

Use of double-bound three-body Coulomb distorted-wave-like basis sets for two-electron wave functions

G. Gasaneo¹ and L. U. Ancarani²¹*Departamento de Física, Universidad Nacional del Sur and Consejo Nacional de Investigaciones Científicas y Técnicas, 8000 Bahía Blanca, Buenos Aires, Argentina*²*Laboratoire de Physique Moléculaire et des Collisions, Université Paul Verlaine–Metz, 57078 Metz, France*

(Received 30 August 2007; revised manuscript received 8 November 2007; published 8 January 2008)

The double-bound analog of the double-continuum three-body Coulomb (C3) wave function, recently introduced by the authors, allows us to propose two different basis sets of correlated functions which can be used for describing double-bound states. The components of the two basis diagonalize the Coulomb interactions but differ in the definition of the distortion factor which depends only on the interelectronic coordinate. In the first set, this factor includes a nonlinear parameter, while the second set contains parameter-free functions. Through an angular correlated configuration interaction method it is possible to generate highly correlated wave functions for S bound states of heliumlike systems. By construction, these states form an orthogonal set, satisfy all two-body cusp conditions, and retain the C3 double-continuum character. Even when a limited number of configurations is included, rather good energy values for the ground and excited states are obtained. A systematic improvement by inclusion of more configurations can be easily achieved, in particular with the computationally efficient, parameter-free basis.

DOI: [10.1103/PhysRevA.77.012705](https://doi.org/10.1103/PhysRevA.77.012705)

PACS number(s): 34.80.Dp, 32.80.Fb, 31.15.V–

I. INTRODUCTION

Understanding the quantum dynamics of a strongly correlated atomic system in collision with charged particles (electrons or ions) and radiation is a fundamental problem in atomic physics. In particular, the double ionization of two-electron atomic systems allows one to gain some knowledge on electron-electron correlations, at the same time, in the initial (bound) and final (continuum) states. Since the three-body quantum problem has no known solution, approximated wave functions are used when calculating double ionization cross sections. A balanced description of the initial and final two-electron states should avoid spurious contributions in collision calculations and seems to play a key role in reproducing experimental data (see more details below). The purpose of this contribution is to investigate this issue in the case of the widely used double-continuum three-body Coulomb (C3) wave function [1] [also called the 3C or Brauner-Briggs-Klar (BBK) model]. A first step toward this aim was achieved in Ref. [2] where the doubly bound analog of the C3 wave function was presented. However, since in that reference the focus was on the ground state, no radial and only a limited amount of angular correlation was included. Here, we pursue the investigation by proposing basis sets of C3-like function. These can be used to construct highly correlated two-electron wave functions for bound S states which are of the same family as that describing the double-continuum C3 wave function.

The motivation behind this investigation comes from a series of recent theoretical results, for both double-photoionization (DPI) and $(e,3e)$ processes on helium, which need further clarification. The theoretical description of the DPI process with wave functions, initial and final, which do not satisfy exactly the same Schrödinger equation yield gauge-dependent results. Thus, even when approximated wave functions for the two-electron initial and final

channels are used, they should be solutions of the same Hamiltonian, or at least treated with the same level of approximation; otherwise, discrepancies between gauges are observed [3,4]. A similar pattern is observed in the case of double ionization by electron impact. When describing $(e,3e)$ processes, for example, on helium, unbalanced approximated wave functions for the initial and final channels lead to disagreement between the calculated [5–8] and the experimental absolute cross sections measured at high incident energy [9]. When the double continuum is described by the C3 wave function [1], magnitude disagreements are observed if angularly and radially correlated initial wave functions are used [6–8,10,11]. On the other hand, agreement is found if the initial state is described by simpler functions which have only angular correlation, defined here as the dependence on the relative interelectronic distance only. Similarly to the C3 double continuum, these functions consist of the product of two bound Coulomb wave functions for the electron-nucleus interactions and a distortion function for the electron-electron interaction; examples used are the Pluvinaige [12,13] and C3-like bound wave functions [6–8], or others [6,7]. However, if more advanced final states are used in combination with these simple initial states, magnitude agreement is lost [5,14] (more details can be found in the Introduction in Ref. [2]).

From these studies, it can be concluded that symmetrical or quasisymmetrical wave functions for the initial and final channels (i.e., those which treat correlation with the same level of approximation) lead to a satisfactory theoretical description of $(e,3e)$ processes, at least in the high incident energy regime. However, this conclusion does not apply to the DPI case [7]. Thus, those functions seem to be balanced only when applied to the $(e,3e)$ process. It is clearly interesting to investigate the possibility of improving the description of both the bound and continuum two-electron states, maintaining a similar treatment, and see the effect on double

ionization cross sections. As concerns the double continuum, improvements of the original C3 wave function can be achieved through the introduction of coordinate- or velocity-dependent effective charges, thus including dynamical screening. However, the choice of effective charges is arbitrary, and the improvement is highly dependent on the kinematical conditions of the double ionization process under scrutiny (see Ref. [2] for a more detailed discussion).

