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Accurate and simple wavefunctions for the helium isoelectronic sequence with correct cusp conditions

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Abstract

Simple and accurate wavefunctions for the He atom and He-like isoelectronic ions are presented. These functions—the product of hydrogenic one-electron solutions and a fully correlated part—satisfy all the coalescence cusp conditions at the Coulomb singularities. Functions with different numbers of parameters and different degrees of accuracy are discussed. Simple analytic expressions for the wavefunction and the energy, valid for a wide range of nuclear charges, are presented. The wavefunctions are tested, in the case of helium, through the calculations of various cross sections which probe different regions of the configuration space, mostly those close to the two-particle coalescence points.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

While a large variety of methods can be applied to the calculation of the wavefunctions and the energies of He-like ions [1–4], finding simple yet accurate wavefunctions for these systems remains an important challenge. Such wavefunctions are of importance for the study of a variety of physical processes such as the double ionization of atoms by ion and electron or photon impact [5–12]. The evaluation of cross sections for those processes demands large dimensional numerical integrations of two-electron wavefunctions both for the initial and the final collisional channels [11, 13, 14]. One way of reducing the difficulty of the calculations is to use simple wavefunctions in both channels. Our work is an attempt in this direction.

The efforts related to the determination of bound states energies and wavefunctions for He-like systems can be roughly separated into two approaches. The first one is based on highly sophisticated calculations, and the second on simple functions with the correct functional structure. Within the first approach, thousands of variational parameters are used in order to produce very highly precise approximations, which are essentially exact for all

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practical purposes [15–20]. It is computationally prohibitive to use these wavefunctions for the calculation of cross sections. Thus, no report can be found in the literature with applications of that kind of functions to collisional problems such as photo-double ionization or (e,2e) and (e,3e) processes. Within the second approach, a very low number of parameters are used to produce quite simple wavefunctions for He-like ions [21–24]. These functions are built with the correct asymptotic behaviour and cusp conditions. The drawback of this approach is that the energies and general characteristics reported are often not good enough to properly describe the systems [9]. The Hylleraas-like functions [25] can be considered an intermediate approach. On the one hand, these types of functions are relatively simple. On the other hand, they have been tested as useful functions for many collisional calculations [26]. For example, the functions given by Green *et al* [27], by Chandrasekhar *et al* [28, 29] and by Hart *et al* [30] use a few dozens of parameters and yield good energies for practical collisional purposes. However, these wavefunctions do not have the correct asymptotic behaviour and fail to describe properties such as the cusp conditions at the two-body coalescences (Kato cusp conditions [31]). Failure to describe these last properties leads to wrong results in the calculations of the cross section of particular physical processes [6, 7, 32, 33]. The importance of the fulfilment of the Kato cusp conditions has been pointed out by many authors [11, 12, 14, 34–38] who have discussed the value of satisfying them in the electron–atom double ionization and (e,3e) processes.

Many simple and accurate wavefunctions are generated, based on the semi-separable method originally proposed by Pluvinage [39]. In this method the wavefunctions are the product of two factors. The first term includes the electron–nucleus interactions. The second term takes into account both the electron–electron interaction and the correlation between all the parts of the system. This method was applied to atoms [22, 24, 40–44] and molecules [45]. Moumeni and co-workers [41] modified Pluvinage's original proposal introducing a screening function to represent the correlation. Siebbeles *et al* [42] and Le Sech [22] further modified the angular correlation factor, and also generalized the idea to other atomic systems [46, 47].

The aim of our work is to construct relatively simple functions having accuracies and shapes similar to those given by Green *et al* [27] or by Chandrasekhar *et al* [28, 29], but with correct cusp conditions. We chose this form for our wavefunctions because it might avoid substantial rewriting of already existing codes designed to evaluate the cross sections based on convergent close-coupling, exterior complex scaling and perturbative calculations based on the continuum distorted wave methods (see, for example, [13, 14]). In a previous paper (see Rodriguez *et al* [44]), simple and accurate wavefunctions were given for the ground state of the He atom, but the method was not discussed in detail. In the present work, a detailed discussion of the method is presented, analysing the different basis set of functions as well as its properties. Furthermore, the application of the method is extended for other ions belonging to the He isoelectronic sequence, from $Z = 1$ to $Z = 10$. Approximate analytical expressions are given, allowing the calculation of the wavefunctions and the energies for other ions in the sequence.

Our work is organized as follows: in section 2 we give a complete description of our method. In section 3, we report the calculated energies for the ground states of helium-like ions, up to $Z = 10$. In sections 3.1 and 3.2, we make a detailed analysis of the convergence of the different types of functions, paying particular attention to the H^- ion and the He atom. For these ions, we give a complete set of variational solutions having an accuracy of about 1.5×10^{-4} for H^- and 4.3×10^{-5} for He. In section 3.3 we present approximate analytic expressions for the wavefunctions and energies which are valid for all the two-electron ions in the isoelectronic sequence with Z starting from $Z = 1$. The behaviour of the bound states near the two-particle coalescence points is studied in section 4. Dynamical quantities associated with photoabsorption processes which probe various parts of the configuration space are evaluated. Some conclusions are given in section 5. Atomic units are used throughout this paper.

