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Excited state entanglement on a two-electron system near the ionization threshold

Omar Osenda and Pablo Serra

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

E-mail: osenda@famaf.unc.edu.ar and serra@famaf.unc.edu.ar

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Abstract

We have investigated the critical properties of the lowest-energy triplet state of the spherical helium atom. Using finite-size scaling methods we calculate critical charge and critical exponents for both the energy and the von Neumann entropy near the ionization threshold. We show that the scaling properties of the energy and the von Neumann entropy for this excited state are qualitatively different from those obtained for the ground state. These scaling properties are quantified in terms of critical exponents; therefore, the analysis is applicable to other few-fermion systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The behaviour of atomic or molecular systems near the ionization threshold is crucial for a number of phenomena, amongst which photoionization is very important [1]. In addition to this, recently, a number of papers have dealt with the application of quantum information concepts, such as entanglement, to atomic systems. For example, Carlier *et al* [2] studied a one-dimensional two-electron atom and calculated the entanglement carried by the two-electron eigenstates. Amovilli and March [3] studied the Shannon and Jaynes entropies for an exactly solvable artificial two-electron atom, and Shi and Kais [4] studied the near-threshold scaling of the Shannon entropy for the two-electron atom. A paper by us [5] dealt with the behaviour of entanglement, determined using the von Neumann entropy, near the ionization threshold of a two-electron atomic-like system, the spherical helium atom. In any case, as noted in the paper of Fedorov *et al* [1], there are some problems facing the choice of which quantity is more useful to quantify the entanglement on a given system. For the problem that they were considering, the photoionization of an atom, they introduced a measure of entanglement that is experimentally accessible. This difficulty is not only associated with which quantities are experimentally accessible, it is more deep rooted and has to do with the quantification of quantum correlations of indistinguishable particles.

From the beginning, it was recognized that the quantification of entanglement of indistinguishable particles is very different from that of distinguishable ones. This is so because of the exchange symmetry which requires the symmetrization or the antisymmetrization of the quantum wavefunctions describing bosons or fermions, respectively. In any case, there are a number of papers dealing with the subject of which quantity could be more useful or appropriate to analyse different situations: Buscemi *et al* [6] analysed the advantages of the linear entropy in a two-fermion system; Nielsen and Chuang [7], Ekert and Knight [8] preferred the Schmidt number; the occupation number basis is used and analysed by Gittings and Fisher [9] and also by Zanardi [10]; while the properties of the von Neumann entropy are discussed by Ghirardi and Marinatto [11]; for two fermions in a four-dimensional Hilbert space, the Slater formation measure [12] is the analogy of the concurrence introduced by Wootters [13] in the context of arbitrary states of two qubits. It is interesting to point out here that most of the quantities previously mentioned depend on the whole spectrum of the reduced density matrix of one of the particles ρ, and that the Schmidt number and the linear entropy are simple functions of $\mathrm{Tr}(\rho^2)$.

Recently, we have studied the behaviour of the entanglement for the ground state of an atomic-like two-

electron system as a function of the nuclear charge [5]. The ionization threshold, or critical point, for atomic-like systems is defined as the value of the nuclear charge for which a bound-state energy becomes absorbed or degenerate with the continuum. In [5] we have shown that the critical behaviour of the entanglement near the ionization threshold of an atomic-like system resembles the one observed for the entanglement near a quantum phase transition [14, 15]. Using the von Neumann entropy as the entanglement measure we found that the spherical helium's ground-state entanglement is discontinuous at the ionization point. It is well known from critical phenomena theory that the critical exponents of physical systems are related to very general characteristics of the system, and not to the details of the particular model under study. Therefore, the classical or quantum phase transitions can be classified as first-, second- (or other-) order transitions, depending on the kind of non-analyticity present in the energy of the ground state. In the same sense, it can be expected that other systems with the same characteristics as those of the spherical helium model have the same critical exponents, so it is not surprising that the helium atom and the spherical helium model have the same critical exponent associated with the energy of the ground state [16].