In this contribution, we shall concentrate on improving the initial double-bound state: our aim is to build highly correlated two-electron wave functions (including both radial and angular correlation), which are constructed in a similar fashion to the continuum C3 wave function. The doubly bound analog for S states of the C3 continuum wave function is given by the product of two Coulomb functions associated to the electron-nucleus dynamics by a distortion factor describing the electron-electron interaction (thus containing angular correlation only) [2]. The result was obtained by double analytic continuation of the relative electron-nucleus momenta to the complex plane [2], leading to a set of two quantum numbers associated to bound states for each electron. The relative momentum appearing in the continuum distortion factor is also analytically continued, and may be considered either as a nonlinear variational parameter, or as a source of a new quantum number associated to the interelectronic distance. According to this selection, the corresponding double-bound C3 analog functions can be used to build basis sets of correlated functions which either depend on variational parameters or contain parameter-free functions. These basis sets allow us to construct approximate two-electron wave functions for S states through an angular correlated configuration interaction (ACCI) method implemented along the lines of Refs. [15,16]. The approach of configuration interaction has been used many times in the past with various basis functions. Here, differently from what was previously proposed, each component of the basis sets preserves the properties of the original C3 bound analog, i.e., (i) it satisfies Kato's cusp conditions [17] at all of the two-body coalescence points and (ii) it includes an angular correlation which diagonalizes the electron-electron Coulomb interaction. With both basis sets, the Schrödinger equation is transformed into a set of linear algebraic equations which can be easily solved by standard matrix methods. The application to the construction of approximate two-electron wave functions for S states with different degrees of radial and angular correlation is presented, not only for the ground state ($Z=1-3$ of the helium isoelectronic sequence) but also for excited states ($Z=2$). It should be mentioned that, though it is feasible, there is no intention here to obtain highly sophisticated two-electron wave functions.

The rest of this paper is structured as follows. In Sec. II, we present the double-bound C3-like functions and introduce the two C3-like basis sets. In Sec. III a configuration interaction approach for bound S states is presented, and numerical results for ground and excited states of two-electron atoms are given in Sec. IV. A summary and some perspectives are given in Sec. V. Atomic units are used throughout.

II. C3-LIKE FUNCTIONS

A. Double-bound C3-like functions

We first recall that the C3 double-continuum wave function is defined by [1] the product of two continuum Coulomb wave functions $C(\alpha, \mathbf{k}, \mathbf{r})$ (for electrons 1 and 2 of, respectively, coordinates \mathbf{r}_1 and \mathbf{r}_2 relative to the infinitely heavy nucleus) and by a distortion factor (for the electron-electron relative vector $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$ part). Using the same notation as in [2], it is given by

$$\Psi_{C3} = N_{C3} C(\alpha_1, \mathbf{k}_1, \mathbf{r}_1) C(\alpha_2, \mathbf{k}_2, \mathbf{r}_2) D(\alpha_{12}, \mathbf{k}_{12}, \mathbf{r}_{12}) \quad (1)$$

(we refer to [2] for the differential equation satisfied by this wave function). \mathbf{k}_1 and \mathbf{k}_2 represent the two electron momenta relative to the nucleus, while the relative momentum \mathbf{k}_{12} is given by

$$\mathbf{k}_{12} = (\mathbf{k}_1 - \mathbf{k}_2)/2. \quad (2)$$

The Sommerfeld parameters α_j ($j=1,2$) and α_{12} defined by $\alpha_j = \frac{Zz_j}{k_j}$ ($j=1,2$) and $\alpha_{12} = \frac{z_1 z_2}{2k_{12}}$ are directly related to the corresponding Coulomb potentials. Here we shall consider the case of two electrons ($z_1=z_2=-1$) in the field of a nucleus of charge Z .

Consider now the negative energy case (bound case, labeled hereafter by a superscript B). To study the double-bound analog of the C3 continuum wave function it is convenient to start from its partial wave expansion [2]

$$\Psi_{C3} = \left(\sum_{l_1} R_{l_1, k_1}(r_1) P_{l_1}(\cos \theta_1) \right) \left(\sum_{l_2} R_{l_2, k_2}(r_2) P_{l_2}(\cos \theta_2) \right) \times \left(\sum_{l_{12}} A_{l_{12}, k_{12}}(r_{12}) P_{l_{12}}(\cos \theta_{12}) \right), \quad (3)$$

where $P_l(\cos \theta)$ are Legendre polynomials, θ_1 (respectively, θ_2, θ_{12}) is the angle between \mathbf{k}_1 and \mathbf{r}_1 (respectively, \mathbf{k}_2 and \mathbf{r}_2 , and \mathbf{k}_{12} and \mathbf{r}_{12}). $R_{l_j, k_j}(r_j)$ are the l_j radial Coulomb partial waves ($j=1,2$),

$$R_{l_j, k_j}(r_j) = e^{-\pi/2\alpha_j} (2l_j + 1) \frac{\Gamma(l_j + 1 - i\alpha_j)}{\Gamma(2l_j + 2)} (2ik_j r_j)^{l_j} \times e^{-ik_j r_j} {}_1F_1(l_j + 1 - i\alpha_j, 2l_j + 2, 2ik_j r_j),$$

and the $A_{l_{12}, k_{12}}$ are given by

$$A_{l_{12}, k_{12}}(r_{12}) = e^{-\pi/2\alpha_{12}} \frac{\Gamma(1 - i\alpha_{12}) \Gamma(l_{12} + i\alpha_{12})}{\Gamma(i\alpha_{12}) (2l_{12} - 1)! l_{12}!} (-ik_{12} r_{12})^{l_{12}} \times {}_1F_1(l_{12} + i\alpha_{12}, 2l_{12} + 2, -2ik_{12} r_{12}).$$

We can now perform the analytic continuation by replacing k_j by iZz_j/n_j , so that $i\alpha_j = n_j$, where $n_j = 1, 2, 3, \dots$ ($j=1,2$) [18]. The two continuum Coulomb partial waves in r_1 and r_2 get transformed into the product $\varphi_{n_1, l_1}(r_1) \varphi_{n_2, l_2}(r_2)$ of two radial hydrogenic bound functions of principal quantum numbers n_1 and n_2 , and orbital numbers l_1 and l_2 ,

$$\varphi_{n, l}(r) = N_{n, l} e^{-Zr/n} {}_1F_1\left(1 + l - n, 2l + 2, \frac{2Zr}{n}\right),$$

where the normalization is given by

$$N_{n,l} = \frac{1}{(2l+1)} \left[\left(\frac{2Z}{n} \right)^3 \frac{(n+l)!}{2n(n-l-1)!} \right]^{1/2}$$