2. Theory

2.1. The method

The non-relativistic Schrödinger equation for a two-electron atomic system is

$$H\Phi(\mathbf{r}_1,\mathbf{r}_2) = \left[T - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\Phi(\mathbf{r}_1,\mathbf{r}_2) = E\Phi(\mathbf{r}_1,\mathbf{r}_2), \tag{1}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the usual vectors describing the electron locations, r_{12} is the relative distance between them and Z is the charge of the nucleus. The total kinetic energy T in terms of these relative coordinates is

$$T = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \nabla_{12}^2 - \nabla_1\cdot\nabla_{12} + \nabla_2\cdot\nabla_{12}. \tag{2}$$

In this paper we report S states having total angular momentum $L = 0$. In this case

$$\begin{aligned} T = {} & -\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1}\right) - \frac{1}{2}\left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2}\right) \\ & - \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right) - t_1\frac{\partial^2}{\partial r_{12}\partial r_1} - t_2\frac{\partial^2}{\partial r_{12}\partial r_2}, \end{aligned} \tag{3}$$

with

$$t_1 = \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1r_{12}} \qquad \text{and} \qquad t_2 = \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2r_{12}}, \tag{4}$$

where the domain of the coordinates r_1, r_2 and r_{12} appearing in the last equation are $r_1 \in [0,\infty)$, $r_2 \in [0,\infty)$ and $|r_1 - r_2| \leqslant r_{12} \leqslant (r_1 + r_2)$, respectively. When the kinetic energy T is replaced in the Schrödinger equation (1), the following expression results:

$$[D_0 + D_1 - E_c]\,\Phi(r_1, r_2, r_{12}) = 0. \tag{5}$$

Here D_0 and D_1 are given by

$$\begin{aligned} D_0 \equiv {} & -\left[\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1}\right) + \frac{Z}{r_1} + E_1\right] - \left[\frac{1}{2}\left(\frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2}\right) + \frac{Z}{r_2} + E_2\right] \\ & - \left[\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right) - \frac{1}{r_{12}} + E_{12}\right], \end{aligned} \tag{6}$$

$$D_1 \equiv -t_1\frac{\partial^2}{\partial r_{12}\partial r_1} - t_2\frac{\partial^2}{\partial r_{12}\partial r_2}, \tag{7}$$

and the total energy E is written as the sum of partial energies $E = E_0 + E_c$, with $E_0 \equiv E_1 + E_2 + E_{12}$ and a correlation energy E_c. The D_0 term in equation (5) does not couple the coordinates; it represents three independent two-body Coulomb problems. The cross derivatives included in D_1 couple the motion of the pairs and lead to a non-separable equation. Thus, equation (5) suggests a possible structure for the wavefunction as the product of two factors: one exactly solving the equation

$$D_0\phi_{n_1,n_2} = 0, \tag{8}$$

and the other taking into account the coupling between the coordinates. In mathematical terms

$$\Phi_{n_1,n_2}(r_1, r_2, r_{12}) = \phi_{n_1,n_2}(r_1, r_2, r_{12})\Omega_{n_1,n_2}(r_1, r_2, r_{12}). \tag{9}$$

The solution of equation (8) is

$$\phi_{n_1,n_2}(r_1, r_2, r_{12}) = \varphi_{n_1}(r_1)\varphi_{n_2}(r_2)\chi_P(r_{12}), \tag{10}$$

where φ_n are the one-electron hydrogenic solutions

$$\varphi_{n_i}(r_i) = \mathrm{e}^{-\frac{Z}{n_i}r_i} F\left[1 - n_i, 2, 2\frac{Z}{n_i}r_i\right], \qquad i = 1, 2, \tag{11}$$

χ_P is the angular correlation factor

$$\chi_P(r_{12}) = \frac{2\beta}{2\beta + 1}\,\mathrm{e}^{-\mathrm{i}\beta r_{12}} F\left[1 - \frac{\mathrm{i}}{2\beta}, 2, 2\mathrm{i}\beta r_{12}\right], \tag{12}$$

F is the confluent hypergeometric function [48], and the energies are $E_i = -\frac{Z^2}{2n_i^2}$ and $E_{12} = \beta^2$.

We impose to the proposed functions to satisfy all the Kato cusp conditions [31]:

$$\begin{aligned}
\left[\frac{\partial\overline{\Phi}}{\partial r_1}\right]_{r_1 \longrightarrow 0} &= -Z\Phi(0, r_2, r_{12})\\
\left[\frac{\partial\overline{\Phi}}{\partial r_2}\right]_{r_2 \longrightarrow 0} &= -Z\Phi(r_1, 0, r_{12})\\
\left[\frac{\partial\overline{\Phi}}{\partial r_{12}}\right]_{r_{12} \longrightarrow 0} &= \frac{1}{2}\Phi(r, r, 0), \qquad r = \frac{1}{2}|\mathbf{r}_1 + \mathbf{r}_2|,
\end{aligned} \tag{13}$$

where $\overline{\Phi}$ means the average of Φ, e.g., in the first term of equation (13), the average is taken over a small sphere of radius r_1 keeping the other values fixed. Since the ϕ part of the function is composed of Coulomb functions that naturally satisfies them, the Kato cusp conditions are fulfilled if the function Ω behaves like

$$\Omega \longrightarrow 1 + O\left(r_1^2, r_2^2, r_{12}^2\right) \tag{14}$$

near the two-particle coalescence points.

Following our previous paper [44], we use

$$\begin{aligned}
\Omega_{(n_1,n_2)}(r_1, r_2, r_{12}) &= \sum_{i,j,k\neq 1} c_{i,j,k}^{(n_1,n_2)} \Omega_{i,j,k}^{(n_1,n_2)}(r_1, r_2, r_{12})\\
&\equiv \sum_{i,j,k\neq 1} c_{i,j,k}^{(n_1,n_2)} r_1^i r_2^j r_{12}^k.
\end{aligned} \tag{15}$$

The coefficients c must be restricted by the condition that the power series should not include first power on the coordinates; otherwise the Kato cusp conditions are not satisfied. This is actually observed in other proposals [22, 40, 41] in which the coupling functions $\sinh(\lambda r)/r$ or $\cosh(\lambda r)$ explicitly exclude the first powers on r.