The picture emerging from our results is the following: if the system under consideration has a normalizable ground state at the threshold then the critical exponent associated with the energy is $\alpha = 1$ [17] and the critical exponent associated with the von Neumann entropy is $\mu = 0$ [5]. So a system that does not have a normalizable ground state at the threshold, and correspondingly has $\alpha > 1$, necessarily must have $\mu \neq 0$. For example, the ground state of a Li-like atom does not have a normalizable ground state at the threshold [18] and could be a good system to test these ideas. However, there are a number of issues to solve in order to effectively study this system, mainly that there is not a clear-cut measure of entanglement to be used and that for three identical fermions the Hilbert space of the system does not decompose in simple factors (an antisymmetric Hilbert space times a symmetric one) as the Hilbert space of two fermions does. For two-fermion systems the von Neumann entropy S is a good entanglement measure. A state ρ is entangled iff $S(\rho) > 1$ or, equivalently, the state cannot be written as a single Slater determinant.

Besides the subtleties involved in how to quantify the entanglement there are some technical issues too: the study of the three-body problem is difficult, even more so if the calculations are performed near the critical region. One way to avoid the aforementioned problems is to study a simpler system with the same critical behaviour, that is, identical critical exponents. The near-threshold behaviour of the ground state of a two-fermion system is qualitatively different from that of a three-electron system. In the first case, the ground state is a singlet state where both electrons have the same quantum numbers except the spin; then both electrons are in the same orbit for all values of the nuclear charge, and the electron density $\rho(r)$ has a simple maximum, giving a ground-state even at the critical charge with the corresponding exponent $\alpha = 1$. The picture is different for a three-fermion system; in this case, by the exclusion

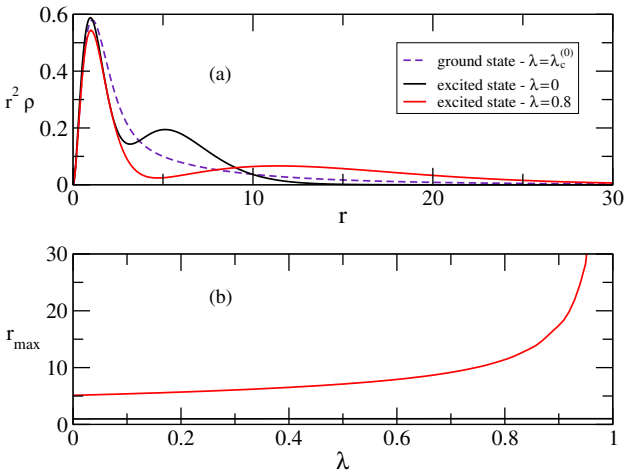

Figure 1. (a) Comparison of $r^2\rho(r)$ for the critical ground state $\lambda = \lambda_c^{(0)} = 1.054$, the non-interacting triplet state $\lambda = 0$ and the triplet state with $\lambda = 0.8$. (b) Both maxima of the density of the triplet state as a function of λ showing that the radius of the inner orbit is almost constant, but the system ionizes continuously for $\lambda \to 1$.

principle, the ground-state configuration has two electrons in the inner orbit and one in the outer orbit. When the nuclear charge goes down to the critical charge $Z = 2$ [18], the radius of the outer orbit goes continuously to infinity, and the outer electron becomes delocalized, therefore there are no bound states at the critical charge, and the critical exponent is $\alpha = 2$. The ground-state density of the Li atom has a peak near the Bohr radius and a second peak in the outer orbit. For values of $Z \to Z_c$ the outer peak goes to infinity. In other words, in the critical region, one electron is weakly bound to the nucleus and the other two remain near it; when the charge reaches its critical value the outer electron is lost.

The ground state of a two-electron atom, a spherically symmetric singlet state, does not have the possibility to lose an electron in such a way. But an excited state with its two electrons belonging to different atomic shells could do it (see figure 1). So, if the argument holds up, an excited state with its electrons on two different atomic orbits should have a critical exponent $\alpha = 2$, and a critical exponent $\mu \neq 0$. The purpose of the paper is to test these ideas. Moreover, as in previous work [5], in order to get accurate results in the critical region, we studied the spherical approximation to the two-electron atom.

