Simple correlated wavefunctions for the K-shell electrons of neutral atoms

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Abstract

Simple correlated wavefunctions considering two K-shell active electrons of neutral atoms from He to Xe are presented in this paper, describing a variational method subject to a local Hartree potential representing the presence of outer shell electrons. Three kinds of electron–electron correlation functions have been studied with rigorous observation of the exact behaviour of the wavefunctions at the electron–electron and electron–nucleus coalescence points (Kato cusp conditions). Global properties, such as the energies and virial coefficients, as well as local properties, such as spatial mean values, together with scaling laws with the nuclear charge for the variational parameters, are also analysed. We calculated the expansion of the functions in terms of bipolar spherical harmonics. Finally, comparisons are made with a more rigorous, fully quantal close-coupling method, which also includes the same Hartree potential for the outer electrons.

1. Introduction

Much effort has been invested since the beginning of quantum theory, to solve the bound three-body Coulombic systems. In particular, the non-relativistic helium atom ground state can be calculated today within a precision better than 19 significant figures (see [1] and references therein). For most practical purposes, simple approximated wavefunctions have been proposed, fulfilling the required global and local properties of the He ground state with the optimization of only a few variational parameters. Some instances are the widely used functions presented by Bonham and Khol [2], Le Sech [3] and Patil [4, 5], applicable to the helium atom and to helium-like systems. Simple variational representations for the low-lying excited states are also available for these systems (see, for example, [6, 7]). However, scientific literature lacks such simple correlated wavefunctions for the two electrons subject to the influence of outer-shell electrons.

New experimental techniques could offer deeper understanding by providing information about the average separation between two electrons in the initial state. Recent measurements

of double ionization of He and Ne by Schultz *et al* [8] confirmed that the correlation function depends sensitively on the correlation introduced by the initial state. Experiments in proton–helium transfer ionization by Mergel *et al* [9] show a particular transfer ionization mechanism which can only be interpreted as a result of strong correlations in the initial He ground-state wavefunction. New experiments involving double photoionization of K- and L-shell electrons of neutral atoms [10, 11] demand knowledge of appropriate functions which account not only for correlation but also for the influence of the passive-shell electrons. Therefore, we intend here to develop fully correlated two-electron wavefunctions of atoms to deal with *double* processes in a way analogous to how the Hartree–Fock method tackled *single* transition processes. For these functions, we require acceptable values for the bound energies and other global properties such as the virial coefficient, together with local properties such as mean radii values to ensure the proper behaviour in all regions.

These functions can specially be useful in the calculation of double photoionization [12–14], dielectronic capture [15] or double ionization of inner shell [16] electrons, where correlation plays a leading role. The wavefunctions must also satisfy the exact behaviour at the electron–electron and electron–nucleus coalescence points (Kato cusp conditions) [17]. For instance, the double photoionization at very high incident energies is extremely sensitive to the electron–nucleus cusp conditions. As is discussed by Åberg [18], the matrix element of this process involves the Fourier transform of the gradient (in velocity gauge) of the initial wavefunction. Thus, the proper limit is obtained only if the cusp condition at the nucleus (see equation (11)) is satisfied. Furthermore, at very-high photon energies, another mechanism, the so-called quasi-free double photoionization, dominates the central part of the single differential electron energy spectrum [19]. In the quasi-free mechanism, both electrons share the energy and are ejected in nearly opposite directions, with no participation of the atomic nucleus [19, 20]. In this case, its matrix element maps the derivative of the ground-state wavefunction at small electron–electron distances. Therefore, the fulfilment of the electron–electron cusp condition (also known as the correlation cusp—see equation (12)) is the relevant criteria in the description of the equal sharing energy region.

Calculations of these processes put severe limitations on the sophistication of the wavefunctions, even when powerful computational facilities are available. Therefore, we are resorted to tractable wavefunctions which allow us to solve these transition matrix elements in the context of simple Nordsieck-type integrals [12].

As a first step, we want to propose simple correlated K-shell wavefunctions which account for the influence of the passive electrons, for many neutral atoms. We compare these functions with a fully quantal close-coupling (CC) calculation, which also includes the same outer-shell influence. The comparison between both methods is performed not only for the total wavefunction, but also for every term in the partial channel expansion in terms of bipolar spherical harmonics. Having established that both calculations are compatible, the CC functions may then be used to provide the necessary constraints for further development of variational methods in the calculation of excited and continuum wavefunctions.

Atomic units are used throughout this paper unless otherwise specified.

2. Theory

2.1. The K-shell model Hamiltonian

Let us consider a system composed of two interacting electrons described by the non-relativistic Hamiltonian

$$H_K = -\frac{\nabla_{\mathbf{r}_1}^2}{2} - \frac{\nabla_{\mathbf{r}_2}^2}{2} + V(r_1) + V(r_2) + \frac{1}{r_{12}}. \tag{1}$$

