

Comment on “Towards a differential equation for the nonrelativistic ground-state electron density of the He-like sequence of atomic ions”

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In a recent paper [Phys. Rev. A **71**, 042501 (2005)], Howard and March presented the exact ground state wave function of the spherical He-like atom, and many physical aspects of this solution were analyzed. We show that this function is not the exact solution of the model.

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In Ref. [1] Howard and March propose an exact solution for S waves for the spherical He-like atom. In this model the Coulombic repulsion between electrons e^2/r_{12} is replaced by its spherical average $e^2/r_>$, where $r_> = \max(r_1, r_2)$. The authors assumed that the radial Schrödinger equation is separable and that an exact solution exists. The equation and the proposed S -wave energies and wave functions (in particular, the ground state energy and wave function) are described in Eqs. (2.1)–(2.8) of Ref. [1].

This model has a long history and it has been used to study bound [2,3] and scattering [4] solutions of the two-electron atomic system. For S states the Schrödinger equation, in atomic units, takes the form

$$\left[-\frac{1}{2r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} - \frac{Z}{r_1} - \frac{1}{2r_2^2} \frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} - \frac{Z}{r_2} + \frac{1}{r_>} \right] \Psi(r_1, r_2) = E\Psi(r_1, r_2), \quad (1)$$

where Z is the nuclear charge. Note that:

(i) There is not angular dependence in the Hamiltonian. Therefore, the S waves have not only total angular momentum equal to zero, but also the individual angular momentum of each electron is zero.

(ii) The repulsive electronic potential does not present a Coulombic divergence at $r_1=r_2$, and therefore, there is no cusp effect at $r_1=r_2$ in the exact solution.

(iii) The potential energy is finite and continuous except in the origin of coordinates. Then the condition for the logarithmic derivate of the wave function at $r_1=r_2$ is [4]

$$\frac{\partial}{\partial r_1} \ln[\Psi(r_1, r_2)] \Big|_{r_1=r_2} = \frac{\partial}{\partial r_2} \ln[\Psi(r_1, r_2)] \Big|_{r_1=r_2}. \quad (2)$$

The radial Schrödinger equation for S waves could be written in $(r_<, r_>)$ coordinates as [3]

$$\left[-\frac{1}{2r_<^2} \frac{\partial}{\partial r_<} r_<^2 \frac{\partial}{\partial r_<} - \frac{Z}{r_<} - \frac{1}{2r_>^2} \frac{\partial}{\partial r_>} r_>^2 \frac{\partial}{\partial r_>} - \frac{Z-1}{r_>} \right] \Psi(r_<, r_>) = E\Psi(r_<, r_>). \quad (3)$$

The correct *nonseparable* boundary condition at $r_<=r_>$ is [3,4]

$$\frac{\partial}{\partial r_<} \ln[\Psi(r_<, r_>)] \Big|_{r_<=r_>} = \frac{\partial}{\partial r_>} \ln[\Psi(r_<, r_>)] \Big|_{r_<=r_>}. \quad (4)$$

Equation (3) together with the boundary condition Eq. (4) conform a nonseparable Hermitian eigenvalue problem [3,4]. With the (wrong) assumption that the model has a separable structure, the normalized symmetric solution proposed in Ref. [1], in $(r_<, r_>)$ coordinates, takes the form

$$\Psi(r_<, r_>) = \sqrt{\frac{(Z-1)^3(2Z-1)^5}{2\pi^2(16Z^2-25Z+10)}} \times \exp[-Zr_< - (Z-1)r_>]. \quad (5)$$

It is straightforward to show that this function, that locally is a solution of the differential equation (3), does not satisfy the boundary condition Eq. (4),

$$\frac{\partial}{\partial r_<} \ln[\Psi(r_<, r_>)] \Big|_{r_<=r_>} = -Z \quad (6)$$

and

$$\frac{\partial}{\partial r_>} \ln[\Psi(r_<, r_>)] \Big|_{r_<=r_>} = -(Z-1). \quad (7)$$

The assumed exact ground state energy is also given in Eq. (2.8) of Ref. [1], $E(Z) = -(Z^2+1/2)+Z$.

We performed an accurate variational calculation with 861 functions of the form $\exp[-\beta(r_1+r_2)](r_1^i r_2^j)$ with $i \leq j = 0, \dots, 40$, and β is an optimization parameter. The variational value for the ground state energy must satisfy $E_0(Z) \leq E_{var}(Z)$, where $E_0(Z)$ is the exact ground state energy for the spherical He-like atom. In Table I we compare our rigorous upper bound for the ground state energy for $Z=1$

TABLE I. Comparison of the ground state energy for $Z=1$ and $Z=2$ of the spherical He-like atom.

	Variational	Ref. [1]
$Z=1$	-0.514 496	-0.5
$Z=2$	-2.879 02	-2.5

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and $Z=2$, giving lower values than those reported in Ref. [1]. Moreover, the ionization ground state energy given in Eq. (4.5) of Ref. [1] is $I(Z) = -(Z-1)^2/2$. Therefore, there should be no bound state for $Z \leq 1$. We find as a rigorous upper bound for the critical charge for bound states $Z_c \leq Z_{var} = 0.948\ 768$. The asymptotic behavior near the critical charge defines the critical exponent α , $I(Z) \sim (Z-Z_c)^\alpha$ for $Z \rightarrow Z_c^+$ [5]. We computed this exponent using a finite size scaling calculation [5] and obtained the value $\alpha = 0.996(5)$, in contradiction with the value $\alpha = 2$ given in Eq. (4.5) of Ref. [1]. This value for the exponent is consistent with the exact value for the exponent $\alpha = 1$ for the He-like atom [6].

We used the variational wave function to calculate the ground-state density $\rho(r)$. In Fig. 1 our result is compared with the (normalized) density presented in Eq. (2.11) of Ref. [1] for $Z=2$.

Summarizing, we showed that the ground-state energy and the corresponding wave function proposed in Ref. [1] are not the exact solution of the spherical He-like atom. Even as an approximate solution, it neither captures the correct near threshold behavior of the exact solution, nor does the corresponding density give a reasonable value for $Z=2$. For large values of Z , the boundary condition Eq. (4) is satisfied in first order in Z , and then, near the limit of two noninteracting electrons, the proposed solution is a good approximation.

Finally, we have to note that recently one of the authors of Ref. [1] and C. Amovilli published a second article [7] study-

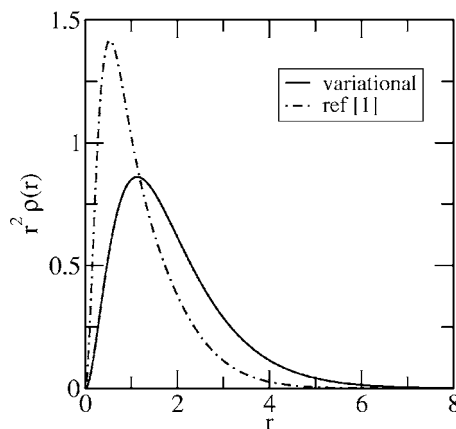


FIG. 1. Ground state density $r^2\rho(r)$ vs r for $Z=2$ from a variational calculation and from Eq. (2.11) of Ref. [1].

ing the one particle density matrix of the spherical He-like atom using the wave function presented in Ref. [1]. Therefore, the main point of this comment is also applicable to Ref. [7].

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