This paper is organized as follows. In section 2 we give a summary of the spherical helium model. In section 3 we discuss the properties of the von Neumann entropy and its near-threshold behaviour; in particular we present in some detail how the entanglement of a degenerate state must be calculated, and the differences with the case of a non-degenerate pure state. Finally, the conclusions are given in section 4.

2. The model

The Hilbert space of the two-electron atom splits into two orthogonal subspaces: one subspace corresponds to spatially symmetric wavefunctions times the (antisymmetric) singlet

spinor, and the other corresponds to spatially anti-symmetric wavefunctions times the (symmetric) triplet spinor. Because many numerical methods, in particular the Ritz variational method that we use in this work, give more accurate results for the lowest-energy state of a given sub-space than for excited states, it is convenient to study the critical behaviour of the lowest-energy state of the triplet subspace. In this case, the electrons are in different orbits giving the desired near-threshold behaviour, and, using the same one-particle basis-set, the variational results are as good as those obtained for the ground state.

As we described above, the lowest-energy triplet is an extended state in the critical region, and it is necessary to expand it in a large basis-set in order to get a reasonable approximation to the critical parameters. Then it is convenient to use, instead of the two-electron atom, the approximation known as the spherical helium model [19]. In the spherical helium model the Coulombic repulsion between electrons, $1/r_{12}$, is replaced by its spherical average, $1/r_>$, where $r_> = \max(r_1, r_2)$, then the Hamiltonian, in atomic units, and applying the standard transformation $\vec{r} \to \vec{r}/Z$; $H \to Z^2 H$, takes the form [20]

$$H = h(1) + h(2) + \lambda V, \tag{1}$$

where

$$h(i) = \frac{1}{2}p_i^2 - \frac{1}{r_i}, \qquad \lambda = \frac{1}{Z}, \qquad V = \frac{1}{r_>}, \tag{2}$$

p_i and r_i are the momentum operator and the position operator, respectively, of the ith electron ($i = 1, 2$), r_{12} is the distance between electrons and Z is the nuclear charge. Note that the two-electron Hamiltonian commutes with the total angular momentum, therefore its s-waves are functions of r_1, r_2 and r_{12}. The Hamiltonian equation (1) has extra symmetries; it commutes with the total angular momentum and also with the one-particle angular momenta, and then the s-waves depend only on r_1 and r_2. Then we have to expand only a two-variable function instead of a three-variable function as in the helium s-waves. That is, the s-waves of Hamiltonian equation (1) take the form

$$\Psi(1, 2) = \Phi_{\substack{\mathrm{S} \\ \mathrm{A}}}(r_1, r_2)\chi_{\substack{\mathrm{sing} \\ \mathrm{trip}}}, \tag{3}$$

where the spatial wavefunction $\Phi_{\mathrm{S}}(\Phi_{\mathrm{A}})$ is symmetric (antisymmetric) under permutation of the particles, and χ_{sing} and χ_{trip} are the singlet and triplet spinors, respectively. Note that, for $\lambda > 0$, the eigenfunctions of the Hamiltonian equation (1) cannot be obtained by antisymmetrizing a factorized state, i.e. they cannot be written as a single Slater determinant [12]. Then, as established by Ghirardi and Marinatto [11], for values of $\lambda > 0$ the states described by bound-state eigenfunctions are entangled states, and the greater the von Neumann entropy, the larger the amount of entanglement of the state.

