



Energy and cusp-conditions study for the He isoelectronic sequence

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Abstract

We present variational wave functions for He-like atoms with nuclear charge $Z = 1, \dots, 10$. We propose modifications of some usual simple correlated wave functions to account for the integration factor required in the evaluation of atomic ionization and excitation amplitudes with distorted wave methods.

We determine the parameters of the trial functions and the resulting energies. We introduce new procedures to test the cusp conditions at the singularities of the Coulomb field.

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1. Introduction

The development of accurate wave functions for atomic bound states has been subject of investigation over the last seventy years [1–5]. The ground state wave function Ψ , for helium and helium-like atoms, is usually constructed as a sum of products of power-exponential terms representing the electron–nucleus and the electron–electron interaction. In this trial function a set of parameters are introduced and obtained from a variational procedure. The quality of the function

is determined by comparing the resulting mean energy with the exact value, and comparing the function's logarithmic derivatives with the expected values at the cusps at the three coordinate-origins [6]. Sophisticated wave functions for the He and other complex atoms were already available by the 1950s [3]. However, their implementation in the calculation of transition amplitudes in atomic collision processes based on perturbative methods becomes involved both analytically and numerically. The increment in the number of variational parameters needed to improve the wave function, generally results in more time-consuming calculations. Even when nowadays computational facilities allow one to deal with these elaborate functions, the analysis is mainly restricted to numerical treatments. However, in many situations it is

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desirable to have simple wave functions in order to obtain analytical results for different cross sections [4,5,7,8]. As an example, we could consider the study of the photo-double ionization amplitude dependence on the nuclear charge. The use of simple wave functions allows partial analytical development of this amplitude by means of Nordsieck-like integrals [9–11]. Otherwise the properties of the system have to be extracted from numerical results.

In this report we focus our work on the determination of the trial parameters for improved versions of ground state ($1S$) wave functions, for He-like atoms. Variational parameters for ions with nuclear charges $Z = 1, \dots, 10$ are determined. One of the contributions of this report is the introduction of modified correlation terms which avoid the use of integration factors in calculations [9–11]. Two simple models are considered: the GS2-type wave function of Bonham and Kohl [4] and a model recently proposed by Le Sech [7]. Distorting effects on the atomic energy and cusp-conditions for the original wave functions when an arbitrary cut-off is introduced are evaluated. New variational parameters and energies are obtained for the improved functions. New criteria to characterize the cusp-conditions deviations from the correct values are introduced. Mean energies and cusp deviations are tabulated for the modified wave functions here posed. Atomic units are used unless otherwise stated.

2. Wave functions

The Schrödinger equation for a two electron atom with nuclear charge Z is given by

$$H\Psi = E\Psi, \quad (1)$$

where E is the binding energy and H is the Hamiltonian of the system

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \quad (2)$$

The exact solution for Schrödinger equation (1) is unknown. Necessary conditions on Ψ , to satisfy Eq. (1) are the cusp conditions [6,12]:

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_1} \right)_{r_1=0} = \left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_2} \right)_{r_2=0} = -Z \quad (3)$$

and $\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2}$.

Deviation from these rules are used as a measure of the quality of the approximate wave function proposed.

The GS2-type function is a correlated open-shell wave function, and is written as

$$\Psi_{\text{GS2}} = N_i (e^{-ar_1-br_2} + e^{-br_1-ar_2}) (1 + C_0 e^{-\lambda r_{12}}). \quad (4)$$

The Le Sech function is defined by

$$\Psi_{\text{LS}} = N_i e^{-Z(r_1+r_2)} (e^{\gamma r_1} + e^{-\gamma r_1} + e^{\gamma r_2} + e^{-\gamma r_2}) \times (1 + 0.5 r_{12} e^{-h r_{12}}). \quad (5)$$

Here a , b , C_0 , λ , γ and h are the variational parameters. These parameters have been determined by Bonham and Kohl [4] for He-like ions with nuclear charge up to $Z = 3$ and by Le Sech up to $Z = 5$ [7]. When using these functions in calculations of transition amplitudes in atomic processes, like ionization of atoms by ion, electron or photon impact, the introduction of exponential convergence factors becomes necessary in order to ensure convergence of the continuum–continuum Nordsieck-like integrals. This cut-off parameter ranges usually between values 10^{-3} and 10^{-2} [11]. This means that the wave function results are modified as is the energy associated with it. In order to properly include a cut-off without losing accuracy on calculations, we propose the following modifications to the functions defined in Eqs. (4) and (5):

$$\Psi_1 = N_i (e^{-ar_1-br_2} + e^{-br_1-ar_2}) (e^{-z_c r_{12}} + C_0 e^{-\lambda r_{12}}), \quad (6)$$

$$\Psi_2 = N_i e^{-Z(r_1+r_2)} (e^{\gamma r_1} + e^{-\gamma r_1} + e^{\gamma r_2} + e^{-\gamma r_2}) \times (e^{-z_c r_{12}} + D_0 r_{12} e^{-h r_{12}}). \quad (7)$$