and we have explicitly set $z_1 = z_2 = -1$. The bound energy E of the system becomes $E^B = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}$. The corresponding Γ factors, $\Gamma(1+l_j-n_j)$, present a pole for zero or negative value of $1+l_j-n_j$. As in the case of the two-body Coulomb problem (see Ref. [18]), these poles (zeros of the S matrix) remove the exponentially divergent part of the continuum wave function leading, thus, to the bound states $\varphi_{n_i}(r)$. Since k_1 and k_2 become imaginary by analytic continuation, it is reasonable to expect the modulus k_{12} to become imaginary as well, so that k_{12} can be replaced by a single value $i\kappa$. However, this assumption ignores the mathematical link between k_{12} and k_1, k_2 [see Eq. (2)]. Indeed, the modulus $k_{12} = \frac{1}{2}(k_1^2 + k_2^2 - 2\mathbf{k}_1 \cdot \mathbf{k}_2)^{1/2}$ depends on k_1, k_2 and the angle between \mathbf{k}_1 and \mathbf{k}_2 .

In terms of the hydrogenic quantum number n_1, n_2, l_1 , and l_2 , and the numbers κ and l_{12} , the doubly bound analog Ψ_{C3}^B of the continuum Ψ_{C3} is thus given as a triple sum of individual terms

$$\begin{aligned} \Psi_{C3}^B &= \Psi_{C3}^B(n_1, n_2, \kappa, l_1, l_2, l_{12}) \\ &= [\varphi_{n_1, l_1}(r_1) P_{l_1}(\cos \theta_1)] [\varphi_{n_2, l_2}(r_2) P_{l_2}(\cos \theta_2)] \\ &\quad \times \left[{}_1F_1\left(l_{12} + \frac{1}{2\kappa}, 2l_{12} + 2, 2\kappa r_{12}\right) P_{l_{12}}(\cos \theta_{12}) \right]. \end{aligned} \quad (4)$$

B. C3-like basis sets

In this paper we are interested in generating a basis set based on the C3 model that can be used to solve the two-electron Hylleraas equation [see Eqs. (14) and (15) below] for S bound states. For this reason we restrict the function given by Eq. (4) to the case $l_1 = l_2 = l_{12} = 0$, so that

$$\begin{aligned} \Psi_{C3}^B(n_1, n_2, \kappa) &= \Psi_{C3}^B(n_1, n_2, \kappa, 0, 0, 0) \\ &= N_{C3}^B(n_1, n_2, \kappa) \varphi_{n_1}(r_1) \varphi_{n_2}(r_2) \\ &\quad \times {}_1F_1\left(\frac{1}{2\kappa}, 2, 2\kappa r_{12}\right), \end{aligned} \quad (5)$$

where we drop the l 's, and $N_{C3}^B(n_1, n_2, \kappa)$ is the bound normalization factor.

Two alternative basis sets for S states can be defined with the bound functions $\Psi_{C3}^B(n_1, n_2, \kappa)$. The first one, $\{\Psi_{C3}^B(n_1, n_2, \kappa_{n_1, n_2})\}_{NL}$, named nonlinear and abbreviated NL hereafter, is constructed in terms of the $\Psi_{C3}^B(n_1, n_2, \kappa)$ themselves. Different nonlinear parameters κ_{n_1, n_2} are used for each pair of n_1 and n_2 values, with $\kappa_{n_1, n_2} = \kappa_{n_2, n_1}$ by symmetry constraints. The inclusion of variational nonlinear parameters in a basis implies the use of optimization techniques which adds an additional degree of numerical difficulty when solving the Hylleraas equation (see Sec. III).

A second basis set, named parameter free and abbreviated PF hereafter, can be constructed by considering κ as a source for a new quantum number. Indeed, by setting

$\kappa = -1/(2n_{12})$ ($n_{12} = 1, 2, \dots$), the correlation function of Eq. (5) reduces to a Laguerre polynomial $L_{n_{12}}^{(1)}\left(-\frac{r_{12}}{n_{12}}\right)$ of order n_{12} . With these parameter-free functions, the PF basis set $\{\Psi_{C3}^B(n_1, n_2, -\frac{1}{2n_{12}})\}_{PF}$ can be defined. It is interesting to mention here that n_{12} might be considered, in addition to n_1 and n_2 , as a third quantum number (one associated to each of the three relative coordinates r_1, r_2 , and r_{12} , similarly to the Sturmian functions used by Li and Shakeshaft [19]). All Laguerre polynomials $L_{n_{12}}^{(1)}\left(-\frac{r_{12}}{n_{12}}\right)$ have in common the first-order polynomial $L_1^{(1)}(-r_{12}) = 1 + \frac{r_{12}}{2}$ which indicates that all basis set elements satisfy the correct electron-electron cusp condition. To avoid repetitions, from a numerical point of view, it is convenient to use a slightly modified—but equivalent—basis $\{\Phi_{C3}^B(n_1, n_2, n_{12})\}_{PF}$, where

$$\Phi_{C3}^B(n_1, n_2, n_{12}) = N_{C3}^B\left(n_1, n_2, -\frac{1}{2n_{12}}\right) \varphi_{n_1}(r_1) \varphi_{n_2}(r_2) \chi_{n_{12}}(r_{12}) \quad (6)$$

and

$$\chi_{n_{12}}(r_{12}) = \begin{cases} L_1^{(1)}(-r_{12}), & n_{12} = 1, \\ L_{n_{12}}^{(1)}\left(-\frac{r_{12}}{n_{12}}\right) - L_1^{(1)}(-r_{12}), & n_{12} > 1. \end{cases}$$

Both the PF and NL basis functions are eigenfunctions of the C3-bound Hamiltonian

$$H_{C3}^B = D_0 - 2\kappa \frac{\partial}{\partial r_{12}}, \quad (7)$$

with D_0 given by

$$\begin{aligned} D_0 &= \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) + \frac{z_1 Z}{r_1} \right] \\ &\quad + \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} \right) + \frac{z_2 Z}{r_2} \right] \\ &\quad + \left[-\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) + \frac{z_1 z_2}{r_{12}} \right], \end{aligned} \quad (8)$$

and $\kappa = -1/(2n_{12})$ in the PF case. By construction, they diagonalize the Coulomb potentials and thus satisfy Kato's cusp conditions [17] at the two-body coalescence points.