In particular, the ground-state eigenfunction has the form

$$\Psi_0(1, 2) = \Phi_0(r_1, r_2)\chi_{\mathrm{sing}}, \tag{4}$$

where Φ_0 is symmetric under permutation of the particles, and the lowest-energy triplet state has the form

$$\Psi(1, 2) = \Phi(r_1, r_2)\chi_{\mathrm{trip}}, \tag{5}$$

where Φ is antisymmetric under permutation of the particles, while χ_{trip} is symmetric under the same symmetry operation. Then this state could be written as an expansion in a complete basis-set

$$\Phi(r_1, r_2) = \sum_{m,n}^{\infty} C_{m,n}\Phi_{m,n}(r_1, r_2). \tag{6}$$

In particular, we choose the orthonormal basis-set

$$\Phi_{m,n}(r_1, r_2) = \frac{1}{\sqrt{2}}(\phi_m(r_1)\phi_n(r_2) - \phi_n(r_1)\phi_m(r_2)), \tag{7}$$

where $\phi_m(r)$ are the one-electron orthonormal s-wavefunctions,

$$\phi_m(r) = \sqrt{\frac{\beta^3}{4\pi(m+1)(m+2)}}\, \mathrm{e}^{-\beta r/2} L_m^{(2)}(\beta r), \tag{8}$$

$L_m^{(2)}$ are the Laguerre polynomials [21] and β is a nonlinear variational parameter.

The ground state equation (4) is non-degenerate, but a state like Ψ is degenerate since choosing as χ_{trip} any of the triplet spinor possibilities gives the same eigenenergy. This should be taken into account when calculating the entanglement.

In order to obtain an approximate wavefunction, we apply the Ritz variational method [22]. The expansion equation (6) is truncated at order N = maximum value of m and n, which corresponds to $(N + 1)(N + 2)/2$ functions in the expansion equation (6). The lowest eigenvalue of the finite Hamiltonian matrix $\langle\Phi_{m,n}|H|\Phi_{m',n'}\rangle$ is a variational upper bound for the state energy and the corresponding eigenvector gives the coefficients $C_{mn}^{(N)}$ for the Nth-order variational wavefunction

$$\Phi^{(N)}(r_1, r_2) = \sum_{m,n}^{N} C_{m,n}^{(N)}\Phi_{m,n}(r_1, r_2). \tag{9}$$

The one-particle basis-set equation (8) is the same used to expand the ground-state function, and explicit expression for the Hamiltonian matrix elements were given in the appendix of [5].

2.1. Near-threshold behaviour

The spherical helium model has at least one bound state for $\lambda \leqslant \lambda_c^0 \simeq 1.054$, and the asymptotic behaviour of the ground-state energy is

$$E_0(\lambda) - E_{\mathrm{th}} \sim \left(\lambda_c^0 - \lambda\right)^{\alpha} \qquad \text{for} \quad \lambda \to \lambda_c^{0-}, \tag{10}$$

where $E_{\mathrm{th}} = -1/2$ is the threshold energy and $\alpha = 1$ [16]. Our numerical results suggest that for $\lambda < 1$ the model has infinitely many bound states, as in the case of the Coulombian potential [23]. For these states $\lambda_c = 1$ and the critical exponent α can be calculated using the finite-size scaling (FSS) method [24, 25].

In the FSS approach, *finite size* corresponds to the order N in the complete basis-set used to expand the Ritz variational wavefunction in equation (9). In the FSS representation, we assume the existence of a scaling function for the truncated

magnitude of any given operator $\mathcal{O}$ such that

$$\langle\mathcal{O}\rangle_\lambda^{(N)} \sim \langle\mathcal{O}\rangle_\lambda \, F_\mathcal{O}(N|\lambda - \lambda_c|^\nu) \tag{11}$$

with a different scaling function $F_\mathcal{O}$ for each different operator but with a unique scaling exponent ν.

Now, to obtain the critical parameters, we define the following function

$$\Delta_\mathcal{O}(\lambda; N, N') = \frac{\ln\left(\langle\mathcal{O}\rangle_\lambda^{(N)} / \langle\mathcal{O}\rangle_\lambda^{(N')}\right)}{\ln(N'/N)}. \tag{12}$$