As usual, r_1 and r_2 represent the distance of the electrons to the nucleus, and $1/r_{12}$ is the electron–electron repulsion. In general, the central potential $V(r)$ for electrons in the K-shell can be written as

$$V(r) = -\frac{2}{r} + \frac{Z_K(r)}{r} \rightarrow \begin{cases} -\dfrac{Z}{r} & \text{as } r \rightarrow 0, \\[2mm] -\dfrac{2}{r} & \text{as } r \rightarrow \infty, \end{cases} \tag{2}$$

where Z is the nuclear charge. In particular, for helium-like ions $Z_K(r) = Z - 2$. For neutral atoms, $Z_K(r)/r$ accounts for the static potential created by the rest of the electrons in the upper shells. In this paper, we will consider the local Hartree potential given by

$$\frac{Z_K(r)}{r} = \frac{(2-Z)}{r} + \sum_{nl \neq 1s^2} \int d\mathbf{x} \frac{|\varphi_{nl}(\mathbf{x})|^2}{|\mathbf{r} - \mathbf{x}|}, \tag{3}$$

where φ_{nl} represents the upper shell wavefunctions (the K-shell electrons are removed from the sum). For the calculation of the static potential (equation (3)), we use Roothaan–Hartree–Fock functions, tabulated by Bunge *et al* [21]. These functions satisfy the electron–nucleus cusp condition required by our purposes. To make the calculation tractable, we have fitted $Z_K(r)$ as a combination of simple exponentials

$$Z_K(r) \simeq -\sum_{j=1}^{3} Z_j \, e^{-\mu_j r}. \tag{4}$$

The asymptotic conditions at $r \rightarrow 0$ (equation (2)) imposes

$$\sum_{j=1}^{3} Z_j = Z - 2. \tag{5}$$

A list of the parameters Z_j and μ_j for atoms from Li to Xe are shown in table 1. As a function of Z, the coefficients follow a simple behaviour. In general, for $5 \leqslant Z \leqslant 10$, two exponentials are enough to represent $Z_K(r)$ within acceptable relative errors (note the similarities between μ_1 and μ_2 from B to Ne).

The potential introduced to account for the influence of the outer electrons is local, and does not include exchange with these electrons. This exchange, however, is not large since the innermost K-shell is well separated, both in energy and coordinate space, from the outer shells. We explicitly calculated the exchange for several atoms and found its contribution negligible. For example, for the Ne atom, the exchange (at the mean ratio of the K-shell orbit) is less than 0.3% of the direct potential at this distance. This is not the case for the subvalence $2s^2$ subshell, where the exchange with the $2p^2$ electrons is very important. In the Ne atom case, an explicit calculation of the exchange potential results in a contribution of about 20% to the total potential, around the L-shell radius. Therefore, the exchange cannot be neglected while considering these wavefunctions calculations.

2.2. The trial wavefunction

The K-shell ground-state electrons will be described here by the following trial wavefunction,

$$\Phi_{1s^2}^x = \Phi_{12}(r_1, r_2)\Phi_3^x(r_{12}), \tag{6}$$

Table 1. Best values of the parameters Z_j and μ_j for the fitting of $Z_K(r)$ (equation (3)), as given in equation (4).

Z	Atom	Z_1	μ_1	Z_2	μ_2	Z_3	μ_3
3	Li	4.324	0.872	0.815	2.010	−4.139	1.216
4	Be	8.057	1.256	1.333	3.067	−7.389	1.768
5	B	14.276	1.414	0.990	1.438	−12.266	1.618
6	C	20.351	1.773	1.359	1.788	−17.710	2.007
7	N	25.005	2.129	1.678	2.148	−21.683	2.413
8	O	29.165	2.448	2.502	2.489	−25.668	2.776
9	F	33.197	2.777	2.460	2.804	−28.657	3.160
10	Ne	31.964	3.080	2.297	3.092	−26.261	3.599
11	Na	33.126	3.482	0.847	0.426	−24.973	4.099
12	Mg	32.638	4.016	2.064	0.634	−24.703	4.723
13	Al	31.919	4.547	3.228	0.722	−24.147	5.354
14	Si	28.996	5.170	4.721	0.897	−21.717	6.144
15	Ph	29.166	5.863	6.206	1.056	−22.372	6.888
16	S	28.319	6.564	7.645	1.192	−21.965	7.679
17	Cl	27.633	7.335	9.121	1.335	−21.754	8.530
18	Ar	17.499	7.837	10.612	1.480	−12.110	9.939
30	Zn	15.268	4.793	13.009	1.711	−0.278	59.768
36	Kr	19.719	5.419	14.654	1.531	−0.373	58.854
54	Xe	34.238	6.114	17.818	0.795	−0.057	84.286

where

$$\Phi_{12} = N\Phi_{1s}(r_1)\cosh(\alpha r_1)\Phi_{1s}(r_2)\cosh(\alpha r_2), \tag{7}$$

and

$$\Phi_{1s}(r) = \sqrt{Z^3/\pi}\,\exp[-Zr]$$

is the hydrogenic 1s state. The factor $\cosh(\alpha r_1)$ ($\cosh(\alpha r_2)$) accounts for the shielding of electron 2 (1) on 1 (2). The main modification introduced in this work is that the two-electron function Φ_{12} consists of a product function rather than a sum of one-electron functions. Thus, we can *no longer* assume that as $r_1 \to \infty$ electron 2 is represented by $\Phi_{1s}(r_2)$, as posed in the model of Patil [5] to treat two electrons in a pure Coulomb field.

Three types of electron–electron (e–e) correlation functions Φ_3^x ($x = a$, b and c) will be considered in this work. The first correlation function studied here, Φ_3^a,

$$\Phi_3^a = 1 - \frac{1}{1+2\lambda_a}\,e^{-\lambda_a r_{12}}, \tag{8}$$

is a generalization of those studied by Bonham and Kohl [2] and Kleinekathöfer *et al* [22]. It is the simplest of the three functions, but there is a setback. As we are interested in using these wavefunctions in double processes, analytical calculations of transition amplitudes are generally demanded. To calculate the matrix elements by means of Nordsieck-type integrals, a Fourier transform is required on the variable r_{12}. This term should be L^2 integrable, and it is built by multiplying the integrand by $\exp(-\varepsilon r_{12})$ and afterwards producing the limit as $\varepsilon \to 0$ [12, 13]. This procedure is clearly very cumbersome. A better strategy is to build the exponential directly in the wavefunction as suggested by Otranto *et al* [23],

$$\Phi_3^b = e^{-\varepsilon r_{12}} - \frac{1+2\varepsilon}{1+2\lambda_b}\,e^{-\lambda_b r_{12}}. \tag{9}$$

A third type of correlation term was introduced by LeSech [3],

$$\Phi_3^c = 1 + \frac{r_{12}}{2} e^{-\lambda_c r_{12}}, \tag{10}$$

This function has largely been used in the case of helium-like ions. However, the use of Φ_3^c in the calculation of double photoionization processes introduces additional terms containing derivatives of the Nordsieck integral respect to λ_c.