We define the angular correlated configuration–interaction (ACCI) solution of equation (1) as

$$\Phi(r_1, r_2, r_{12}) = \sum_{n_1,n_2} \Phi_{n_1,n_2}(r_1, r_2, r_{12}). \tag{16}$$

The coefficients c from equation (15) are obtained by solving the generalized eigenvalue problem [49]:

$$\sum_{n_1,n_2,i,j,k} [\hat{H} - E\hat{S}]c_{ijk}^{(n_1,n_2)} = 0, \tag{17}$$

where $\hat{S}$ is the overlap matrix

$$S^{n_1,n_2,m_1,m_2}_{ijk,lmn} = \langle \phi_{m_1,m_2}(r_1, r_2, r_{12}) r_1^l r_2^m r_{12}^n | \phi_{n_1,n_2}(r_1, r_2, r_{12}) r_1^i r_2^j r_{12}^k \rangle, \tag{18}$$

and $\hat{H}$ is the Hamiltonian matrix

$$H^{n_1,n_2,m_1,m_2}_{ijk,lmn} = \langle \phi_{m_1,m_2}(r_1, r_2, r_{12}) r_1^l r_2^m r_{12}^n | \hat{H} | \phi_{n_1,n_2}(r_1, r_2, r_{12}) r_1^i r_2^j r_{12}^k \rangle. \tag{19}$$

2.2. The angular correlation factor $\chi(r_{12})$

In many *ab initio* electron structure methods such as the different variants of the quantum Monte Carlo methods (see, for example, [50–52]), the correlation effects are often taken into account by the introduction of a correlation function, generally known as a Jastrow-type function [53]. These functions are included in different manners, but it is standard practice to use a trial function, chosen to reflect particular characteristics desired for the wavefunctions, and parametrized efficiently.

Exponential correlation factors, similar to the function χ_P (equation (12)), have been employed in various guises in many explicitly correlated wavefunction methods. The function χ_P is the continuum Coulomb solution of the third term of equation (6). This continuum function presents many nodes, as is typical for any continuum function. However, there is no physical reason for such nodes in a distortion factor introduced to represent the angular correlation. There is a way to avoid these unphysical nodes by taking $E_{12} = 0$ as used, for example, in [54]. However, setting $E_{12} = 0$ has the effect of eliminating the variational parameter β, which we have found to have a significant effect on the energy. In a previous paper [44], an angular correlation factor χ_E different from the continuum Coulomb wavefunction χ_P was used, and here we will explain its origin. The factor χ_E is the solution of the equation

$$\left[-\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right) + V_E(r_{12}) - E_{12}\right]\chi_E = 0, \tag{20}$$

where V_E is a particular case of the Eckart potential [55]

$$V_E = b\frac{\mathrm{e}^{-\beta r_{12}}}{1 + c\,\mathrm{e}^{-\beta r_{12}}}. \tag{21}$$

The Eckart potential V_E is plotted as a function of r_{12}, for different parameters b, β and c, in figure 1. This potential has an exponentially decreasing behaviour $\mathrm{e}^{-\beta r_{12}}$ at large distances representing the screening produced by the nucleus over the electron–electron interaction.

The zero energy solution ($E_{12} = 0$) of equation (20) can be written in terms of the Gauss hypergeometric function ${}_2F_1\,[a, b, c, z]$ as follows [56]:

$$\chi_E(\beta, b, c, r_{12}) = \frac{2\beta + 1}{2\beta}\,{}_2F_1\left[\frac{\mathrm{i}}{\beta}\sqrt{\frac{b}{c}}, -\frac{\mathrm{i}}{\beta}\sqrt{\frac{b}{c}}, 1, -c\,\mathrm{e}^{-\beta r_{12}}\right]. \tag{22}$$

where it has been assumed that $b, \beta > 0$ and $c > -1$. The constant in front of the ${}_2F_1$ has been introduced for convenience. The function $\chi_E(\beta, b, c, r_{12})$ is plotted in figure 2(a) for different values of the parameters β, b and c as a function of r_{12}. The figure shows that for particular combinations of the coefficients, the function χ_E has a monotonically increasing behaviour approaching a constant, as is expected for a correlation factor (see, for example, [57]). The different angular correlation functions $\chi_E(r)$ and $\chi_P(r)$ are compared in figure 2(b). As can be seen from the figure, these functions have a completely different behaviour for large values of the coordinate. When r_{12} is very large, the solution of the atom must be separable, and that is in agreement with the constant asymptotic behaviour presented by χ_E and not given by χ_P

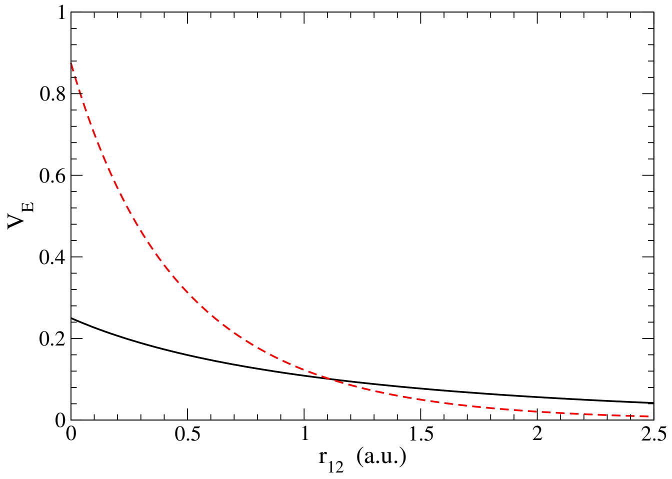

Figure 1. Eckart potential $V_E(r_{12})$. Solid line: $\beta = 0.5$, $b = 0.125$ and $c = -0.5$. Dashed line: $\beta = 1.75$, $b = 0.6806$ and $c = -0.22$.

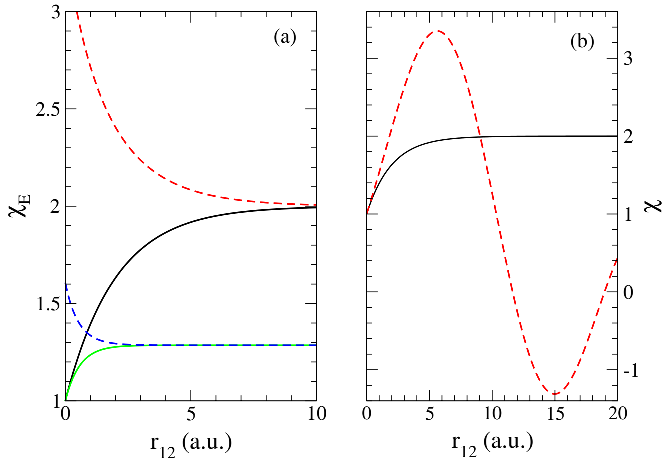

Figure 2. (a) The solution $\chi_E(\beta, b, c, r_{12})$ of the Eckart potential for different parameters: Upper curves: $\beta = 0.5$ and $c = -0.5$; solid curve: $b = 0.125$ and dashed curve: $b = -0.125$. Lower curves: $\beta = 1.75$ and $c = -0.22$; solid curve: $b = 0.68$ and dashed curve: $b = -0.68$. (b) Comparisons between the solutions of the Coulomb and Eckart potentials. Solid line: $\chi_E(0.5, 0.125, -0.5, r_{12})$. Dashed line: the Pluvinage angular correlation factor $\frac{2\beta+1}{2\beta}\chi_P(0.5, r_{12})$.