If one takes the operator $\mathcal{O} = \mathcal{H}$, then $\langle\mathcal{H}\rangle^{(N)} = E_\lambda^{(N)}$ is the usual Ritz variational approximation to the ground-state energy E_λ. From $\mathcal{O} = \partial\mathcal{H}/\partial\lambda$ we obtain a second equation that, together with equation (12), is used to define the following function:

$$\Gamma(\lambda; N, N') = \frac{\Delta_\mathcal{H}(\lambda; N, N')}{\Delta_\mathcal{H}(\lambda; N, N') - \Delta_{\partial\mathcal{H}_\lambda/\partial\lambda}(\lambda; N, N')}, \tag{13}$$

which is independent of the values of N and N' at the critical point $\lambda = \lambda_c$. The particular value of Γ at $\lambda = \lambda_c$ is the critical exponent α for the ground-state energy as defined in equation (10) [25]:

$$\alpha = \Gamma(\lambda = \lambda_c; N, N'). \tag{14}$$

Actually, equations (13) and (14) are asymptotic expressions. For three different values of N, N', N'' (we choose $N' = N - 2$ and $N'' = N + 2$), the curves of $\Gamma(\lambda, N)$ as a function of λ will intersect at sequences of pseudo-critical points $\lambda_c^{(N)}$

$$\Gamma\left(\lambda = \lambda_c^{(N)}; N - 2\right) = \Gamma\left(\lambda = \lambda_c^{(N)}; N\right), \tag{15}$$

giving also a set of pseudo-critical exponents

$$\alpha^{(N)} = \Gamma\left(\lambda_c^{(N)}; N\right). \tag{16}$$

The sequences of values of $\lambda_c^{(N)}$ and $\alpha^{(N)}$ can be used to obtain the extrapolated value of λ_c and α [24].

The FSS calculation of the critical parameters for the ground state of the spherical helium atom were done in [5]. Here we study the critical behaviour of the lowest-energy triplet state. As mentioned before, the near-threshold behaviour of this state, with antisymmetrical spatial wavefunction, is qualitatively different from the ground state. To put the differences in evidence we studied the electron density $\rho(r)$ for the lowest-energy state in both, singlet and triplet, subspaces. The electron density is defined for an arbitrary state Φ as

$$\rho(\vec{x}) = \langle\Phi| \sum_{i=1,2} \delta(\vec{x} - \vec{x}_i)|\Phi\rangle. \tag{17}$$

For the ground state, $r^2\rho(r)$ presents one peak for all values of $0 \leqslant \lambda \leqslant \lambda_c^{(0)} \simeq 1.054$, according to the fact that both electrons are in the same orbit even at the critical charge. In the case of the triplet state, $r^2\rho(r)$ presents two peaks for $0 \leqslant \lambda < \lambda_c = 1$. In figure 1(a), $r^2\rho(r)$ is shown for the ground state at $\lambda_c^{(0)}$, and for the triplet state for $\lambda = 0$ and $\lambda = 0.8$. Except in the case of the exact density at $\lambda = 0$, the calculations were done with the basis-set truncated at $N = 50$. The outer maximum, localized at $r_{\max} \simeq 5.12$ for the non-interacting case $\lambda = 0$, goes to infinity for $\lambda \to \lambda_c = 1$,

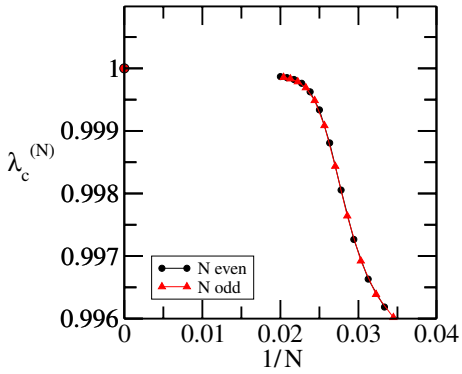

Figure 2. $\lambda_c^{(N)}$ versus $1/N$ obtained with FSS from the variational energies for even and odd values of N. The suggested value $\lambda_c = 1$ is shown with a dot.