Since the three types of functions described above have the following properties,

$$\frac{1}{\Phi_{12}} \frac{d\Phi_{12}}{dr_j}\bigg|_{r_j=0} = -Z \qquad j = 1, 2, \tag{11}$$

$$\frac{1}{\Phi_3^x} \frac{d\Phi_3^x}{dr_{12}}\bigg|_{r_{12}=0} = \frac{1}{2} \qquad x = a, b, c, \tag{12}$$

then, $\Phi_{1s^2}^x$ satisfies the three Kato cusp conditions as a starting condition. At the very end, our wavefunction Φ_{1s^2} can be expressed in terms of a simple sum of products of exponentials of the type

$$\Phi_{1s^2}^{a,b} = \sum_j N_j (e^{-\beta_{1j}r_1} e^{-\beta_{2j}r_2} e^{-\beta_{3j}r_{12}}), \tag{13}$$

where the terms β_{ij} and N_j can easily be derived from the definition of the wavefunctions. In this way, all calculations in the context of double processes become easier and faster. An additional factor r_{12} emerges if $\Phi_{1s^2}^c$ is used instead.

3. Results

The matrix elements involved in the variational expression,

$$E_{1s^2} = \frac{\langle \Phi_{1s^2}|H_K|\Phi_{1s^2}\rangle}{\langle \Phi_{1s^2}|\Phi_{1s^2}\rangle}, \tag{14}$$

can then be cast in terms of simple integrals of the type solved by Bonham and Kohl [2], which have closed forms. It is also important to consider the virial coefficient $\mathcal{V}$, no longer given by the ratio of the mean values of the total potential and the kinetics energies but by

$$\mathcal{V} = -\frac{\langle \Phi_{1s^2}|\mathcal{W} - Z_K'(r_1) - Z_K'(r_2)|\Phi_{1s^2}\rangle}{\langle \Phi_{1s^2}|\mathcal{K}|\Phi_{1s^2}\rangle}, \tag{15}$$

where

$$\mathcal{W} = V(r_1) + V(r_2) + \frac{1}{r_{12}}, \tag{16}$$

and

$$\mathcal{K} = -\frac{\nabla_{r_1}^2}{2} - \frac{\nabla_{r_2}^2}{2}, \tag{17}$$

are the total potential and kinetics energies, respectively and $Z_K'(r)$ is the derivative of Z_K defined in equation (3), and approximated as in equation (4), i.e.,

$$Z_K'(r) = \sum_{j=1}^{3} -\mu_j Z_j e^{-\mu_j r}. \tag{18}$$

In table 2, we present the variational values of the parameters α and λ_a, along with the variational energy E_{1s^2}, the normalization factor N, and the mean values of $\langle r_{12}\rangle = \langle \Phi_{1s^2}|r_{12}|\Phi_{1s^2}\rangle$, and $\langle 1/r_{12}\rangle = \langle \Phi_{1s^2}|1/r_{12}|\Phi_{1s^2}\rangle$, for the wavefunction $\Phi_{1s^2}^a$. For the case of

Table 2. Variational values obtained for $\Phi_{1s^2}^a$ (equation (8)), for neutral atoms.

Z	Atom	E_{1s^2}	$\frac{\alpha}{\sqrt{Z}}$	$\frac{\lambda_a}{Z}$	N	$\langle Zr_{12}\rangle$	$\langle\frac{1}{Zr_{12}}\rangle$	Virial
2	He	−2.899 88	0.3406	0.1900	1.298	2.817	0.4780	2.0081
3	Li	−6.631 44	0.3457	0.2439	1.153	2.587	0.5234	2.0028
4	Be	−11.731 2	0.3537	0.2701	1.100	2.486	0.5463	2.0008
5	B	−18.304 3	0.3446	0.2951	1.074	2.412	0.5636	2.0026
6	C	−26.144 8	0.3500	0.3083	1.056	2.375	0.5730	2.0025
7	N	−35.319 6	0.3558	0.3185	1.044	2.350	0.5797	2.0024
8	O	−45.946 4	0.3627	0.3261	1.035	2.331	0.5846	2.0023
9	F	−57.907 1	0.3696	0.3325	1.029	2.317	0.5885	2.0023
10	Ne	−71.206 2	0.3764	0.3380	1.023	2.306	0.5916	2.0023
11	Na	−87.068 1	0.3870	0.3412	1.019	2.299	0.5938	2.0021
12	Mg	−104.655	0.3938	0.3451	1.015	2.291	0.5959	2.0021
13	Al	−124.059	0.4003	0.3482	1.013	2.285	0.5977	2.0021
14	Si	−145.158	0.4055	0.3513	1.010	2.279	0.5993	2.0020
15	Ph	−167.937	0.4108	0.3539	1.009	2.274	0.6007	2.0020
16	S	−192.451	0.4160	0.3561	1.007	2.270	0.6019	2.0020
17	Cl	−218.656	0.4206	0.3582	1.006	2.266	0.6030	2.0019
18	Ar	−246.547	0.4251	0.3628	1.005	2.262	0.6040	2.0019
30	Zn	−720.815	0.4673	0.3601	0.9993	2.238	0.6109	2.0011
36	Kr	−1057.27	0.4721	0.3635	0.9989	2.230	0.6131	2.0009
54	Xe	−2473.27	0.5408	0.3469	0.9966	2.222	0.6155	2.0000

helium, we obtain a ground-state energy $E_{1s^2} = -2.89988$, which means that our calculation takes into account 88.3% of the correlation energy ($E_{exact} = -2.9037$, $E_{HF} = -2.8617$). In all the cases, $\mathcal{V}$ differs from 2 (exact value) only in the fourth significant figure.