[58, 59]. However, in the region where the electrons spend more time—around the $\langle r_{12}\rangle \approx 1.4$ au—the functions are quite similar.

Choosing the parameter $b = -c\beta^2$ and using the relation ${}_2F_1\,[-1, 1, 1, z] = 1 - z$, then

$$\chi_E(\beta, -c\beta^2, c, r_{12}) = \frac{2\beta+1}{2\beta}\,{}_2F_1[-1, 1, 1, -c\,\mathrm{e}^{-\beta r_{12}}] = \frac{2\beta+1}{2\beta}(1 + c\,\mathrm{e}^{-\beta r_{12}}). \tag{23}$$

Defining $c = -\frac{1}{1+2\beta}$ the zero energy solution χ_E of equation (20) reads

$$\chi_E\left(\beta, \frac{\beta^2}{1+2\beta}, -\frac{1}{1+2\beta}, r_{12}\right) = \frac{2\beta+1}{2\beta}\, {}_2F_1\left[-1, 1, 1, \frac{\mathrm{e}^{-\beta r_{12}}}{1+2\beta}\right] = \frac{2\beta+1-\mathrm{e}^{-\beta r_{12}}}{2\beta}. \tag{24}$$

The replacement of χ_P by the χ_E defined in equation (24) produces a new ϕ function (equation (10)) which still satisfies all the correct cusp conditions. Now ϕ includes a free parameter β, to be fixed by variational methods. The numerical procedure requires the redefinition of the operators D_0 and D_1. The new $\widetilde{D}_0$ operator should be defined as in equation (6), but the Coulomb potential $\frac{1}{r_{12}}$ is replaced now by the Eckart potential V_E. On the other hand, D_1 should be replaced by $\widetilde{D}_1 = D_1 + \left(\frac{1}{r_{12}} - V_E\right)$.

3. Results

The method described in section 2 is now applied to the study of the ground state of He-like systems. In this case the wavefunction (9) becomes

$$\Phi_{\mathrm{GR}N}(r_1, r_2, r_{12}) = A\,\mathrm{e}^{-Z(r_1+r_2)}\chi_E(r_{12}) \sum_{n_1,n_2,i,j,k} c_{i,j,k}^{n_1,n_2} r_1^i r_2^j r_{12}^k, \tag{25}$$

where A is a normalization factor. We denote the function $\Phi_{\mathrm{GR}N}$ following the notation used in our previous paper [44], where N indicates the total number of different parameters included in the function. Since the He ground state has $S = 0$ (antisymmetric spin function), the spatial function Φ must be symmetric under the exchange of the electron coordinates, imposing the constraints $c_{i,j,k} = c_{j,i,k}$ and $i_{\max} = j_{\max}$. Assuming only $n_1 = n_2 = 1$, the function acquires a shape quite similar to that given by Green *et al* [27] and by Chandrasekhar *et al* [28, 29]. Even though in our assumption we are using only combinations of 1s one-electron functions, the method also provides reasonable good wavefunctions for the low-lying excited states. Including other n quantum numbers has improved considerably the wavefunctions for these levels. We are currently investigating this subject.

The simplest of the $\Phi_{\mathrm{GR}N}$ functions is obtained by keeping powers up to order 2 on the coordinates r_1 and r_2 in equation (25). Thus, the Φ_{GR2} function results:

$$\Phi_{\mathrm{GR2}}(r_1, r_2, r_{12}) = A\,\mathrm{e}^{-Z(r_1+r_2)}\chi_E(r_{12})\left[1 + c_{200}\left(r_1^2 + r_2^2\right)\right]. \tag{26}$$

We present, in table 1, the mean energies obtained for the H$^-$ and He ground states by using the Φ_{GR2} function. For comparison, the table displays the results obtained with the angular correlation factor χ_E (equation (24)) together with those obtained by using the Pluvinage factor χ_P (equation (12)). The table shows that the best values are obtained with χ_E for both ions. For H$^-$, the parameter β is much smaller than for He, allowing the wavefunction χ_E to attain greater distances from the origin before reaching its asymptotic region.

3.1. Correlated open-shell-type functions

A separable function such as

$$\Phi_{\mathrm{GRO}N}(r_1, r_2, r_{12}) = A\{\mathrm{e}^{-Zr_1}g(r_2) + \mathrm{e}^{-Zr_2}g(r_1)\}\chi_E(r_{12}), \tag{27}$$

where $g(r_i)$ is defined according to equation (15) in terms of the power series

$$g(r_i) = \mathrm{e}^{-Zr_i}\left[\tfrac{1}{2} + c_{200}r_i^2 + c_{300}r_i^3 + c_{400}r_i^4 + c_{500}r_i^5 + c_{600}r_i^6 + \cdots\right], \tag{28}$$

Table 1. Parameters and mean energies for the H^- and He ground states obtained by using the $\Phi_{GR2}(r_1, r_2, r_{12})$ function. Values obtained by using χ_P (equation (12)) in place of χ_E (equation (24)) are also given for comparison.

	χ_E	χ_P	χ_E	χ_P
Z	1	1	2	2
A	0.0769	0.1615	1.3891	2.3170
β	0.0374	0.42	0.4435	0.7
c_{200}	0.1030	0.0795	0.1556	0.1306
$\langle -E \rangle$	0.5199	0.5166	2.9013	2.898
$-E^{a}_{exact}$	0.5277		2.9037	

[a] Pekeris [63].