The fixed parameter z_c is the same in both cases. The D_0 is a parameter introduced in order to fulfill the electron–electron cusp condition. These proposals, of course, modify the associated binding energies and strengthen the decreasing exponential behavior at large distances.

It is easy to verify that these functions are eigenfunction of the total angular momentum:

$$L^2 = |\mathbf{l}_1 + \mathbf{l}_2|^2, \quad (8)$$

with zero eigenvalue. Here \mathbf{l}_i ($i = 1, 2$) is the orbital angular momentum of electron i . Application of the Hamiltonian operator to the trial functions Eqs. (6) and (7) results in the following kind of equation:

$$H\Psi_i = S_i\Psi_i, \quad (9)$$

where S_i is a operator. That makes clear that the trial functions Eqs. (6) and (7) are not exact solution of the Eq. (1). However the Schrödinger equation could be satisfied in a weak functional sense when the parameters in these trial functions are determined by minimizing the mean energy

$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (10)$$

Even though this is one of the existent methods of determining the wave function and energy, we use this to easily compared our results with those of [4,7]. When applying Eq. (10), the quality of the trial function is specified by the accuracy of the resulting energy. In Table 1, we present the values for the variational parameters for He-like atoms from H^- to Ne^{8+} , calculated with bound states of the form given by Eq. (6), and $z_c = 0.01$. The binding energies are given and compared with the assumed exact values of Pekeris [13]. We have tested the sensitivity of the energies with the z_c value. We have evaluated the variation of the en-

ergy using the bound state wave function given by Eq. (6) with the original Bonham and Kohl parameters, for z_c ranging up to 0.03 and we observed differences up to 1%. Meanwhile, the energies evaluated with Eq. (7) exhibit little sensitivity with the z_c value in that range.

Further test conditions are given by Eq. (3) concerning the logarithmic derivatives of the wave function at the singular points of the potentials. It has been shown that fulfillment of these conditions is essential in order to obtain an appropriate description of electron energy distributions in double photo ionization [14]. The function given by Eq. (7) exactly satisfies the electron–nucleus cusp conditions given by the first two relations in Eq. (3), but gives for the third:

$$\left(\frac{1}{\Psi_2} \frac{\partial \Psi_2}{\partial r_{12}} \right)_{r_{12}=0} = D_0 - z_c. \quad (11)$$

If D_0 is chosen according to Le Sech, a $z_c = 0.01$ value leads to a 2% deviation from the true value. To avoid this error we propose $D_0 = 0.5 + z_c$ to exactly satisfy the electron–electron cusp condition. Table 2 displays the parameters values for the bound states given by Eq. (7) for the same atoms and z_c values considered in Table 1.

The Kato cusp conditions as written in Eq. (3), require a coordinate-independent right hand side. Meanwhile, the logarithmic derivatives of the function Ψ_1 are not constants at the singular points of the Hamiltonian, but depend on the remaining spatial variables and parameters. The electron–electron cusp condition gives

Table 1

Variational parameters, ground state energies and Kato cusp conditions calculated using the wave function given in Eq. (6)

Atom	a	b	λ	C_0	$\langle E \rangle$	$\langle E \rangle_{\text{exact}}$	$R_{\text{eN}}(0)$	$R_{\text{eN}}(r_{2m})$	\bar{R}_{eN}	R_{ee}
H^-	0.4666	1.0721	0.0373	-0.9307	-0.5259	-0.5277	-0.799	-0.9618	-0.9875	0.3566
He	1.4126	2.2068	0.1990	-0.6649	-2.9019	-2.9037	-1.809	-1.9158	-1.9588	0.3650
Li^+	2.3328	3.3006	0.3911	-0.4951	-7.2780	-7.2799	-2.816	-2.9109	-2.9531	0.3637
Be^{2+}	3.2614	4.3781	0.5892	-0.3918	-13.6536	-13.6555	-3.819	-3.9092	-3.9507	0.3631
B^{3+}	4.1973	5.4456	0.7896	-0.3236	-22.0290	-22.0309	-4.821	-4.908	-4.9493	0.3628
C^{4+}	5.1387	6.5064	0.9911	-0.2754	-32.4043	-32.4062	-5.822	-5.9076	-5.9485	0.3629
N^{5+}	6.0846	7.5620	1.1932	-0.2396	-44.7795	-44.7814	-6.823	-6.9076	-6.9479	0.3628
O^{6+}	7.0341	8.6137	1.3957	-0.2120	-59.1546	-59.1565	-7.823	-7.9072	-7.9476	0.3628
F^{7+}	9.6622	7.9865	1.5984	-0.1901z	-75.5297	-75.5317	-8.824	-8.906	-8.9473	0.3628
Ne^{8+}	10.7079	8.9414	1.8013	-0.1723	-93.9048	-93.9068	-9.8246	-9.9068	-9.947	0.3629