The stability of the variational parameters α and λ is worth noting when they are scaled with Z. Since Zr_i is the Coulomb (natural) scaling, then we can write $\lambda r_{12} = (\lambda/Z)(Zr_{12})$, and that is why (λ/Z) is a quasi-universal parameter. The scaling of α with $\sqrt{Z}$ was rather unexpected but it is a consequence of the solution of the Bonham and Kohl integrals [2]. We can attribute the slight increase of $\alpha/\sqrt{Z}$ as Z increases, to the effect of the passive electrons of the upper shells that shield the nucleus, relaxing the ground state. Such an influence affects the electron–nucleus interaction but not the electron–electron interaction; therefore, (λ/Z) remains almost unaffected. It is interesting that this scaling seems to be general, and probably holds for several types of trial wavefunctions. For example, we have found that the results reported by LeSech in [3] also follow this scheme; λ and a in table 1 of this paper can be scaled quite well with $\lambda/\sqrt{Z}$ and a/Z, respectively. Moreover, λ and a in table 2 of [23] follow the same scaling pattern as well.

To evaluate the influence of the upper shells along the isoelectronic sequence, in table 3, we have reported the parameter values for the helium-like ions, from H$^-$ to Xe^{52+}, with the use of the Φ_3^a approximate function. As we are dealing with pure Coulomb potentials ($Z_K(r) = Z - 2$), the virial coefficients can be calculated as the ratio of the mean values of the total potential and the kinetics energies. The values closely approach 2. The values of $\langle Zr_{12}\rangle$ and $\langle\frac{1}{Zr_{12}}\rangle$ are the indicator of accuracy of the level of correlation in the wavefunctions. For helium, we have from table 3 $\langle Zr_{12}\rangle_a = 2.817$ and $\langle\frac{1}{Zr_{12}}\rangle_a = 0.4780$, closely approaching the values reported by Pekeris [24], which are $\langle Zr_{12}\rangle_a = 2.844$ and $\langle\frac{1}{Zr_{12}}\rangle_a = 0.4729$. This prediction improves as Z increases [25]. The values of α and λ scale very well with Z. The variational parameter α, when scaled with $\sqrt{Z}$, is nearly a constant for the three correlation functions. The impressive stability of α is due to the lack of passive electrons, therefore, the

Table 3. Variational values obtained for $\Phi^a_{1s^2}$ (equation (8)), for helium-like ions.

Z	Ion	E_{1s^2}	$\frac{\alpha}{\sqrt{Z}}$	$\frac{\lambda_a}{Z}$	N	$\langle Zr_{12} \rangle$	$\langle \frac{1}{Zr_{12}} \rangle$	Virial
1	H⁻	−0.518 48	0.3364	0.0313	4.782	3.747	0.6876	2.0294
2	He	−2.899 88	0.3406	0.1900	1.298	2.817	0.4780	2.0081
3	Li⁺	−7.276 67	0.3400	0.2453	1.156	2.579	0.5250	2.0034
4	Be²⁺	−13.652 5	0.3394	0.2732	1.106	2.471	0.5493	2.0018
5	B³⁺	−22.028 0	0.3389	0.2900	1.081	2.409	0.5641	2.0011
6	C⁴⁺	−32.403 3	0.3386	0.3013	1.065	2.370	0.5741	2.0007
7	N⁵⁺	−44.778 6	0.3383	0.3093	1.055	2.342	0.5812	2.0005
8	O⁶⁺	−59.153 7	0.3381	0.3154	1.047	2.322	0.5866	2.0004
9	F⁷⁺	−75.528 9	0.3379	0.3201	1.042	2.306	0.5908	2.0003
10	Ne⁸⁺	−93.904 0	0.3378	0.3238	1.037	2.294	0.5942	2.0002
18	Ar¹⁶⁺	−312.904	0.3372	0.3390	1.020	2.246	0.6078	2.0000
36	Kr³⁴⁺	−1273.65	0.3367	0.3484	1.009	2.216	0.6164	2.0000
54	Xe⁵²⁺	−2882.40	0.3366	0.3513	1.006	2.207	0.6193	2.0000

Table 4. Variational values obtained for $\Phi^b_{1s^2}$ (equation (9)), for neutral atoms.

Z	Atom	$\frac{100\varepsilon}{Z}$	$\frac{\alpha}{\sqrt{Z}}$	$\frac{\lambda_b}{Z}$	N
2	He	0.633	0.3410	0.1760	1.406
3	Li	0.813	0.3466	0.2183	1.253
4	Be	0.900	0.3550	0.2342	1.198
5	B	0.987	0.3462	0.2457	1.175
6	C	1.025	0.3518	0.2482	1.157
7	N	1.062	0.3579	0.2476	1.147
8	O	1.087	0.3649	0.2451	1.140
9	F	1.109	0.3719	0.2418	1.135
10	Ne	1.128	0.3788	0.2379	1.131
11	Na	1.137	0.3895	0.2333	1.128
12	Mg	1.150	0.3964	0.2288	1.126
13	Al	1.165	0.4029	0.2238	1.126
14	Si	1.176	0.4082	0.2192	1.126
15	Ph	1.186	0.4135	0.2145	1.126
16	S	1.194	0.4187	0.2098	1.126
17	Cl	1.202	0.4233	0.2053	1.127
18	Ar	1.209	0.4279	0.2008	1.128
30	Zn	1.225	0.4700	0.1570	1.145
36	Kr	1.237	0.4744	0.1410	1.158
54	Xe	1.167	0.5407	0.1074	1.182