Table 2. Variational calculations of the parameters and energies for the H^- ion, calculated with the open-shell-type Φ_{GRON} functions (equation (27)).

	GRO2	GRO3	GRO4*A*	GRO4*B*	GRO5*A*
β	0.0374	0.1065	0.1142	0.1248	0.1246
c_{200}	0.1030	0.0608	0.1026	0.0828	0.0295
c_{300}			−0.0188		0.0300
c_{400}		0.0034	0.0059	0.0017	−0.0033
c_{600}				0.000 05	0.000 08
$\langle -E \rangle$	0.5199	0.5258	0.5260	0.5265	0.5267

Table 3. Variational calculations of the parameters and energies for the He atom, calculated with the open-shell-type Φ_{GRON} functions (equation (27)).

	GRO2	GRO3	GRO4*A*	GRO4*B*	GRO5*A*
β	0.4435	0.4519	0.4493	0.4511	0.4709
c_{200}	0.1556	0.1346	0.1138	0.1330	0.1351
c_{300}			0.0193		0.0008
c_{400}		0.0057	0.0012	0.0063	0.0062
c_{600}				−0.000 06	−0.000 06
$\langle -E \rangle$	2.9013	2.9020	2.9020	2.9020	2.9020

is called an *open-shell-like* function [57]. This is a separable function, in the sense discussed in section 2.1, in which the exponential term describes the Coulomb interaction between the inner electron and the nucleus, while the function g describes the dynamics of the 'outer' electron. A number of combinations of linear parameters c_{i00} was performed in order to get the best representation of the electron–electron correlation. The mean ground state energies for the H^- ion, obtained for the polynomials in the expansion (28) up to order 6, are shown in table 2.

The same results are given for the He atom in table 3. Besides the GRO*N* label to identify the number of independent parameters, we include capital letters A and B to denote different functions. It can be seen from the table that the effect of the inclusion of different terms is much more significant for the H^- ion than for the He atom. This can be associated with the fact that the H^- ion is larger than the He atom; thus it is necessary to include higher powers to appropriately represent the regions of the ion farther from the origin. Another conclusion drawn by analysing the results is that for He the series rapidly saturates the convergence. Adding more terms to the expansion (28) hardly changes the final energy. The best function obtained for the H^- ion is the GRO5A which includes the powers 2, 3, 4 and 6. For the He atom, the GRO5A function does not improve the GRO3 function. We found that including a r^5 term did not significantly improve the accuracy of the solution beyond that of the function having only powers r^2, r^3 and r^4. The r^3 term seems to produce some effect for the H^- ion when combined with the r^6 (see GRO5A). We noticed that the most important contributions to the energy are due to the even powers in agreement with the $\cosh(\lambda r)$ function used by Le Sech [22]. Still, our H^- energies with only two parameters are better than those obtained by Le Sech.

3.2. Highly correlated wavefunctions

Highly correlated wavefunctions can be obtained including more terms in the polynomial representation of the correlation. We consider non-separable functions by adding the crossed terms not included in expansion (28), and adding powers of r_{12} representing the angular correlation.

In table 4 we present the mean ground state energies of He and H^- for the GRN functions having $N = 5, 9, 14$ and 29 parameters. We have used the χ_E angular correlation function in all the calculations due to its simple form and its correct asymptotic behaviour. In our study, we have tried to keep the expansion degree as low as possible.

The best functions obtained with two and three parameters (GR2 and GR3 functions) are the GRO2 and GRO3 functions, respectively, already listed in tables 2 and 3. The first function listed in table 4, including powers up to order 3 on all the Hylleraas coordinates, is the GR5B, with four linear parameters. All the functions listed satisfy all the two-body Kato cusp conditions. In every case, the energy does not vary significantly in a wide range around the minimum value of the nonlinear parameter β. Therefore, the accuracy required for this parameter is not high.

The functions listed in table 4 for the He atom are alternative proposals to the Hylleraas functions with 6, 10, 14 and 20 parameters given by Green *et al* [27], by Chandrasekhar *et al* [28, 29] and by Hart *et al* [30], respectively. The mean energies obtained for these functions are similar to the corresponding functions denoted number 9 and 10 in Bonham and Kohl [21], and are better than the values presented by Le Sech [22], Moumeni *et al* [41] and Siebbeles *et al* [42]. The most accurate function (GR29) presented in this report yields energies with an accuracy of 4.3×10^{-5}. We analysed the quality of our wavefunctions testing local properties which probe the function in different regions. All the mean values are in excellent agreement with those given by the high-order parameter Hylleraas functions. Another global property of interest is the Virial coefficient which converges very rapidly to the exact value of −2: it is −2.012 for the GR3, −2.002 for the GR5B and −2.0003 for the GR9.

For the case of the H^- ion, two highly correlated functions are reported in table 4, with 14 and 29 parameters. Note that two parameters are zero on the definition of the GR29 function for the H^- ion; thus, our best function effectively has 27 parameters. The energies of our functions are in very good agreement with the energies calculated by Henrich [60] (−0.527 559 au, obtained with an 11-parameter function) and by Hart *et al* [30] (−0.527 645 au, 20 parameters). Recently, Qiu *et al* [61] reported a 43-parameter function (parameters not reported) to study one- and two-electron emission from H^- by high-energy photons. This function, written in terms of Hylleraas coordinates, gives a mean energy of −0.527 68 au, and does not satisfy the cusp conditions. Our best function produces almost the same mean energy, but with a considerably smaller number of parameters and with the correct cusp conditions. In contrast to the open-shell-like expansion, the expansion for the correlated wavefunctions

Table 4. Parameters and energies for the He atom and the H^- ion, corresponding to highly correlated Φ_{GRN} wavefunctions (equation (25)).

