



# Improved Le Sech wavefunctions for two-electron atomic systems



Rabeet Singh Chauhan\*, Manoj K. Harbola

Department of Physics, Indian Institute of Technology – Kanpur, Kanpur 208 016, India

## ARTICLE INFO

### Article history:

Received 7 July 2015

In final form 21 September 2015

Available online 28 September 2015

## ABSTRACT

For two electron atoms the ground-state wavefunctions of the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)(\cosh ar_1 + \cosh ar_2)(1 + 0.5r_{12}e^{-br_{12}})$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of two electrons and  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ , is made accurate by optimizing  $a$ ,  $b$  and  $\phi(\mathbf{r})$ . This is done by solving a variationally derived equation for  $\phi(\mathbf{r})$  and optimizing  $a$  and  $b$  to minimize  $\langle H \rangle$ . This wavefunction gives accurate energies and other properties of these systems.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The simplest of many-electron systems are those with two electrons like ions of the helium isoelectronic series or a harmonium atom [1]. Since the Schrödinger equation for these systems cannot be solved analytically, accurate solutions are obtained by using the variational principle for the energy. Thus an approximate parameterized form of the wavefunction is chosen incorporating the effects of electron–electron interaction in the wavefunction and the expectation value of the Hamiltonian (atomic units are used)

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_{ext}(\mathbf{r}_1) + v_{ext}(\mathbf{r}_2) + \frac{1}{r_{12}} \quad (1)$$

is minimized with respect to the parameters in the wavefunction, where  $v_{ext}(\mathbf{r}) = -\frac{Z}{r}$  for He isoelectronic series. This leads to an optimized approximate wavefunction and the corresponding energy. The various forms used for the wavefunctions are those by Hylleraas [2–6], Chandrasekhar [7] and Kinoshita [8,9]. As an example of how these forms simulate the effects of electron–electron interaction, we consider the Chandrasekhar wavefunction for a two-electron atom which is given as

$$\Psi_C(r_1, r_2) = C_N(e^{-ar_1}e^{-br_2} + e^{-ar_2}e^{-br_1}) \quad (2)$$

where  $a$  and  $b$  are the parameters to be optimized and  $C_N$  is the normalization constant. The idea behind writing the wavefunction in the form above is as follows. In the ground state of a two electron atom, each electron moves essentially in a hydrogen-atom like 1s

orbital (of the form  $e^{-ar}$ ). However, because of the electron closer to the nucleus, the effective nuclear charge is different for the outer electron. Hence the orbitals of the two electrons are different. Symmetrization of the resulting product wavefunction then leads to the form given in Eq. (2).

Another way of obtaining accurate wavefunctions has been given by Hylleraas [2–6] where the wavefunction is expressed as

$$\Psi_H(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{l_i} t^{m_i} u^{n_i} \quad (3)$$

where  $s = r_1 + r_2$ ,  $t = r_1 - r_2$ ,  $u = |\mathbf{r}_1 - \mathbf{r}_2|$ , and  $\zeta$  and  $c_i$  are variational parameters. The most accurate calculation using this form of the wavefunction has been that of Frankowski and Pekeris [10], who used a 246-term wavefunction to get highly accurate energies for the helium isoelectronic series. Employing a 230-term wavefunction Freund et al. [11] got essentially the same results as those of [10]. Using another modification to Hylleraas type wavefunction, Koga et al. [12] constructed a 204-term wavefunction that gives energy within 16 nano-Hartree of the energy given in [11]. In addition, usefulness of the work of [12] lies in the fact that the electronic density of the 204-parameter wavefunction is expressed in a simple analytical form with 43 parameters. Along similar lines, Umrigar and Gonze [13] constructed very accurate densities for He isoelectronic series by using 491-term wave function having the same form of the basis set as used by Freund et al. The resulting densities have been used in the past to construct exchange–correlation potential [13] and to calculate [14] polarizability of two electron atoms and also to study derivative discontinuity [15] of the Kohn–Sham exchange–correlation [16] potential of density functional theory [17]. Examples of Refs. [13,14,16] are sufficient to show that the

\* Corresponding author.

E-mail addresses: [rabeet@iitk.ac.in](mailto:rabeet@iitk.ac.in) (R.S. Chauhan), [mkh@iitk.ac.in](mailto:mkh@iitk.ac.in) (M.K. Harbola).

**Table 1**

Total energies for He-like systems using approximate wavefunction  $\Psi_L$  of Eq. (4) and  $\Psi_{ML}$  of Eq. (9). Their comparison with the energies given in [12] (given in the column under  $\Psi_K$ ) is also made in the table. The differences of each energy from that given in [12] is given in ppm under the energies.