Table 2
Variational parameters and ground state energies using the wave function given in Eq. (7) with $z_c = 0.01$

Atom	λ	a	$\langle E \rangle$	$\langle E \rangle_{\text{exact}}$
H ⁻	0.5829	0.0599	-0.5267	-0.5277
He	0.7243	0.1983	-2.9019	-2.9037
Li ⁺	0.8658	0.3492	-7.2778	-7.2799
Be ²⁺	0.9890	0.5018	-13.6533	-13.6555
B ³⁺	1.0994	0.6562	-22.0286	-22.0309
C ⁴⁺	1.1997	0.8097	-32.4038	-32.4062
N ⁵⁺	1.2928	0.9650	-44.7789	-44.7814
O ⁶⁺	1.3790	1.1190	-59.1541	-59.1565
F ⁷⁺	1.4576	1.2673	-75.5291	-75.5317
Ne ⁸⁺	1.5348	1.4212	-93.9042	-93.9068

$$R_{\text{ee}} = \left(\frac{1}{\Psi_1} \frac{\partial \Psi_1}{\partial r_{12}} \right)_{r_{12}=0} = -\frac{z_c + C_0 \lambda}{1 + C_0}. \quad (12)$$

In Table 1 we show the values of R_{ee} , and observe that they are almost Z -independent and smaller than the correct value 0.5. This could be interpreted as an underestimation of the interelectronic repulsion by the function given by Eq. (6).

In Fig. 1 we show $-R_{\text{eN}}(r_2)/Z$, where

$$R_{\text{eN}}(r_2) = \left(\frac{1}{\Psi_1} \frac{\partial \Psi_1}{\partial r_1} \right)_{r_1=0} \quad (13)$$

for the parameters obtained variationally. We observe a strong variation with the r_2 coordinate,

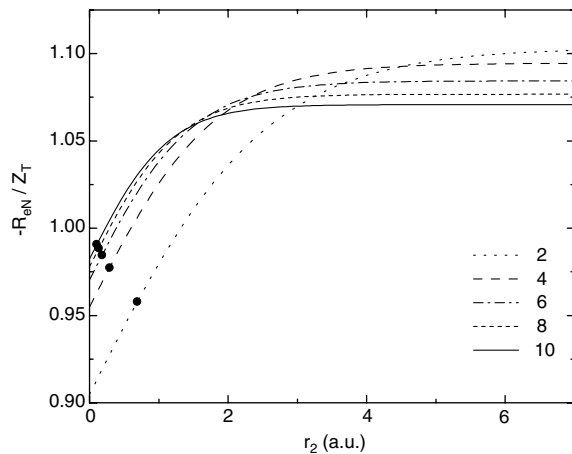


Fig. 1. R_{eN} as a function of r_2 . Dotted line: He; dashed line: Be²⁺; dot-dashed line: C⁴⁺; short-dashed line: O⁶⁺; solid line: Ne⁸⁺. The dots represent $R_{\text{eN}}(r_{2m})$.

which decreases for increasing Z . One way to evaluate a coordinate-dependent cusp condition is by considering the double coalescence limit

$$\begin{aligned} R_{\text{eN}}(r_2 = 0) &= \left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_1} \right)_{r_1=r_2=0} \\ &= \left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_2} \right)_{r_1=r_2=0}. \end{aligned} \quad (14)$$

This corresponds to the limit $r_{1,2} = 0$ in Fig. 1 [11,15]. In Table 1 we show $R_{\text{eN}}(r_2 = 0)$ for Ψ_1 , and observe a deviation of 10% for He, which diminishes for increasing Z .

