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ScienceDirect
Journal of Electron Spectroscopy and Related Phenomena 161 (2007) 204–206
JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena
www.elsevier.com/locate/elspec

Hylleraas-like functions with the correct cusp conditions: K-shell electrons for the neutral atoms

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Available online 31 March 2007

Abstract

We present simple correlated wavefunctions for the two K-shell electrons of neutral atoms. A variational method was chosen to calculate the mean energy of the ground state, in which the electrons are subject to a local Hartree potential representing the presence of the outer shell electrons. The functions are constructed in terms of exponential and power series, where special care has been taken in order to fulfill the exact behavior 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, are also analyzed.

Keywords: K-shell electrons; Variational method; Kato cusp conditions

1. Introduction

The wavefunctions of two-electron atoms and ions have been investigated in great detail since the early days of quantum mechanics. It is the simplest of all quantum systems in which electron–electron correlations have an important effect. Many authors have worked in the search of accurate and simple functions [1–5].

Recent measurements of double ionization of He and Ne by Schulz et al. [6] confirmed that the correlation function for back to back emission of two electrons with equal energy depends sensitively on the electron–electron correlation effects in the initial state. Experiments in proton-Helium transfer ionization by Mergel et al.[7] 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 [8,9] demand knowledge of appropriate functions which account not only for correlation but also for the influence of the passive-shell electrons.

We describe here simple and fully correlated two-electron wavefunctions for the K-shell inner electrons of many neutral atoms. The method is based on the semi-separable strategy originally proposed by Pluvinage [10]. Hylleraas-like wavefunctions [11,12] are constructed in terms of exponential and power series. In our approach, special care has been taken in order to fulfill all the coalescence (Kato) cusp conditions [13]. The importance of fulfilling these conditions has been pointed out by many authors [14–21] who have discussed the value of satisfying them in the electron-atom double ionization and (e,3e) processes.

The form of the wavefunctions proposed, and the method for their calculations are introduced in Section 2. A local Hartree potential representing the presence of outer shell electrons is also presented in this section. In Section 3 we report the results of the calculations of a set of wavefunctions and the mean values describing different physical properties, for selected atoms. Atomic units are used throughout this paper.

2. Theory

Let us consider a system composed of two interacting electrons described by the nonrelativistic Hamiltonian

$$H_{\mathrm{K}} = T + V(r_1) + V(r_2) + \frac{1}{r_{12}}. \tag{1}$$

Here r_1 and r_2 represent the distance of the electrons to the nucleus and $1/r_{12}$ is the electron–electron repulsion. T is the

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doi:10.1016/j.elspec.2007.03.013

total kinetic energy

$$T = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \nabla_{12}^2 - \nabla_1 \cdot \nabla_{12} - \nabla_2 \cdot \nabla_{12}, \tag{2}$$

which for the levels considered in our work (with total $L = 0$) can be written as

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

with

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

The central potential $V(r)$ for electrons in the K-shell can be written [22] as,

$$V(r) = -\frac{2}{r} + \frac{Z_K(r)}{r} \to \begin{cases} -\dfrac{Z}{r} & \text{as } r \to 0, \\ -\dfrac{2}{r} & \text{as } r \to \infty, \end{cases} \tag{5}$$

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 article we will consider the local Hartree potential given by

$$\frac{Z_K(r)}{r} = \frac{(2 - Z)}{r} + \sum_{nl \neq 1s^2} \int d\mathbf{x} \frac{|\varphi_{nl}(\mathbf{x})|^2}{|\mathbf{r} - \mathbf{x}|}, \tag{6}$$

where φ_{nl} represents the upper shells wavefunctions (the K-shell electrons are removed from the sum). For the calculation of the static potential (Eq. (6)), we use Roothaan–Hartree–Fock functions, tabulated by Bunge et al. [23]. These functions satisfy the electron–nucleus cusp condition required for our purposes. The potential introduced to account for the influence of the outer electrons is local, and does not include exchange with these electrons. However, the effect of this exchange is not appreciable since the innermost K-shell is well separated, both in energy and coordinate space, from the outer shells. We explicitly calculated the exchange potential for several atoms, and found its contribution negligible.

To make the calculation tractable, we have fitted $Z_K(r)$ as a combination of simple exponentials

$$Z_K(r) \simeq -\sum_{j=1}^{3} Z_j e^{-\mu_j r}. \tag{7}$$

The asymptotic conditions at $r \to 0$ (Eq. (5)) imposes

$$\sum_{j=1}^{3} Z_j = Z - 2. \tag{8}$$

A list of the parameters Z_j and μ_j for atoms from Li to Xe are shown in Table 1 of our previous work [22].

Table 1
Parameters and mean energy for the K-shell electrons in the ground state of some neutral atoms

	Z	β	α	c_{200}	c_{400}	$\langle E \rangle$
GR2	10	3.48199		0.75224		−71.1955
GR3	10	3.38635		0.679698	0.429059	−71.1959
Ψ_{MM}	10	3.38409	1.19155			−71.1952
Ψ_{LeSech}	10	1.52516	1.71493			−71.1955
GR2	18	6.67782		1.69		−246.564
GR3	18	6.39091		1.50418	3.55039	−246.564
Ψ_{MM}	18	6.53434	1.8049			−246.563
Ψ_{LeSech}	18	2.89978	2.58327			−246.564
GR2	36	13.5696		4.12732		−1057.25
GR3	36	13.6759		3.90963	19.7189	−1057.25
Ψ_{MM}	36	13.3912	2.84307			−1057.25
Ψ_{LeSech}	36	5.89382	4.04847			−1057.25
GR2	54	19.1875		8.09173		−2473.17
GR3	54	19.8356		8.32169	−33.8045	−2473.17
Ψ_{MM}	54	18.8523	3.98216			−2473.17
Ψ_{LeSech}	54	8.45105	5.66696			−2473.17

GR3: Gasaneo–Rodriguez [5], MM: function $\Phi^a_{1s^2}$ from Mitnik–Miraglia [22], LeSech: function $\Phi^c_{1s^2}$ from [22]. (In both last cases, the name of the parameter β given in [22] is λ.)