For the ground state the double-bound C3 model wave function $\Psi_{C3}^B(n_1, n_2, -\frac{1}{2n_{12}})$ reduces to

$$\Psi_{C3}^B\left(1, 1, -\frac{1}{2n_{12}}\right) = N_{C3}^B\left(1, 1, -\frac{1}{2n_{12}}\right) e^{-Zr_1 - Zr_2} L_{n_{12}}^{(1)}\left(-\frac{r_{12}}{n_{12}}\right). \quad (9)$$

In particular, when $n_{12} = 1$, the first-order polynomial leads exactly to the correlation function suggested by Patil [20] and the ground-state wave function of our model coincides with Patil's proposal,

$$\Psi_{C3}^B\left(1,1,-\frac{1}{2}\right) = N\left(1,1,-\frac{1}{2}\right) e^{-Zr_1-Zr_2} \left(1 + \frac{r_{12}}{2}\right). \quad (10)$$

On the other hand, when $n_{12} \rightarrow \infty$ [or alternatively $\kappa \rightarrow 0$ in Eq. (5)], we obtain the wave function [2]

$$\Psi_{C3}^B(1,1,0) = N_{C3}^B(1,1,0) e^{-Zr_1-Zr_2} \frac{I_1(2\sqrt{r_{12}})}{\sqrt{r_{12}}}, \quad (11)$$

where $I_1(z)$ represents a Bessel function [21]. The use of these wave functions, as well as the optimized NL one of Eq. (5), as approximated solutions for the He ground state ($Z=2$) have been discussed in more details in Ref. [2].

Since the basis sets $\{\Psi_{C3}^B(n_1, n_2, \kappa_{n_1, n_2})\}_{NL}$ and $\{\Psi_{C3}^B(n_1, n_2, -\frac{1}{2n_{12}})\}_{PF}$ include only double-bound functions, they cannot be considered as complete. For the purpose of writing the S -state solutions of the Hylleraas equation, one should complete the basis set with C3-like functions having (a) one bound (n_2) and one continuum (p_1) electron states (labeled $B-C$)

$$\Psi_{C3}^{B-C}(p_1, n_2, p_{12}) = R_{0, p_1}(r_1) \varphi_{n_2}(r_2) A_{0, p_{12}}(r_{12}), \quad (12)$$

or a symmetrized version; and (b) double-continuum states (p_1, p_2) (labeled $C-C$), i.e., the zero angular momentum radial functions of Eq. (3),

$$\Psi_{C3}^{C-C}(p_1, p_2, p_{12}) = R_{0, p_1}(r_1) R_{0, p_2}(r_2) A_{0, p_{12}}(r_{12}). \quad (13)$$

We have defined the basis functions $\Psi_{C3}^{B-C}(p_1, n_2, p_{12})$ and $\Psi_{C3}^{C-C}(p_1, p_2, p_{12})$ in terms of general momenta p_1 , p_2 , and p_{12} to have the chance to associate a momentum to each coordinate as in the case of the double-bound wave functions $\Psi_{C3}^B(n_1, n_2, -\frac{1}{2n_{12}})$. By including the functions defined by Eqs. (12) and (13) the two complete basis sets become nonlinear $\{\Psi_{C3}^B(n_1, n_2, \kappa_{n_1, n_2}), \Psi_{C3}^{B-C}(p_1, n_2, p_{12}), \Psi_{C3}^{C-C}(p_1, p_2, p_{12})\}_{NL}$ and parameter free $\{\Psi_{C3}^B(n_1, n_2, -\frac{1}{2n_{12}}), \Psi_{C3}^{B-C}(p_1, n_2, p_{12}), \Psi_{C3}^{C-C}(p_1, p_2, p_{12})\}_{PF}$. As discussed in Ref. [2] the double-bound analog of the double-continuum C3 wave functions are not orthogonal with each other; the same applies with the continuum functions.

Before proceeding, in the next section, with the construction of approximate two-electron S bound states, it is worth adding a comment on the basis set built on Pluvillage-type functions [12]. In Ref. [2] we have underlined the fact that these are not the correct analog of the C3 double-continuum wave function contrary to a common belief (see, e.g., [10, 13, 22]). Indeed, a Coulomb function $e^{-i\kappa r_{12}} {}_1F_1(1 - \frac{i}{2\kappa}, 2, 2i\kappa r_{12})$ is used to represent the electron-electron correlation [instead of ${}_1F_1(\frac{1}{2\kappa}, 2, 2\kappa r_{12})$ as in Eq. (5)], and correspond to a bound energy $E_{PLU}^B = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} + \kappa^2$. A nonlinear basis set $\{\Psi_{PLU}^B(n_1, n_2, \kappa)\}_{PLU, NL}$ has nevertheless been suggested, whether with a constant variational parameter κ [10] or with variational parameters κ_{n_1, n_2} [11, 14]. Moreover, by setting $\kappa = \frac{i}{2N_{12}}$, $N_{12} = 1, 2, \dots$ (negative energy contribution to E_{PLU}^B) one gets parameter-free functions [6] and one may construct a parameter-free basis set $\{\Psi_{PLU}^B(n_1, n_2, N_{12})\}_{PLU, PF}$.

III. SUPERPOSITION OF CONFIGURATIONS FOR TWO-ELECTRON BOUND S STATES WAVE FUNCTIONS

In this section we want to use the basis discussed above to construct double-bound approximated solutions Ψ^B for the S bound states. We thus use the Hylleraas equation

$$H_S \Psi^B = E_S^B \Psi^B, \quad (14)$$

where we label E_S^B the energy, and H_S is given by

$$H_S = D_0 + \left(-\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_{12} \frac{\partial}{\partial r_1} + \hat{\mathbf{r}}_2 \cdot \hat{\mathbf{r}}_{12} \frac{\partial}{\partial r_2} \right) \frac{\partial}{\partial r_{12}}. \quad (15)$$

The last term in H_S involves mixed partial derivatives and introduces the nonseparability character of the three-body system.

