratoire de Physique Moléculaire et des Collisions, Université Paul Verlaine–Metz, is gratefully acknowledged. This work has been supported by PICT Grant Nos. 08/0934 and 20548/04 of the ANPCYT (Argentina) and PGI Grant No. 24/F049, Universidad Nacional del Sur (Argentina).

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