	He				H^-	
	GR5*B*	GR9	GR14	GR29	GR14	GR29
N	1.403 9859	1.390 9157	1.385 8475	1.381 633 5	0.073 386 239	0.073 293 631
β	0.70	0.56	1.43	1.80	0.15	0.82
c_{200}	0.132 7041	0.166 6377	0.194 1680	0.216 445 3	0.116 972 024	0.106 045 350
c_{220}	−0.024 9529	−0.090 2841	−0.114 7580	−0.265 781 3	−0.013 888 435	−0.043 414 801
c_{300}	0.026 3593	0.011 4176	−0.011 3241	−0.017 856 7	−0.017 928 453	0.000 963 730
c_{320}		0.014 3997	0.015 9012	0.078 584 6	0.000 694 004	0.006 839 546
c_{400}			0.010 9928	0.015 622 5	0.006 978 128	0.005 774 476
c_{420}				−0.012 325 5		−0.000 845 991
c_{430}				−0.000 369 3		0.000 025 452
c_{002}	0.022 0519	−0.010 0572	0.140 8332	0.206 031 0	0.001 100 876	0.107 959 091
c_{202}		0.017 0400	0.031 9705	0.091 479 0	0.006 191 243	0.024 586 696
c_{222}			0.004 0334	0.036 830 6	0.000 253 537	0.001 827 515
c_{302}		−0.008 7965	−0.015 0901	−0.068 119 57	−0.002 251 535	−0.012 163 022
c_{322}				−0.014 091 6		−0.000 305 902
c_{402}		0.001 2633	0.001 8194	0.011 978 2	0.000 183 044	0.001 710 909
c_{422}				0.002 153 9		0.000 032 183
c_{432}				0.000 188 8		0
c_{552}				−0.000 001 2		0
c_{003}			−0.070 530 4	−0.151 308 7	−0.006 861 951	−0.044 690 827
c_{203}				−0.023 988 8		−0.001 939 658
c_{223}			−0.000 848 4	0.036 830 67	−0.000 018 989	0.000 027 058
c_{303}				0.030 739 7		0.002 211 197
c_{403}				−0.008 158 6		−0.000 498 590
c_{423}				−0.000 209 9		−0.000 001 354
c_{503}				0.000 405 7		0.000 018 019
c_{004}			0.009 1852	0.043 703 0	0.000 795 513	0.006 765 652
c_{204}				−0.010 544 4		−0.000 723 228
c_{304}				0.002 617 3		0.000 148 783
c_{324}				0.000 030 6		0.000 000 395
c_{405}				−0.000 006 4		−0.000 000 225
$\langle -E \rangle$	2.902 86	2.903 27	2.903 42	2.903 60	0.527 432	0.527 673

corresponding to the H^- ion converges slowly. The most accurate function (GR29) presented in this report yields energies with an accuracy of 1.5×10^{-4}.

It should be noticed that the wavefunctions here proposed do not have the appropriate asymptotic behaviour in the region where one of the electrons is close to the nucleus and the other is far from the origin [62]. In our proposal, a power series expansion is used to build that behaviour. We decided to use power series instead of exponential functions time powers to keep the wavefunctions as similar as possible to the Hylleraas functions which are currently used in collisional calculations. The inclusion of the appropriate asymptotic behaviour within the angular correlated method will be presented elsewhere.

3.3. The He-like isoelectronic sequence

We extended our calculations for other helium-like ions. Systematic calculations were performed for the simplest variational functions along the whole isoelectronic sequence. The values of the coefficients and energies given in table 5 correspond to the correlated

Table 5. Variational coefficients β and c_{200} for the GR2 function along the He-like isoelectronic sequence.

Z	A	β	c_{200}	$\langle -E\rangle$	$-E^{\mathrm{a}}_{\mathrm{exact}}$
1	0.0769	0.0374	0.1030	0.5199	0.5277
2	1.3891	0.4435	0.1556	2.9013	2.9037
3	5.8526	0.8122	0.2102	7.2777	7.2799
4	15.379	1.1726	0.2652	13.6535	13.6556
5	31.876	1.5313	0.3208	22.0290	22.0309
6	57.252	1.8895	0.3768	32.4043	32.4062
7	93.417	2.2476	0.4330	44.7795	44.7814
8	142.28	2.6055	0.4893	59.1545	59.1566
9	205.75	2.9635	0.5457	75.5295	75.5317
10	285.75	3.3214	0.6021	93.9044	93.9068

[a] Pekeris [63].

Table 6. Variational coefficients β, c_{200}, and c_{400} for the GR3 function along the He-like isoelectronic sequence.

Z	A	β	c_{200}	c_{400}	$\langle -E\rangle$	$-E^{\mathrm{a}}_{\mathrm{exact}}$
1	0.0801	0.1065	0.0608	0.0034	0.5258	0.5277
2	1.4054	0.4519	0.1346	0.0057	2.9020	2.9037
3	5.8738	0.8062	0.1965	0.0075	7.2778	7.2799
4	15.396	1.1660	0.2576	0.0072	13.6534	13.6556
5	31.871	1.4709	0.3122	0.0044	22.0287	22.0309
6	57.248	1.9261	0.3834	−0.0071	32.4039	32.4062
7	93.379	2.2446	0.4394	−0.0212	44.7790	44.7814
8	142.21	2.6036	0.4998	−0.0446	59.1542	59.1566
9	205.65	2.9648	0.5604	−0.0776	75.5293	75.5317
10	285.59	3.3174	0.6200	−0.1205	93.9043	93.9068

[a] Pekeris [63].

wavefunction GR2 obtained by the variational procedure of equation (17), for the He isoelectronic sequence up to charge $Z = 10$.

Table 6 shows the variational parameters and the resulting energy, though now using the GR3 function. As can be seen from these tables, the energies obtained with the GR2 and the GR3 functions are almost identical for charges higher than 4.