In the numerical calculations which shall be presented in the next section, we shall restrict the use of the basis sets to double-bound functions; the (more delicate) inclusion of the bound-continuum and the double-continuum functions will be considered in a separated contribution. With the PF and NL basis sets, we define the angular correlated configuration interaction solutions of Eq. (14) as either

$$\Psi_{PF}^B = \sum_{n_1, n_2, n_{12}} c_{n_1, n_2, n_{12}} \Psi_{C3}^B\left(n_1, n_2, -\frac{1}{2n_{12}}\right) \quad (16)$$

or

$$\Psi_{NL}^B = \sum_{n_1, n_2} b_{n_1, n_2, \kappa_{n_1, n_2}} \Psi_{C3}^B(n_1, n_2, \kappa_{n_1, n_2}). \quad (17)$$

In either case, the approximated wave functions Ψ^B satisfy Kato's cusp conditions [17] since each basis set function does.

The coefficients $c_{n_1, n_2, n_{12}}$ in Eq. (16) are obtained by solving the generalized eigenvalue problem

$$\sum_{n_1, n_2, n_{12}} (\hat{H}_S - E_S^B \hat{S}) c_{n_1, n_2, n_{12}} = 0, \quad (18)$$

where \hat{S} is the overlap matrix of elements

$$S_{m_1, m_2, m_{12}, n_1, n_2, n_{12}} = \left\langle \Psi_{C3}^B\left(m_1, m_2, \frac{-1}{2m_{12}}\right) \middle| \Psi_{C3}^B\left(n_1, n_2, \frac{-1}{2n_{12}}\right) \right\rangle,$$

and \hat{H}_S is the Hamiltonian matrix of elements

$$H_{S, m_1, m_2, m_{12}, n_1, n_2, n_{12}} = \left\langle \Psi_{C3}^B\left(m_1, m_2, \frac{-1}{2m_{12}}\right) \middle| H_S \middle| \Psi_{C3}^B\left(n_1, n_2, \frac{-1}{2n_{12}}\right) \right\rangle.$$

Standard matrix methods (diagonalization) are used. The task of evaluating the Hamiltonian matrix elements is considerably reduced because the basis elements $\Psi_{C3}^B(n_1, n_2, -\frac{1}{2n_{12}})$ are eigenfunctions (diagonal functions) of the Hamiltonian H_{C3}^B [Eq. (7)]. Hence, only the matrix elements of the mixed partial derivatives appearing in the definition of the full Hamiltonian H_S [Eq. (15)] must be evaluated. Besides,

TABLE I. Mean energy for the ground state of the He atom obtained with $\Psi_{C3}^B(1, 1, -\frac{1}{2n_{12}})$ for $n_{12}=1, 2, \dots, \infty$.

| n | n_{12} | $\langle E \rangle$ | $-E_{\text{exact}}$ |
|-----|----------|---------------------|---------------------|
| 1 | 1 | 2.87658 | |
| 1 | 2 | 2.87854 | |
| 1 | 3 | 2.87816 | |
| 1 | ∞ | 2.87462 | 2.9037 ^a |

^aDrake [23].

analytical expressions for $S_{m_1, m_2, m_{12}, n_1, n_2, n_{12}}$ and $H_{S, m_1, m_2, m_{12}, n_1, n_2, n_{12}}$ can be derived. Note also that the fact of having a parameter-free basis set implies that the diagonalization of Eq. (18) leads directly to the energies E_S^B and the coefficients (linear parameters) $c_{n_1, n_2, n_{12}}$ corresponding to a given number of basis functions.

If the NL basis functions $\Psi_{C3}^B(n_1, n_2, \kappa_{n_1, n_2})$ are used, a set of equations similar to (18) is obtained for coefficients (linear parameters) $b_{n_1, n_2, \kappa_{n_1, n_2}}$; again, only the matrix elements of the mixed partial derivatives must be evaluated. The difference with the PF case is that the energies E_S^B obtained by diagonalization will depend on the nonlinear parameters κ_{n_1, n_2} . Thus, an optimization procedure should be implemented, implying that a large number of diagonalization must be performed in the minimization process. In addition, both the Hamiltonian and the overlap matrix elements must be evaluated numerically, clearly increasing the numerical difficulties in comparison to the PF basis.

IV. NUMERICAL RESULTS

The basis sets and the method described in the preceding sections are now applied to the study of approximated ground and excited states of two-electron atoms (helium isoelectronic sequence). Different classes of approximated double-bound states can be generated with the proposal of Eqs. (16) and (17). We shall denote by n the total number of functions included in the series. In each case, the mean energies $\langle E \rangle$ are calculated with the full three-body Hamiltonian H_S , and are compared to the numerically exact value taken from Ref. [23].

A first class is obtained with functions which have the same structure as the double-continuum C3 wave function (i.e., functions with angular but no radial correlation), built with one of the functions ($n=1$) belonging to either the PF or the NL basis set [2]. For example, with the PF basis set, we can vary the degree of angular correlation of the ground-state function $\Psi_{C3}^B(1, 1, -\frac{1}{2n_{12}})$ [Eq. (9)]. For the He atom ($Z=2$), the differences observed in the mean energies for $n_{12}=1, 2, 3, \dots, \infty$ (Table I) are directly associated to their angular correlation factors. Within this class the best energy of functions is obtained for $n_{12}=2$, while a mean energy of -2.87462 a.u. is found for the limit $n_{12} \rightarrow \infty$. The NL basis set, on the other hand, does not offer the chance of including different degrees of angular correlation without including radial correlation (see below). The function $\Psi_{C3}^B(1, 1, \kappa_{1,1})$ is

the only one associated to the ground state and only one parameter can be adjusted. The optimization of Eq. (18) yields $\kappa_{1,1} = -0.255$, and a mean energy of -2.87854 a.u. [2], a result which is almost identical to that obtained with $\Psi_{C3}^B(1, 1, -\frac{1}{4})$ (second row of Table I, $n_{12}=2$) because of the value $\kappa_{1,1} = -0.255$.