The structure of Eq. (1) suggests a suitable form for the variational wavefunction. We can write it as a product of two factors, one is an approximate solution of the separable parts of the equation, and the second takes into account the coupling between the motion of the coordinates. This is similar to the method of pseudo-separability originally proposed by Pluvinage [10] and generalized, later on, by other authors [3,24–26,5]. In this report we propose a simple approximate solution where the effects of the Coulomb interactions are included in the wavefunctions and all the coalescence cusp conditions [13] are satisfied. In mathematical terms, we write the variational wavefunction as

$$\Phi(r_1, r_2, r_{12}) = \phi(r_1, r_2, r_{12})\Omega(r_1, r_2, r_{12}), \tag{9}$$

where $\phi(r_1, r_2, r_{12})$ is written as the product of three-separable functions

$$\phi(r_1, r_2, r_{12}) = e^{-Z(r_1 + r_2)}\left(\frac{1 + 2\beta}{2\beta} - \frac{1}{2\beta}e^{-\beta r_{12}}\right) \tag{10}$$

and

$$\Omega(r_1, r_2, r_{12}) = \sum_{i,j,k} c_{i,j,k} r_1^i r_2^j r_{12}^k = \sum_{i,j,k} c_{i,j,k}\Omega_{i,j,k}(r_1, r_2, r_{12}). \tag{11}$$

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. The same is observed in the functions proposed by other authors [24,25,3] in which the functions $\sinh(\lambda r)/r$ or $\cosh(\lambda r)$ explicitly excludes first powers of r. The function Φ depends on a nonlinear parameter β, and on a set of linear parameters c. The variational method can be used to optimize all these parameters. The equations for the c coefficients become a generalized eigenvalue problem [27].

Table 2
Mean radial values obtained for neutral atoms

	Z	$\langle r_{12}\rangle$	$\langle r_{12}^2\rangle$	$\langle 1/r_{12}\rangle$	$\langle R\rangle$	$\langle \mathbf{r}_1 \cdot \mathbf{r}_2\rangle$	Virial
GR2	10	0.23063	0.06666	5.91411	0.236797	−0.00037	−2.0027
GR3	10	0.23077	0.06681	5.91472	0.236904	−0.00038	−2.0017
Ψ_{MM}	10	0.2306		5.916			−2.0023
GR2	18	0.12568	0.01981	10.8713	0.129453	−0.00006	−2.0021
GR3	18	0.12573	0.01984	10.8726	0.12949	−0.00006	−2.0013
Ψ_{MM}	18	0.12566		10.872			−2.0019
GR2	36	0.06197	0.00482	22.0835	0.0639333	-7.4918×10^{-6}	−2.001
GR3	36	0.06195	0.00482	22.0746	0.0639381	-7.4342×10^{-6}	−2.0007
Ψ_{MM}	36	0.06194		22.0716			−2.0009
GR2	54	0.04115	0.00212	33.2352	0.0425003	-2.3519×10^{-6}	−2.00004
GR3	54	0.04115	0.00212	33.2355	0.0424993	-2.2817×10^{-6}	−2.0001
Ψ_{MM}	54	0.04115		33.237			−2.0000

3. Results and conclusions

The aim of this paper is to use the simple and accurate wavefunctions (denoted as GR) presented in a previous work [5], to study complex systems. These functions have three variational parameters. Therefore, we compare them with the similar functions $\Phi^{x}_{1s^2}$ obtained by Mitnik and Miraglia [22](denoted here Ψ_{MM} and Ψ_{LeSech}). The functions Ψ_{LeSech} have the same type of angular correlation as the function proposed by Le Sech [3] for the He-like ions. In Table 1, we present the results obtained for minimizing the mean energy of the K-shell electrons in the ground state of neutral atoms. Four neutral atoms with nuclear charge Z equal to 10, 18, 36 and 54 are studied. The Ψ_{MM} and Ψ_{LeSech} functions have been recalculated in order to obtain the same level of accuracy as the new proposed GR functions.

The best ground state mean energy for the Ne atom ($Z = 10$) is obtained with the GR3 wavefunction. However, the similar Ψ_{LeSech} function gives an energy comparable to the much simpler GR2 function (with only two parameters). The energies obtained for the Ar, Kr and Xe atoms are similar for the three types of wavefunctions. However, the energy is not the only criterion to evaluate the quality of a trial wavefunction. Thus, in Table 2, we analyze several local properties, such as spatial mean values, and the hyperspherical radius $R = (r_1^2 + r_2^2)^{1/2}$. We also analyzed another global property, the virial coefficient, which departs from 2 (the exact value) only in the fourth significant figure, in almost every case.

In conclusion, continuing with the line of our previous works [22,5] we have introduced a set of simple and accurate wavefunctions to describe K-shell electrons of neutral atoms. These functions are strongly correlated and satisfy all the cusp conditions. Their simple form makes them very tractable for the calculation of atomic processes involving two active electrons. They describe very well the global and local parameters (mean energy, virial coefficient, spatial mean values, etc.).

Acknowledgments

This work has been supported by PICTR 2003/0437 of the ANPCYT, PGI 24/F027 Universidad Nacional del Sur, and UBACyT X075 (Argentina). Computational work was carried out at the High-Performance Opteron Parallel Ensemble (HOPE) cluster at IAFE.

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