Coulomb scaling applies naturally, leading to the conclusion that the method is very robust, and the wavefunctions have an appropriate structure. The influence of the passive outer shells in the atoms considered here is generally very small, as can be seen by comparing the parameters of the neutral atoms and the corresponding positive ions. This is clearly seen comparing tables 2 and 3. For instance, the difference between the mean separation $\langle Zr_{12} \rangle$ in neutral Ne and in the Ne⁸⁺ ion is only 0.5%. The same similarity holds for $\langle \frac{1}{Zr_{12}} \rangle$. However, the value of α, which is directly related to the energy, differs by about 11%.

In the case of the function $\Phi^b_{1s^2}$, the best variational values for the parameter ε, α, λ_b and N are given in table 4. There is no need to display E_{1s^2}, $\mathcal{V}$, $\langle r_{12} \rangle$ and $\langle 1/r_{12} \rangle$, since there is no

Table 5. Variational values obtained for $\Phi^c_{1s^2}$ (equation (10)), for neutral atoms.

Z	Atom	E_{1s^2}	$\frac{\alpha}{\sqrt{Z}}$	$\frac{\lambda_c}{Z}$	N	Virial
2	He	−2.899 91	0.3421	0.0884	0.5589	2.0085
3	Li	−6.631 49	0.3480	0.1117	0.6827	2.0034
4	Be	−11.731 2	0.3563	0.1229	0.7501	2.0014
5	B	−18.304 2	0.3471	0.1326	0.8004	2.0031
6	C	−26.144 7	0.3525	0.1379	0.8299	2.0029
7	N	−35.319 5	0.3584	0.1419	0.8514	2.0029
8	O	−45.946 3	0.3652	0.1449	0.8674	2.0027
9	F	−57.906 9	0.3721	0.1474	0.8800	2.0027
10	Ne	−71.206 0	0.3789	0.1495	0.8902	2.0026
18	Ar	−246.547	0.4285	0.1599	0.9319	2.0021
36	Kr	−1057.27	0.4747	0.1611	0.9620	2.0010
54	Xe	−2473.27	0.5409	0.1502	0.9705	2.0000

noticeable change of these magnitudes from those displayed in table 2, except in the fourth (for $\langle r_{12} \rangle$ and $\langle 1/r_{12} \rangle$), fifth (for $\mathcal{V}$) or sixth (for E_{1s^2}) figures.

In the case of the function $\Phi^c_{1s^2}$, we report the best values for α, λ_c and N in table 5. No important improvement is observed in relation to the simplest case $\Phi^a_{1s^2}$ to justify an additional derivative of the Nordsieck integral. For helium, the correlation energy increases to 91%, but the virial coefficient does not improve. The original LeSech function, as given by equation (2) of [3], has a correlation energy of 96%, but its structure differs from ours as it contains the sum of cosh's instead of the product of cosh's, as used here. Although it is more precise, equation (3) of [3] complicates the calculation of the matrix elements even more.

4. Comparison with the close-coupling method

In this section, we will compare our variational functions $\Phi^x_{1s^2}$ with a nonperturbative, fully quantal close-coupling calculation of the exact wavefunctions of K-shell electrons in a numerical lattice. The main purpose of the comparison between the variational $\Phi^x_{1s^2}$ and the nonperturbative functions $\Phi^{cc}_{1s^2}$ is threefold. First, it tests the quality of the variational functions, since an accurate energy value does not warrant that the function has the right spatial behaviour. Second, it provides a good test to the convergence of the partial waves expansion in the CC calculation. Since our variational functions contain all the cusp conditions, it is useful to know how many partial waves are needed to fulfil these conditions. If we can find a general agreement between both methods, a top-up procedure can be developed for a complete extension of the close-coupling wavefunctions to higher partial waves. Third, if both methods are compatible, we could be able to develop further variational methods for the excited and continuum wavefunctions, constrained with the exact CC wavefunctions behaviour (for example, imposing the zeros of the functions).

In [26], a complete description of the theoretical procedure used here was presented for helium within a spherical symmetric model (also known as the Temkin–Poet model or the S-wave model [27, 28]). The same method was also used before for real helium in a full CC calculation by Mitnik *et al* [29], and the detailed description of the theory for this case will appear in a forthcoming paper. The main difference with these previous calculations resides in the fact that as we are dealing now with general atoms and ions, the influence of the outer-shell electrons is taken into account here through the inclusion of the Hartree potential (equation (2)) in the close-coupling equations.

The CC ground-state wavefunction is calculated by relaxing the initial wavefunction (it can be a simple product of one-electron wavefunctions) in a fictitious imaginary time $\tau = it$ [30].

$$\frac{\partial}{\partial \tau} \Phi_{1s^2}^{cc}(\vec{r}_1, \vec{r}_2, \tau) = -H_K \Phi_{1s^2}^{cc}(\vec{r}_1, \vec{r}_2, \tau). \tag{19}$$

With no constraints, this imaginary time propagation will relax to the solution with the smallest eigenvalue of H_K. Thus, after many iterations (continuously renormalizing the wavefunction), only the lowest level eigenvalue (i.e. the ground state, or the first metastable level, according to the parity of the initial function) survives the relaxation. The computer codes that implement this method are also adapted to run on parallel computers. In this case, the wavefunctions are partitioned over many processors in such a way that the communications between the processors are minimized and performed at every time step only for the partitioned domain borders. This parallelization scheme is a standard procedure for many of the time-dependent-close-coupling works (for example [31]).