In the next step, we consider the function Eq. (16) keeping $n_1 = n_2 = 1$ but including more angular correlation to the trial wave function by adding—up to saturation—several n_{12} terms (n of them). This leads to functions with the structure $\varphi_1(r_1)\varphi_1(r_2)\chi(r_{12})$, where $\chi(r_{12})$ represents the global angular correlation factor. No radial correlation is included. Using the numerically convenient basis elements $\Phi_{C3}^B(n_1, n_2, n_{12})$ [see Eq. (6)], the mean energies are found by solving Eq. (18). Saturation in energy is reached with $n=5$, for both the He atom $\langle E \rangle = -2.87935$ a.u. (2.9037 a.u. [23]) and the H⁻ ion $\langle E \rangle = -0.49844$ a.u. (0.5277 a.u. [23]). For illustration, when including up to three n_{12} terms, the normalized two-electron wave function for the He ground state reads

$$\Psi_{1s^2}^B = 0.62096[\Phi_{C3}^B(1, 1, 1) - 19.0708\Phi_{C3}^B(1, 1, 2) + 14.0106\Phi_{C3}^B(1, 1, 3)] \quad (19)$$

[although the coefficients look large, one should keep in mind that the powers in r_{12} in the $\chi_{n_{12}}(r_{12})$ functions are multiplied by small numbers]. The result for the H⁻ ion shows that it is not possible to get a bound state for this system without adding radial correlation. This fact has important consequences in collision problems. If symmetrical theories are going to be used to evaluate cross sections of, e.g., $(e, 3e)$ processes, there is no way to treat the double ionization of H⁻ with the C3 double continuum and an equivalent wave function for the initial channel. Some degree of radial correlation must be included in the initial, double-bound state, and thus an equivalent step beyond the C3 approach is necessary.

Note that the functions so far considered are said to include angular correlation only, a terminology which we now briefly discuss. When compared to those of the independent particle model (IPM), these functions differ by the correlation factor $\chi(r_{12})$ which depends purely on the r_{12} coordinate, and not (explicitly) on the r_1 and/or r_2 coordinates (the only dependence on r_1 and r_2 is indirect, through r_{12}). Thus, we define correlation with respect to the IPM, and define angular correlation as the amount of correlation included by factors which depend only on the interparticle distance r_{12} . Moreover, since the basis functions, and the functions built in terms of them, diagonalize all the Coulomb potentials, the correlation is mathematically related to the cross derivatives of the three-body Hamiltonian, and hence to the coupling that they produce between the two-body problems (which are exactly solved by the basis functions).

A more advanced and more interesting class of approximated two-electron bound wave functions can be constructed with the PF basis by including multiple configurations. It is obtained by summing several n_1 and n_2 terms in the series of Eq. (16), thus including both radial and angular correlation. In Table II we present the optimized ground state energies

TABLE II. Mean energies for the ground state of H^- ($Z=1$), He ($Z=2$), and Li^+ ($Z=3$) obtained with the PF and NL functions, Eqs. (16) and (17), with n_1 and n_2 up to 2, and including up to $n_{12}=5$ angular correlation factors in the PF case.

| | n | n_1 | n_2 | n_{12} | $-\langle E \rangle_{PF}$ | $-\langle E \rangle_{NL}$ | $-E_{\text{exact}}$ |
|-------|-----|-------|-------|-----------|---------------------------|---------------------------|---------------------|
| $Z=1$ | 4 | 1,2 | 1,2 | 1 | 0.5226 | 0.5231 | |
| | 8 | 1,2 | 1,2 | 1,2 | 0.5255 | | |
| | 12 | 1,2 | 1,2 | 1,2,3 | 0.5265 | | |
| | 16 | 1,2 | 1,2 | 1,2,3,4 | 0.5269 | | |
| | 20 | 1,2 | 1,2 | 1,2,3,4,5 | 0.5270 | | 0.5277 ^a |
| $Z=2$ | 4 | 1,2 | 1,2 | 1 | 2.8882 | 2.8897 | |
| | 8 | 1,2 | 1,2 | 1,2 | 2.8952 | | |
| | 12 | 1,2 | 1,2 | 1,2,3 | 2.8986 | | |
| | 16 | 1,2 | 1,2 | 1,2,3,4 | 2.9002 | | |
| | 20 | 1,2 | 1,2 | 1,2,3,4,5 | 2.9009 | | 2.9037 ^a |
| $Z=3$ | 4 | 1,2 | 1,2 | 1 | 7.2621 | 7.2649 | |
| | 8 | 1,2 | 1,2 | 1,2 | 7.2698 | | |
| | 12 | 1,2 | 1,2 | 1,2,3 | 7.2736 | | |
| | 16 | 1,2 | 1,2 | 1,2,3,4 | 7.2756 | | |
| | 20 | 1,2 | 1,2 | 1,2,3,4,5 | 7.2764 | | 7.2799 ^a |

^aDrake [23].

obtained for the He atom, the H^- and the Li^+ ions, by solving Eq. (18) when including the configurations $1s1s$, $1s2s$, $2s1s$, and $2s2s$ (i.e., n_1 and n_2 up to 2), and with n_{12} up to 5. By increasing the total number n of basis functions, the mean energies are improved, and a bound state is predicted for the H^- ion. The comparison of the mean energies with the numerically exact values [23] shows that relative accuracies of 1.33×10^{-3} , 1.14×10^{-3} , and 4.80×10^{-4} are obtained for the H^- , He, and Li^+ systems, respectively. Our energy values are much better than those obtained with the Hartree-Fock method and even better than those obtained with the transcorrelated variational Monte Carlo method [24]. A result obtained with the NL proposal, Eq. (17), is also shown in Table II. Two observations can be done: (i) there is no way of improving the value obtained without including other configurations; (ii) the optimization procedure of the nonlinear parameters is computationally much more expensive than the procedure required for the PF basis set.