In order to obtain analytical approximate expressions for the wavefunctions and energies, we first neglected the angular correlation factor χ_E. The two-electron uncorrelated system admits an analytical solution of the variational equations for the GR2U function (the analogous uncorrelated version of the GR2 function). Details about the theoretical procedure and the analytical expressions obtained for the coefficients are given in [64]. Once we had these analytical expressions for the uncorrelated GR2U functions, we tried the same functional form, in order to produce a numerical fitting for the coefficients of the completely correlated GR2 function. We obtained then general formulae for the coefficient values, along the isoelectronic series. All of them have the appropriate asymptotic behaviour as a function of the nuclear charge. The best fitting for the GR2 functions are

$$\beta^{(\mathrm{GR2})}(Z) = \frac{Z^2}{77.8498 - 66.0392Z + \sqrt{4737.8518Z^2 - 10436.7557Z + 5922.2474}}, \tag{29}$$

$$c_{200}^{(\mathrm{GR2})}(Z) = \frac{1.9945Z^2}{-16.3362 + 32.969Z + \sqrt{4.934\,01Z^2 - 19.5053Z + 22.0567}}, \tag{30}$$

and for the energy $E^{(\mathrm{GR2})}(Z)$ is

$$E^{(\mathrm{GR2})}(Z) = -Z(0.599\,107 + 0.033\,295Z - \sqrt{1.067\,596Z^2 - 0.051\,764Z + 0.312\,009}). \tag{31}$$

The coefficients and the energies obtained by using the fitting expressions agree with the variational results up to the last figure given in the tables. These energy values are in excellent agreement with the *exact* results of Pekeris [63]. The accuracy of the calculated energies ranges from about 1.4×10^{-2} for $Z = 1$ to 2.5×10^{-5} for $Z = 10$. Moreover, formulae (29)–(31) are valid for ions with higher degree of ionization, giving excellent values for the energies. As an example, the energy $E^{(\mathrm{GR2})}$ corresponding to $\mathrm{Ti}^{20+}(Z = 22)$ is -470.395 au. The value obtained by solving the variational system of equations (17) with $\beta^{(\mathrm{GR2})}(Z = 22)$ is -470.40 au. It is worth noting the value of -470.361 au reported by Koga *et al* [65] obtained using a Hartree–Fock calculation.

Using the technique developed by Bonham and Kohl [21] to evaluate the integrals involving the coordinates r_1, r_2 and r_{12} and the analytic expression given for GR2 function, it is possible to obtain analytic expressions for different expectation values, dipolar and quadrupolar polarizabilities and other physical atomic properties for the two-electron isoelectronic sequence. In addition, it might be useful to study different collisional problems as a function of the nuclear charge similar to that described in, e.g., [66].

4. Dynamical tests for the correlated wavefunctions

The simultaneous excitation and ionization, as well as double ionization of atoms by photon impact, offers a series of dynamical tests for the bound state wavefunctions. The ejection or excitation of two electrons strongly depends on the electron-electron correlation of both initial and final states [33]. In particular, in the asymptotically high-energy regime, the photoionization cross sections are closely linked to the Coulomb singularities of the electron–nucleus and electron–electron interactions [33]. The photoabsorption might occur through the shake-off (SO) and quasi-free (QF) mechanisms. The SO process corresponds to the case where one of the electrons is ejected with high energy while the second remains bound to the nucleus (ionization–excitation) or leaves the atom with low velocity. The QF mechanism, on the other hand, is associated with the situation where both electrons share the absorbed photon without any participation of the nucleus. The ratio of cross sections for double photoionization to single photoionization

$$R(\omega) = \frac{\sigma^{2+}(\omega)}{\sigma^{+}(\omega)} \tag{32}$$

can be written, in the asymptotic region of very high photon energies ω, as

$$R(\omega) = R_{\mathrm{SO}} + R_{\mathrm{QF}}(\omega). \tag{33}$$

The photoionization cross sections for both mechanisms are related to the correlation matrix defined by Dalgarno and Sadeghpour *et al* [67, 68],

$$M_n = \left| \int \mathrm{d}\mathbf{r}_2 \varphi_n^*(\mathbf{r}_2) \Phi\,(0, \mathbf{r}_2) \right|^2, \tag{34}$$

where $\varphi_n(\mathbf{r}_2)$ is a hydrogenic bound-state wavefunction.

Table 7. Relative Ratio R_n of single-to-total photoionization given by the shake-off mechanism (equation (36)) for helium. n denotes the principal quantum number of the hydrogenic bound states of the residual ion.

n	GR5*B*	GR9	Hy6	Hy10	Hy20
1	0.931 96	0.930 02	0.926 65	0.927 20	0.929 41
2	0.044 26	0.044 81	0.045 33	0.045 20	0.044 49
3	0.005 67	0.005 37	0.006 11	0.005 64	0.005 54
4	0.001 85	0.001 82	0.002 00	0.001 89	0.001 83
5	0.000 85	0.000 85	0.000 94	0.000 88	0.000 85
6	0.000 46	0.000 47	0.000 52	0.000 48	0.000 46

The shake-off ratio of double-to-single ionization cross section at high photon energies is given by

$$R_{\mathrm{SO}} = 1 - \sum_n R_n, \tag{35}$$

where

$$R_n = \frac{M_n}{\int \mathrm{d}\mathbf{r}_2 |\Phi(0, \mathbf{r}_2)|^2}, \tag{36}$$

and the sum runs over all possible bound states of the residual ion. The shake-off photoabsorption process, in the asymptotic high-energy regime, probes the wavefunction at the origin of coordinates of the fast emitted electron. The expression for the ratio R_{SO} given by equation (36) is obtained using the sudden approximation, i.e., by projecting the initial state wavefunction onto the final state of the shaken-up electron. As demonstrated by Åberg [32], this expression is valid only if the electron–nucleus cusp conditions are satisfied.

On the other hand, the total cross section for double ionization through the quasi-free mechanism, in the asymptotic high-energy regime, is found to be proportional to [33]

$$\sigma_{\mathrm{QF}} \propto \int \mathrm{d}\mathbf{r} |\Phi(\mathbf{r}, \mathbf{r})|^2. \tag{37}$$

As explained by Drukarev [69], the contribution to the asymptotic ratio of double-to-single photoionization given by the quasi-free mechanism can be written as

$$R_{\mathrm{QF}}(\omega) = \frac{8\sqrt{2}}{5Z^2} C \frac{\omega}{m}, \tag{38}$$

where m is the electron mass and Z is the effective charge. The quantity C is given by

$$C = \frac{\int \mathrm{d}\mathbf{r} |\Phi(\mathbf{r}, \mathbf{r})|^2}{\sum_n M_n}. \tag{39}$$

The quasi-free mechanism is associated with the electron–electron cusp condition; it thus tests a different part of the configuration space, the region where the electrons are close to each other.