4.1. Energy and mean values

In first place, we have tackled the energy of the ground state of helium, obtained by means of this relaxation technique. For a numerical lattice having 500 points with a mesh spacing $\Delta r_1 = \Delta r_2 = 0.05$, and for seven coupled channels ($l_1 l_2 =$ ss, pp, dd, ff, gg, hh, ii), we obtain $E_{1s^2}^{cc} = -2.896$ which is no better than the energy of our variational wavefunctions. With this numerical grid, the energy of the one-electron He$^+$ ion is $E_{1s} = -1.9889$, compared with the exact value of $E_{1s} = -2$. In order to improve these results, the CC method needs to decrease the mesh step size, increasing the number of points. Convergence is demonstrated by using a grid with $\Delta r_1 = \Delta r_2 = 0.01$, where $E_{1s} = -1.9998$ and $E_{1s^2}^{cc} = -2.9030$, much better than the variational predictions.

We have also considered the K-shell electrons of neon and argon as a benchmark to illustrate neutral atoms. For neutral Ne, the total energy was calculated with the CC method, by using a numerical grid of 500 points with $\Delta r_1 = \Delta r_2 = 0.005$ and including the same seven channels in the calculation. We obtain $E_{1s^2}^{cc} = -71.127$, which reproduces the value shown in table 2 with an agreement close to the 0.1%. Other parameters of interest are the mean orbital radii. The CC method yields $\langle r_1 \rangle_{cc} = 0.154$, $\langle r_1^2 \rangle_{cc} = 0.032$ and $\langle 1/r_1 \rangle_{cc} = 9.78$ while the use of $\Phi_{1s^2}^a$ produces instead $\langle r_1 \rangle_a = 0.156$, $\langle r_1^2 \rangle_a = 0.033$ and $\langle 1/r_1 \rangle_a = 9.66$. These values are similar to the Hartree–Fock values $\langle r_1 \rangle_{HF} = 0.1576$, $\langle r_1^2 \rangle_{HF} = 0.0335$, and $\langle 1/r_1 \rangle_{HF} = 9.618$, as tabulated by Bunge et al [21]. As noted before, the close-coupling results can be improved by using a better numerical lattice.

For neutral Ar, the CC calculation uses a 500-points numerical grid, with $\Delta r_1 = \Delta r_2 = 0.001$, and includes four channels ($l_1 l_2 =$ ss, pp, dd, ff). We obtain the following results: $E_{1s^2}^{cc} = -246.52$, $\langle r_1 \rangle_{cc} = 0.085$, $\langle r_1^2 \rangle_{cc} = 0.0096$ and $\langle 1/r_1 \rangle_{cc} = 17.7$ while the use of $\Phi_{1s^2}^a$ produces $\langle r_1 \rangle_a = 0.086$, $\langle r_1^2 \rangle_a = 0.0098$ and $\langle 1/r_1 \rangle_a = 17.6$. The corresponding Hartree–Fock values [21] are $\langle r_1 \rangle_{HF} = 0.0861$, $\langle r_1^2 \rangle_{HF} = 0.009\,96$ and $\langle 1/r_1 \rangle_{HF} = 17.55$. Therefore, we conclude that our correlated wavefunctions describe the global parameters quiet well.

4.2. Coupled spherical harmonics expansion

In general, the total wavefunction Φ^{LM} can be expanded in terms of coupled spherical harmonics as follows:

$$\Phi^{LM} = \sum_{l_1, l_2} \frac{P_{l_1 l_2}^{LM}(r_1, r_2)}{r_1 r_2} \times \sum_{m_1, m_2} C_{m_1 m_2 M}^{l_1 l_2 L} Y_{l_1}^{m_1}(\widehat{\mathbf{r}}_1) Y_{l_2}^{m_2}(\widehat{\mathbf{r}}_2), \tag{20}$$
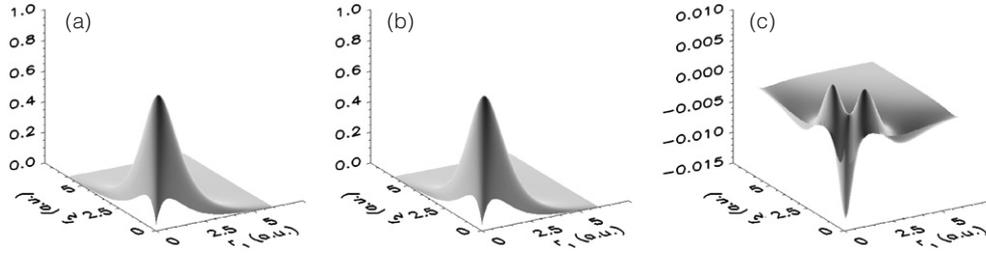
Figure 1. (a) P_{00}^a, the s–s radial part of $\Phi_{1s^2}^a$ (the variational approximated wavefunction), (b) P_{00}^{CC}, the s–s radial part of $\Phi_{1s^2}^{cc}$ (the CC wavefunction) and (c) the difference between both radial wavefunctions.
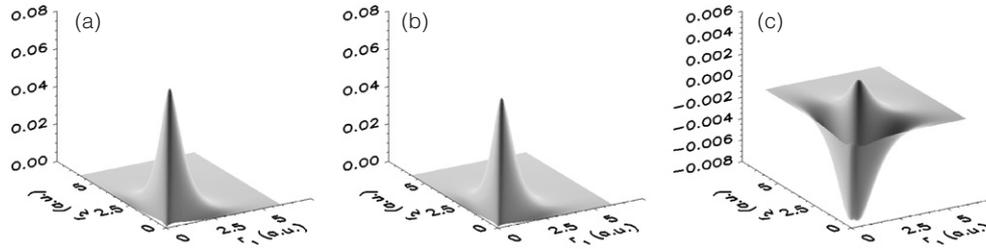
Figure 2. (a) P_{11}^a, the p–p radial part of $\Phi_{1s^2}^a$ (the variational approximated wavefunction), (b) P_{11}^{CC}, the p–p radial part of $\Phi_{1s^2}^{cc}$ (the CC wavefunction) and (c) the difference between both radial wavefunctions.