For comparison we have also performed calculations with the parameter-free basis set $\{\Psi_{PLU}^B(n_1, n_2, N_{12})\}_{PLU,PF}$. The convergence rate observed with these functions is smaller

than that with the C3-like PF basis set. As an example, the energies resulting for the He atom with the same $1s1s$, $1s2s$, $2s1s$, and $2s2s$ configurations are -2.8555 a.u. with $n_{12}=1$ ($n=4$), -2.8859 a.u. with $n_{12}=1, 2$ ($n=8$), and -2.8906 a.u. with $n_{12}=1, 2, 3$ ($n=12$). A few calculations with the nonlinear basis set $\{\Psi_{PLU}^B(n_1, n_2, \kappa)\}_{PLU,NL}$ have been performed whether with a constant variational parameter κ [10] or with variational parameters κ_{n_1, n_2} [11, 14]. Similarly to what was observed with the NL basis set $\{\Psi_{C3}^B(n_1, n_2, \kappa_{n_1, n_2})\}_{NL}$, convergence toward good energy values is rather slow and the calculations are computationally expensive, as a delicate optimization of the nonlinear parameters κ_{n_1, n_2} is required.

The calculation performed to obtain the results of Table II provide us also with wave functions and energies of excited states. In Table III we show the results for excited states 2^1S , 2^3S , 3^1S , and 3^3S , obtained when including the configurations $1s1s$, $1s2s$, $2s1s$, $1s3s$, $3s1s$, and $2s2s$ (i.e., n_1 and n_2 up to 3) and with n_{12} up to 5. We can see how the energies of the 2^1S , 2^3S , 3^1S , and 3^3S states are improved when the terms with either n_1 or $n_2=3$ are included. On the other hand, the quality of the energies is not improved by including the

TABLE III. Mean energies for the ground state and the first excited states for the He atom ($Z=2$) obtained with wave functions, Eq. (16), with n_1 and n_2 up to 3 as indicated, and including up to $n_{12}=5$ angular correlation factors.

| Configurations included | n | $-\langle E \rangle_{1s^2}$ | $-\langle E \rangle_{2^1S}$ | $-\langle E \rangle_{2^3S}$ | $-\langle E \rangle_{3^1S}$ | $-\langle E \rangle_{3^3S}$ |
|-------------------------------------|-----|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $1s1s+(1s2s+2s1s)$ | 15 | 2.9003 | 2.1136 | 2.1549 | 1.7905 | 1.8107 |
| $1s1s+(1s2s+2s1s)+2s2s$ | 20 | 2.9009 | 2.1137 | 2.1549 | 1.7905 | 1.8155 |
| $1s1s+(1s2s+2s1s)+(1s3s+3s1s)$ | 25 | 2.9009 | 2.1454 | 2.1748 | 2.0468 | 2.0597 |
| $1s1s+(1s2s+2s1s)+(1s3s+3s1s)+2s2s$ | 30 | 2.9014 | 2.1453 | 2.1748 | 2.0486 | 2.0598 |
| Exact | | 2.9037 ^a | 2.1459 ^a | 2.1752 ^a | 2.0612 ^a | 2.0687 ^a |

^aDrake [23].

$2s2s$ configuration in the calculations except for the 1^1S level for which a non-negligible contribution is observed. Also the doubly excited state $2s^2^1S$ can be obtained. For example, with a wave function generated with the $1s1s$, $1s2s$, $2s1s$, $1s3s$, $3s1s$, and $2s2s$ configurations, and with up to $n_{l2}=5$ angular functions ($n=20$), one finds a mean energy of -0.7659 a.u. which is in good agreement with the value -0.7685 a.u. reported by Lipsky *et al.* [25] and the value -0.7776 a.u. reported by Dulieu and Le Sech [26].

It is interesting to underline the fact that the constructed functions for ground and excited states form an orthogonal set of wave functions because all of them are obtained in the same diagonalization process of an approximated Hermitian Hamiltonian. Moreover, the energies for all of these states can be systematically further improved by increasing the number of configurations and/or angular correlation functions. While this is quite computationally expensive for the NL basis, it is rather easy and efficient with the PF basis set. As mentioned in the Introduction, we should remind the reader, however, that the two-electron wave functions proposed here cannot compete with advanced variational wave functions. The aim here is to build approximated wave functions of a certain class, i.e., C3-like.

V. SUMMARY AND PERSPECTIVES

In this paper we have addressed three different but closely related issues.

First, two alternative C3-like basis sets of angular correlated functions for S states are defined. The basis sets include both double-bound, bound-continuum, and double-continuum functions. Due to the fact that they diagonalize all the Coulomb interactions, they satisfy all the two-body Kato cusp conditions at the divergence of the Coulomb potentials. They are defined as the product of two two-body Coulomb functions (for the electron-nucleus parts) multiplied by a distortion function for the electron-electron interaction. One of the basis sets, named NL, includes nonlinear parameters in the double-bound part of the distortion factor. On the other hand, the second basis set, named PF, is parameter free.

Second, we implement an ACCI method where a linear combination of the double-bound basis functions is used to write the solution of the Hylleraas equation for heliumlike S states. The use of both the NL and the PF basis sets transforms the Hylleraas equation into an algebraic set of equations that can be solved by standard matrix methods. A single diagonalization provides the linear coefficients and the level energies; an orthogonal set of wave functions for ground and excited states is obtained. With the PF basis set, the Hamiltonian and overlapping matrix elements can be derived analytically, and the energy values are directly obtained. With

the NL basis, on the other hand, the algebraic equations must be solved many times in the optimization process of the nonlinear parameters. This, together with the fact that the matrix elements are not analytical, increases considerably the numerical difficulty.