We have calculated several of these quantities in the case of He. In tables 7 and 8, we give the results obtained by using our simple wavefunctions GR5B and GR9. For comparison we have included the values obtained by using different Hylleraas functions, with the 6 [27], 10 [28] and 20 parameters [30], noted here Hy6, Hy10 and Hy20, respectively.

In table 7, we show the results obtained for the ratios R_n leaving the residual ion in the ns state ($n = 1$–6). The main discrepancies appear for $n = 1$. The sum of the R_n values reported by Dalgarno and Sadeghpour [67] is in excellent agreement with the experimental

Table 8. Values of the quantity C calculated by using equation (39) for He. This quantity is the proportionality constant which defines the asymptotic ratio of double-to-single photoionization as a linear function of the photon energy ω for the quasi-free mechanism (equation (38)).

	GR5B	GR9	Hy6	Hy10	Hy20
C	0.0608	0.0602	0.0625	0.0617	0.0601

values reported by Spielberger *et al* [70]. Although the energies of our GR5B and GR9 functions are similar to the energy of the 6-parameter function reported by Green [27], our R_n ratios are in better agreement with the highly correlated Hy20 function. Therefore, the energy is not the most relevant magnitude related to the quality of a wavefunction when dealing with particular dynamical processes. In this case the probability density to find the electrons around the nucleus is the relevant one, and this is better described by our simple GR5B and GR9 wavefunctions rather than by the Hy6 and Hy10. Note also that some Hylleraas wavefunctions can produce remarkable disagreements in the ratios of double-to-single ionization cross sections at asymptotically high energies, either when these ratios are calculated by using equation (36), or by the explicit calculation of the cross sections. This is a direct consequence of the fact that the electron–nucleus cusp conditions are not satisfied [32].

In table 8, we present the results obtained for the quantity C given by equation (39). The value $C = 0.053$ reported by Surić *et al* [33] was estimated by using a very simple approximate ground-state wavefunction which only takes care for the fulfilment of the Kato cusp conditions. Drukarev [69] obtained a value $C = 0.055$ using the 39-parameter Kinoshita function [71]. Later on, Krivec *et al* [72] reported a value of $C = 0.0597$ using the correlation function hyperspherical harmonic method. However, they also reported a value of $C = 0.068$ using a Hylleraas 6-parameter wavefunction. This value is not in good agreement with our calculations. Therefore, for a consistent comparison, we have calculated the C values using different Hylleraas functions (6-, 10- and 20-parameter). The results calculated with our GR5B and GR9 functions are in agreement with the value obtained by using the Hy20 function. This shows, again, that the peculiarities that characterize the functions at the coalescence points must be reproduced well by the wavefunctions used in order to obtain reliable values of double-photoionization cross-sections at high energies.

5. Conclusions

In this report we have introduced the angular correlated configuration–interaction method to carry out highly accurate calculations for He-like systems. All the wavefunctions were constructed satisfying the correct cusp conditions at the two-body coalescence where the Coulomb potentials diverge. The procedure presented in section 2 constitutes an extension of the semi-separable method. The approximate solutions are the product of two functions. One function describes a separable problem involving three non-interacting subsystems, while the second function introduces the couplings. The separable part was written as the product of functions depending on each of the three relative coordinates, r_1, r_2 and r_{12}.

For the angular correlation part of the wavefunction, two different analytical proposals were studied. We first considered a pure Coulomb wavefunction χ_P and discarded it later as a correlation factor due to its oscillatory behaviour which introduces a number of nonphysical nodes. Secondly, we studied a correlation factor χ_E which is the analytical solution of the Eckart potential for zero–energy. The efficiency and simplicity of the definition of χ_E, together with the fact that it has the proper asymptotic behaviour, led us to adopt this angular correlation factor for all the other calculations to be performed in these systems.

In the first part of section 3 we discussed different proposals for the factor which correlates the non-interacting subsystems. This factor is defined in terms of power series, giving a Hylleraas-like shape to the ground state wavefunction. We compared the energies of H^- and He given by two-parameter functions corresponding to the Coulomb χ_P, and the Eckart χ_E angular correlation factors. The Eckart factor proves to be more efficient.

In the second part of section 3 functions with different numbers of linear parameters were analysed. We discussed the separable part of the two-electron wavefunction and the relative importance of the different powers included in the coupling factor Ω. In section 3.1 different types of open shell-like functions were studied. The results obtained with these simple wavefunctions for the H^- and He agreed with Pekeris' results [63] up to three significant figures. A set of more accurate wavefunctions including up to 29 linear parameters was presented in section 3.2, and accuracies 1.5×10^{-4} for H^- and 4.3×10^{-5} for He were obtained.

Following our goal of providing both simple and accurate wavefunctions, in section 3.3 we studied the solutions for many ions along the isoelectronic sequence. Analytical expressions for all the coefficients and energies were given for the simplest correlated functions. The expressions are valid for a wide range of charges.

Different dynamical tests of the He wavefunctions have been performed. They are associated with cross sections corresponding to photoabsorption processes at asymptotically high photon energies. The values for R_n and C calculated with the wavefunction GR5B and GR9 were compared with the highly correlated 6-, 10- and 20-parameter Hylleraas functions. The calculations show that good descriptions of the configuration space are given by our functions, even better than those obtained with the 6- and 10-parameters Hylleraas functions. That means that the quality of the wavefunctions is improved by satisfying the cusp conditions.

Although our method is valid also for excited levels, we have only considered the ground states in the present work. The extension of the method to n-electron atoms and its application to the ground and excited states will be presented in a separate contribution.

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