where L and M are the total orbital and azimuthal angular momentum of the system, $Y_l^m(\hat{\mathbf{r}})$ are spherical harmonics, and $C_{m_1 m_2 M}^{l_1 l_2 L}$ are Clebsch–Gordan coefficients. In particular, for the ground-state wavefunction Φ_{1s^2} (in which $L = 0$ and $M = 0$) is reduced to

$$\Phi_{1s^2} = \frac{1}{r_1 r_2} \sum_{lm} P_{ll}(r_1, r_2) \frac{(-1)^l}{\sqrt{2l+1}} Y_l^{m*}(\hat{\mathbf{r}}_1) Y_l^m(\hat{\mathbf{r}}_2). \tag{21}$$

The normalization of Φ_{1s^2} imposes $\sum_l C_{ll} = 1$, where

$$C_{ll} = \int \mathrm{d}r_1 \, \mathrm{d}r_2 |P_{ll}(r_1, r_2)|^2. \tag{22}$$

The first term, C_{00}, is the so-called s–s correlation, C_{11} is the p–p correlation, and so on.

In order to compare the variational wavefunctions with the CC wavefunctions, we expanded both functions in terms of coupled spherical harmonics, and compared every term in the partial expansion. Figure 1 shows (a) P_{00}^a, the s–s radial part of $\Phi_{1s^2}^a$ (the variational approximated wavefunction), (b) P_{00}^{CC}, the s–s radial part of $\Phi_{1s^2}^{cc}$ (the CC wavefunction), and (c) the difference between both radial wavefunctions. As is shown in the figure, the difference between both functions is very small (the amplitude of the differences is less than 0.01). The figure shows a deeper zone along the diagonal $r_1 = r_2$, which is a clear demonstration that the individual partial wave P_{00}^{CC} does not properly satisfy the electron–electron cusp condition.

The excellent agreement between the variational and the close-coupling radial wavefunctions is not limited to the s–s term in the expansion. Figure 2 shows P_{11}^a and P_{11}^{CC}, and the difference between both radial wavefunctions. In this case, the overall agreement is still very good, and the effect of the lack of the electron–electron cusp condition in the CC wavefunction is less pronounced. It must be mentioned that the variational and the CC
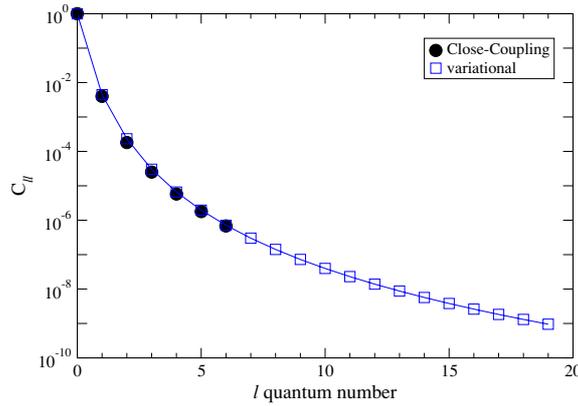
Figure 3. Correlation values C_{ll} (equation (22)) for He, as a function of the l quantum number, for the close-coupling expansion of $\Phi_{1s^2}^{cc}$, compared with the $\Phi_{1s^2}^a$ approximated function.

functions are normalized in a completely separate calculation. So, it will be natural to find such differences between the partial expansion terms.

The correlation terms C_{ll} (equation (22)) can be calculated from the variational wavefunctions by simply projecting $\Phi_{1s^2}^x$ into the coupled spherical harmonic base. This projection has been achieved here by numerical calculation. Alternatively, one may obtain closed forms for the first l's by using the technique derived by Swiatecki [32], as described in the appendix.

Figure 3 shows the partial contribution of the different terms in the expansion (21), by plotting the C_{ll} values (equation (22)), as a function of the quantum number l, for neutral He. The figure shows the expansion terms for both the CC calculations (full circles) and for $\Phi_{1s^2}^a$ (empty squares) connected with a solid line ($\Phi_{1s^2}^c$ produces very similar values which are undistinguishable in the present plot). Note that, by construction, $\sum_l C_{ll} = 1$ in the CC calculations. As we show in the figure, the agreement between the different methods is excellent.

Two important dependences can be extracted from the expansion of $\Phi_{1s^2}^a$ as discussed next.

(i) From the closed forms displayed in the appendix, we have noted that for neutral atoms the expansion of $\Phi_{1s^2}^a$ in terms of the correlation terms C_{ll}^a (equation (22)) obeys a scaling law with the nuclear charge. They can roughly be fitted for large Z, ($Z \gtrsim 4$), as follows

$$C_{11}^a \approx \frac{0.017}{Z^2}, \qquad C_{22}^a \approx \frac{0.0012}{Z^2} \tag{23}$$

This relation can be predicted by scaling the electron coordinates in the natural ones, i.e. $\rho_i = Z r_i$. In this way the integral given by equation (22) reduces from $\int dr_1 \, dr_2$ to $Z^{-2} \int d\rho_1 \, d\rho_2$, given the so-called Coulomb or Schrödinger scaling.