Atom	$\Psi_L$		–Energy a.u.	$\Psi_K$	–Energy a.u.	$\Psi_{ML}$	
	$a$	$b$				$a$	$b$
H <sup>-</sup>	0.58	0.06	0.5267 (1899)	0.5277	0.5271 (1137)	0.62	0.06
He	0.72	0.20	2.9020 (586)	2.9037	2.9028 (310)	0.93	0.20
Li <sup>+</sup>	0.87	0.36	7.2778 (289)	7.2799	7.2788 (151)	1.19	0.36
Be <sup>2+</sup>	0.99	0.52	13.6533 (161)	13.6555	13.6544 (81)	1.48	0.54
B <sup>3+</sup>	1.10	0.67	22.0286 (104)	22.0309	22.0297 (55)	1.72	0.70
Ne <sup>8+</sup>	1.54	1.47	93.9042 (28)	93.9068	93.9054 (15)	2.78	1.54

availability of accurate densities facilitates studies in fundamental aspects of density functional theory. Therefore methods that can give accurate densities with relative computational ease are desirable to facilitate such studies. With this in mind Le Sech [18] introduced a semianalytical wavefunction for the ground state of two electron atoms and ions that gives energy within parts per million (ppm) of the values of energies in Refs. [10–12]. Furthermore, the wavefunction is simple so that it can be employed with ease for other investigations. We have tried to use this wavefunction for fundamental studies in density functional theory. In doing so, we find that while the wavefunction gives good energies, the densities given by it are not accurate enough for such studies. The question it raises is if Le Sech wavefunction can be improved further while maintaining its simple form but making the densities accurate enough so that they can be employed with confidence for further research. The work presented in this Letter describes our attempts in this direction.

In the following we first discuss the Le Sech wavefunction, the corresponding densities, the degree of accuracy of the satisfaction of ionization potential theorem [15] and the exchange-correlation potential [16] obtained from those densities. We then introduce an improved version of these wavefunctions and show that they lead to better accuracy without any significant increase in the computational effort.

## 2. Le Sech wavefunction and its accuracy

The wavefunction proposed by Le Sech is motivated by the intuitive aspects of the Chandrasekhar wavefunction and correlation factor given by earlier studies [19]. The wavefunction is given as

$$\Psi_L(\mathbf{r}_1, \mathbf{r}_2) = C_N e^{-Z(r_1+r_2)} f(r_1, r_2, r_{12}) \quad (4)$$

where

$$f(r_1, r_2, r_{12}) = (\cosh ar_1 + \cosh ar_2)(1 + 0.5r_{12}e^{-br_{12}})$$

**Table 2**

Densities and their derivatives at  $r=0$  calculated by using  $\Psi_L$  and  $\Psi_{ML}$ . For the density given by Koga et al. [12] (given in the column under  $\psi_K$ ) we have used the exact expression given in their paper to calculate  $\rho(r=0)$  and  $-\frac{d\rho}{dr}(r=0)$ . Numbers given are in atomic units.

Atom	$\rho(r=0)$			$-\frac{d\rho}{dr}(r=0)$		
	$\Psi_L$	$\Psi_K$	$\Psi_{ML}$	$\Psi_L$	$\Psi_K$	$\Psi_{ML}$
H <sup>-</sup>	0.310	0.323	0.329	0.621	0.649	0.657
He	3.554	3.621	3.616	14.214	14.483	14.462
Li <sup>+</sup>	13.552	13.704	13.693	81.312	82.223	82.185
Be <sup>2+</sup>	34.180	34.396	34.384	273.438	275.167	275.077
B <sup>3+</sup>	69.164	69.517	69.501	691.640	695.165	695.011
Ne <sup>8+</sup>	594.067	595.245	595.210	11 881.332	11 904.788	11 904.200

and  $C_N$  is the normalization constant and  $Z$  is the atomic number of the atomic system. The factor  $(\cosh ar_1 + \cosh ar_2)$  is chosen so that its product with  $e^{-Z(r_1+r_2)}$  resembles the wavefunction of Eq. (2) and the cusp condition [20] is satisfied exactly by the wavefunction. The parameters  $a$  and  $b$  are obtained variationally by minimizing the expectation value of the Hamiltonian with respect to them. The values of parameters  $a$  and  $b$  and the corresponding energies so obtained for H<sup>-</sup>, He, Li<sup>+</sup>, Be<sup>2+</sup>, B<sup>3+</sup> and for Ne<sup>8+</sup> are given in Table 1 along with the exact total energies obtained in [12]. The differences between the two energies are also shown. We mention that the values of parameters  $a$  and  $b$  and the corresponding energies obtained by us are slightly different from those reported in Ref. [18].

It is clear from Table 1 that the wavefunction  $\Psi_L$  of Eq. (4) leads to accurate total energies with the difference from those of [12] becoming smaller with increasing  $Z$ . The difference for H<sup>-</sup> is 1899 parts per million (ppm) and goes down to 28 ppm for Ne<sup>8+</sup>. We note that the wavefunction of Eq. (4) can be improved further [18] with the inclusion of one more parameter and leads to a closer agreement with the exact energies.

The question we now ask is how accurate are the densities given by  $\Psi_L$ ? This is important from the point of view of having an accurate and easily accessible density of two electron systems if we were to employ them to investigate the foundational aspects of density functional theory of many electron systems in general and two electron systems in particular. The density  $\rho(\mathbf{r})$  is obtained from  $\Psi_L(\mathbf{r}_1, \mathbf{r}_2)$  from the formula

$$\rho(\mathbf{r}) = 2 \int |\Psi_L(\mathbf{r}, \mathbf{r}_2)| d\mathbf{r}_2. \quad (5)$$

The integral over  $\mathbf{r}_2$  is carried out numerically.

We present in Table 2 the values of  $\rho(r=0)$ ,  $\frac{d\rho}{dr}|_{r=0}$  and in Tables 3 and 4 various moments of the densities obtained from the Le Sech wavefunction. A comparison of the results is made with the

Download English Version:

<https://daneshyari.com/en/article/5379854>

Download Persian Version:

<https://daneshyari.com/article/5379854>

[Daneshyari.com](https://daneshyari.com)