Finally, the ACCI method with the proposed basis sets is applied to construct correlated bound wave functions for heliumlike systems. For both the ground and excited states we have obtained quite good results with just a few terms; systematic improvement can be easily achieved by including more configurations (and hence more correlation) in the trial wave function, retaining the same C3-like properties. While the proposed wave functions cannot compete with sophisticated variational wave functions, our energy values are quite good when compared, for example, to Hartree-Fock results.

The present study of the C3-like correlated wave functions could be extended along several lines. First, bound states other than S states could be investigated. This would require defining a basis set including nonzero angular momentum values. Second, the inclusion of bound-continuum and continuum-continuum functions to complete the basis set should be investigated. Third, a systematic procedure to improve the two-electron trial wave functions, without breaking the cusp conditions, has been recently explored in Refs. [15,16]. A preliminary investigation has shown that the approximated wave functions discussed above can be easily and effectively improved. This approach, however, destroys the C3-like character of the present study.

In this paper we have addressed the two-electron problem case. The generalization to the case of N -electron systems is straightforward as indicated in [2]. The PF basis set for S states can be defined as the product of N Coulomb wave functions multiplied by $M=N(N-1)/2$ Coulomb distortion factors, see Eq. (6),

$$\Psi_{CN}^B = \prod_{m>l,j=1}^N \varphi_{n_j}(r_j) L_{n_{lm}}^{(1)}\left(-\frac{r_{lm}}{n_{lm}}\right).$$

The combination with bound-continuum and continuum-continuum functions allows one to define a complete basis set for N electrons as shown in this paper for the $N=2$ case. These functions diagonalize all the Coulomb potentials, thus satisfying all the two-body cusp conditions. The extension to general masses and charges is straightforward.

ACKNOWLEDGMENTS

One of the authors (G.G.) would like to acknowledge support from ANPCYT (Argentina) Grant No. PICTR 2003/00437, CONICET (Argentina) Grant No. PICT 5595, and Universidad Nacional del Sur (Argentina) Grant No. PGI 24/F038.

- [1] C. R. Garibotti and J. E. Miraglia, *Phys. Rev. A* **21**, 572 (1980); M. Brauner, J. Briggs, and H. Klar, *J. Phys. B* **22**, 2265 (1989).
- [2] L. U. Ancarani and G. Gasaneo, *Phys. Rev. A* **75**, 032706 (2007).
- [3] A. S. Kheifets and I. Bray, *Phys. Rev. A* **58**, 4501 (1998).
- [4] S. P. Lucey, J. Rasch, C. T. Whelan, and H. R. J. Walters, *J. Phys. B* **31**, 1237 (1998).
- [5] A. S. Kheifets and I. Bray, *Phys. Rev. A* **69**, 050701(R) (2004).
- [6] L. U. Ancarani, T. Montagnese, and C. Dal Cappello, *Phys. Rev. A* **70**, 012711 (2004).
- [7] F. D. Colavecchia, G. Gasaneo, and K. V. Rodriguez, *J. Electron Spectrosc. Relat. Phenom.* **161**, 73 (2007).
- [8] L. U. Ancarani, T. Montagnese, and C. Dal Cappello, in *Electron and Photon Impact Ionization and Related Topics*, edited by B. Piraux, IOP Conf. Proc. No. 183 (Institute of Physics, London, 2005), p. 21.
- [9] A. Lahmam-Bennani, I. Taouil, A. Duguet, M. Lecas, L. Avaldi, and J. Berakdar, *Phys. Rev. A* **59**, 3548 (1999).
- [10] S. Jones, J. H. Macek, and D. H. Madison, *Phys. Rev. A* **70**, 012712 (2004).
- [11] L. U. Ancarani and C. Dal Cappello, *J. Electron Spectrosc. Relat. Phenom.* **161**, 22 (2007).
- [12] P. Pluvinaige, *Ann. Phys.* **5**, 145 (1950); *J. Phys. Radium* **12**, 789 (1951).
- [13] S. Jones and D. H. Madison, *Phys. Rev. Lett.* **91**, 073201 (2003).
- [14] L. U. Ancarani, C. Dal Cappello, and T. Montagnese, in *Ionization, Correlation, and Polarization in Atomic Collisions*, edited by A. Lahmam-Bennani and B. Lohmann, AIP Conf. Proc. No. 811 (AIP, Melville, NY, 2006), p. 1.
- [15] K. V. Rodriguez and G. Gasaneo, *J. Phys. B* **38**, L259 (2005).
- [16] K. V. Rodriguez, G. Gasaneo, and D. M. Mitnik, *J. Phys. B* **40**, 3923 (2007).
- [17] T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).
- [18] C. R. Garibotti, G. Gasaneo, and F. D. Colavecchia, *Phys. Rev. A* **62**, 022710 (2000).
- [19] T. Li and R. Shakeshaft, *Phys. Rev. A* **71**, 052505 (2005).
- [20] S. H. Patil, *Eur. J. Phys.* **25**, 91 (2004).
- [21] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
- [22] J. R. Götz, M. Walter, and J. S. Briggs, *J. Phys. B* **38**, 1569 (2005).
- [23] W. F. Drake, *Springer Handbook of Atomic, Molecular, and Optical Physics* (Springer, New York, 2005).
- [24] N. Umezawa and S. Tsuneyuki, *J. Chem. Phys.* **119**, 10015 (2003).
- [25] L. Lipsky, R. Anania, and M. J. Conneely, *At. Data Nucl. Data Tables* **20**, 127 (1977).
- [26] O. Dulieu and C. Le Sech, *Z. Phys. D: At., Mol. Clusters* **13**, 9 (1989).