(ii) It is also noticeable in figure 3 that beyond a certain l, the C_{ll}^a behaves as $C_{ll}^a \approx l^{-5.7}$, which may be very important to estimate the importance of higher angular momentum in the close-coupling method.

The interesting point to observe is that C_{ll}^c follows a similar scaling to equation (23) for large Z. Even for neutral helium, we find similar correlation terms. For example, for $\Phi_{1s^2}^a$, we find $C_{11}^a = 0.0044$ and $C_{22}^a = 0.000\,23$, while for $\Phi_{1s^2}^c$, $C_{11}^c = 0.0044$ and $C_{22}^c = 0.000\,57$.

These results do not differ much from those obtained by using a nonperturbative CC method, which produces $C_{11}^{cc} = 0.0040$ and $C_{22}^{cc} = 0.000\,18$.

For larger Z, the correlation terms are also quite similar. For example, for neutral Ne we find $C_{11}^{a} = 1.60 \times 10^{-4}$ and $C_{22}^{a} = 1.2 \times 10^{-5}$, which compares very well with $C_{11}^{c} = 1.68 \times 10^{-4}$ and $C_{22}^{c} = 1.4 \times 10^{-5}$. They are in good agreement with the CC results $C_{11}^{cc} = 1.39 \times 10^{-4}$ and $C_{22}^{cc} = 4.0 \times 10^{-5}$. It seems that the Kato cusp conditions impose an appropriate decomposition in spherical harmonics.

5. Conclusions

We have introduced simple variational wavefunctions to describe the K-shell orbital electrons of neutral atoms and helium-like ions. These functions are strongly correlated and satisfy the Kato cusp conditions. Their structure makes them very tractable for atomic physics processes involving two active electrons. They describe very well the global and local parameters (energy, mean orbital radius, virial coefficient, etc). From the comparison with the rigorous CC method, we find that our variational functions yields a good description when expanded in coupled spherical harmonics. Compatibility between both methods will allow us to rely on the exact CC functions, for imposing constraints to the variational calculation of excited and continuum states. Summing up, the simple wavefunctions here proposed appear to be excellent candidates for the calculation of double processes in atomic physics.

Acknowledgments

Appendix. Analytical angular momentum expansion

In this appendix, we will show how to expand our simple wavefunctions in coupled spherical harmonics, as in equation (21), though applying an analytical approach. The general technique has been detailed by Swiatecki [32], and we will follow these procedures to obtain the P_{ll}^{x} terms for the approximated functions $x = a$ and c. For the first kind of functions $\Phi_{1s^2}^{a}$, after some algebra, we obtain

$$P_{ll}^{a}(r_1, r_2) = \frac{(-1)^l}{\sqrt{2l+1}} \Phi_{12}(r_1, r_2) \left[r_1 r_2 \delta_{l0} - \frac{T_l^{a}(r_1, r_2)}{2 + 4\lambda_a} \right], \quad (A.1)$$

where

$$T_l^{a}(r_1, r_2) = \sum_{j=0}^{l} \sum_{k=0}^{j} L_{l,j,k} I(1 + 2j - 2k, \lambda_a, r_0, R_0), \quad (A.2)$$

$$L_{l,j,k} = \binom{j}{k} \frac{(-l)_j (l+1)_j}{(j!)^2 (4r_1 r_2)^j} \binom{j}{k} (-1)^k r_0^{2k}, \quad (A.3)$$

and

$$I(n, \lambda, r_0, R_0) = \int_{r_0}^{R_0} \mathrm{d}x\, x^n\, \mathrm{e}^{-(\lambda x)} = \frac{1}{\lambda^{n+1}} \left[\Gamma(n+1, \lambda r_0) - \Gamma(n+1, \lambda R_0) \right]. \quad (A.4)$$

In the last expressions, $r_0 \equiv |r_1 - r_2|$ and $R_0 \equiv r_1 + r_2$.

The first terms in equation (A.2) are

$$T_0^a = I_1, \qquad T_1^a = I_1 Y_a + I_3 Y_b, \qquad T_2^a = I_1 Y_c + I_3 Y_d + I_5 Y_e, \qquad (A.5)$$

where

$$Y_a = 1 + \frac{r_0^2}{2r_1 r_2}, \qquad Y_b = -\frac{1}{2r_1 r_2}, \qquad Y_e = \frac{3}{8r_1^2 r_2^2},$$
$$Y_c = 1 + \frac{3r_0^2}{2r_1 r_2} + \frac{3r_0^4}{8r_1^2 r_2^2}, \qquad Y_d = -\frac{3}{2r_1 r_2} - \frac{3r_0^2}{4r_1^2 r_2^2}, \qquad (A.6)$$

and, for the sake of simplicity, we have denoted here $I_n \equiv I(n, \lambda, r_0, R_0)$.

For $\Phi_{1s^2}^c$, we find an expansion similar to equation (A.1) but now

$$P_{ll}^c(r_1, r_2) = \frac{(-1)^l}{\sqrt{2l+1}} \Phi_{12}(r_1 r_2) \left[r_1 r_2 \delta_{l0} + \frac{1}{4} T_l^c(r_1, r_2) \right], \qquad (A.7)$$

and

$$T_l^c(r_1, r_2) = \sum_{j=0}^{l} \sum_{k=0}^{j} L_{l,j,k} I(2 + 2j - 2k, \lambda_c, r_0, R_0). \qquad (A.8)$$

The first terms in equation (A.8) are

$$T_0^c = I_2, \qquad T_1^c = I_2 Y_a + I_4 Y_b, \qquad T_2^c = I_2 Y_c + I_4 Y_d + I_6 Y_e. \qquad (A.9)$$

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