Concerning the electron–nucleus coalescence other criteria can be introduced. When the electron labeled by r_1 coalesces with the nucleus, the wave function describing the spatial distribution of the remaining electron has a maximum radial probability at the point r_{2m} . Therefore, this point is physically more relevant than $r_2 = 0$ (the double coalescence limit), for He-like atoms. For many-electron atoms, double coalescence could nevertheless be meaningful [16]. Then the Kato cusp conditions for approximated wave functions could be evaluated with these r_{2m} values for different Z charges. The values

$$R_{\text{eN}}(r_{2m}) = \left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_1} \right)_{r_1=0; r_2=r_{2m}} \quad (15)$$

are given in Table 1, and are represented by dots in Fig. 1.

In most applications the cusp condition for one electron appears integrated over the spatial distribution of the other electron [14]. The high energy limit for the photo excitation–ionization amplitude depends on the spatially weighted values of the electron–nucleus Kato condition:

$$\left\langle \phi(r_2) \left| \frac{\partial \Psi}{\partial r_1} \right| (r_1 = 0, r_2) \right\rangle = -Z \langle \phi(r_2) | \Psi(r_1 = 0, r_2) \rangle, \quad (16)$$

where $\phi(r_2)$ is the final excited ionic state [15]. Therefore, an alternative test would be to check the mean value of the Kato condition

$$\overline{R}_{\text{eN}} = \frac{\left\langle \Psi(r_1 = 0, r_2) \left| \frac{\partial \Psi}{\partial r_1} \right| (r_1 = 0, r_2) \right\rangle}{\langle \Psi(r_1 = 0, r_2) | \Psi(r_1 = 0, r_2) \rangle}. \quad (17)$$

An equivalent relation operates at $r_2 = 0$. These mean cusp-conditions also seem more correct, in a “weak” functional sense, than Eq. (14) giving a further measure of the convenience of the function. Note that Eq. (17) is similar to that used for the mean energy.

The values of cusp conditions resulting from Eqs. (14), (15) and (17) for Ψ_1 , are shown in Table 1. We observe quite large differences for low ion charges that become smaller as Z increases. Deviation from the exact Kato value is smaller for \bar{R}_{eN} and larger for $R_{eN}(r_2 = 0)$. The two new criteria introduced here have a more sound physical base, and furthermore seem to give more appropriate values than the usual double coalescence rule.

3. Conclusions

Simple analytic variational wave functions are proposed for the ground states of two electron atoms, by modifying the Bonham and Kohl and Le Sech functions used so far [4,7]. These new functions avoid the need of convergence factors in the evaluation of atomic ionization and excitation transition amplitudes.

We have determined the atomic energy when cut-offs are introduced, and the original parameters obtained for Eqs. (4) and (5) are kept. We have shown that these cut-offs lead to a modification of the binding energy and the cusp conditions, distorting in this sense the wave function’s quality. We have also determined the variational parameters for the wave functions proposed and evaluated the corresponding binding energies, for nuclear charges up to $Z = 10$. The energies were compared with the exact values. For the two wave functions here used, we have obtained very close agreement for the atomic energies. Those corresponding to the wave function given by Eq. (6) are slightly closer to the exact values for $Z > 2$ by about 5 or 6 in the fourth decimal place.

The Kato cusp conditions at the coalescence points are exactly fulfilled by the function given by Eq. (7), but for the function in Eq. (6), these conditions are coordinate-dependent. We have discussed this dependence and performed the usual test at the three body coalescence point. Further-

more, two new procedures were proposed to test the electron–nucleus cusp condition, based on the relevant region and mean values of the wave functions. One of them considers the remaining electron at the radius corresponding to the maximum radial probability. In other words, it considers that this is the relevant region in which the cusp condition contributes when the wave function is applied in distorted-wave models. On the other hand, the latter criterion projects the cusp conditions with the second-electron spatial distribution. This is the usual form appearing in transition amplitudes.

Comparing the three criteria for cusp conditions we observe that R_{eN} gives very large deviations from the true value for low charged ions. For low Z values, when one of the electrons coalesces with the nucleus the radial distribution of the second electron extends over several atomic units and therefore a criterion based on three-body coalescence appears incorrect. As the charge increases, the second electron moves nearer to the nucleus and R_{eN} improves. The two new criteria consider the real distribution of the second electron and could be applied for any charge.

In any case, for two electron atoms these criteria appear to be more appropriate than the double-coalescence limit. In this sense, they could be useful to characterize wave functions which do not exactly fulfill the cusp conditions.

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