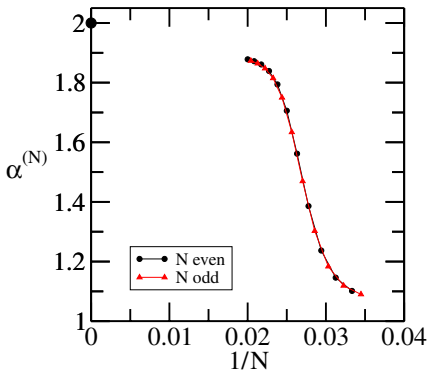

Figure 3. The critical exponent associated with the energy $\alpha^{(N)}$ versus $1/N$. The suggested value $\alpha = 2$ is also shown.

describing a continuous ionization as a function of the nuclear charge as is shown in figure 1(b).

The FSS calculation applied to the triplet state corroborates the hypothesis that the helium and spherical helium models have the same critical behaviour. The numerical calculations are in excellent agreement with the assumptions $\lambda_c = 1$ (see figure 2) and $\alpha = 2$ (see figure 3).

3. von Neumann entropy

For a two-particle system in a pure state $|\Psi\rangle$, the density operator ρ takes the form

$$\rho = |\Psi\rangle\langle\Psi|. \tag{18}$$

But, for a degenerate energy level, the density operator is an equal mixture of all eigenstates with the same eigenenergy (see, for example, [26]) so, for an excited state like the triplet state equation (5) the density operator takes the form

$$\rho = |\Phi\rangle\langle\Phi|\rho_s, \tag{19}$$

where the spin contribution to the density operator is

$$\rho_s = \tfrac{1}{3}\big[|\uparrow\uparrow\rangle\langle\uparrow\uparrow| + \tfrac{1}{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)(\langle\uparrow\downarrow| + \langle\downarrow\uparrow|) + |\downarrow\downarrow\rangle\langle\downarrow\downarrow|\big]. \tag{20}$$

The reduced density operator is [27, 28]

$$\hat{\rho}^{\mathrm{red}}(\vec{x}_1, \vec{x}_1') = \mathrm{tr}_2[|\Phi\rangle\langle\Phi|\rho_s]; \tag{21}$$

here the trace is taken over one electron.

The von Neumann entropy is given by

$$\mathbf{S} = -\mathrm{tr}(\hat{\rho}^{\mathrm{red}} \log_2 \hat{\rho}^{\mathrm{red}}), \tag{22}$$

which separates in two contributions, one corresponding to the spin degrees of freedom plus one corresponding to the spatial degrees of freedom,

$$\mathbf{S} = S_s + S = S_s - \sum_i \Lambda_i \log_2(\Lambda_i), \tag{23}$$

where Λ_i are the eigenvalues of the spatial part of the reduced density operator

$$\int \mathrm{d}^3x_1' \int \mathrm{d}^3x_2 \Phi(r_1, r_2)\Phi^*(r_1', r_2)\varphi_i(r_1') = \Lambda_i\varphi_i(r_1), \tag{24}$$

and

$$S_s = -\mathrm{Tr}\left(\rho_s^{\mathrm{red}} \log_2 \rho_s^{\mathrm{red}}\right) \quad \text{and} \quad \rho_s^{\mathrm{red}} = \begin{pmatrix} 1/2 & 1/6 \\ 1/6 & 1/2 \end{pmatrix}. \tag{25}$$

Clearly, the additive constant S_s does not change the behaviour of the von Neumann entropy near the critical point, nor its scaling properties. Thus, from now on we will refer to the spatial contribution S in equation (23) as the von Neumann entropy.

Similarly to the critical exponent α for the lowest triplet state, the critical exponent μ for the von Neumann entropy for this excited state is different than the ground state exponent. The entropy has a singular behaviour at the critical point $\lambda_c = 1$,

$$S(\lambda) - S(\lambda_c) \sim (\lambda_c - \lambda)^{\mu} \qquad \text{for} \quad \lambda \to \lambda_c^-, \tag{26}$$

with a critical exponent $\mu \neq 0$.

Introducing the Nth-order variational approximation to the ground-state function equation (9) in the integral equation (24), we obtain

$$\int \mathrm{d}^3x_1' \int \mathrm{d}^3x_2\, \Phi_0^{(N)}(r_1, r_2)\left(\Phi_0^{(N)}(r_1', r_2)\right)^* \varphi_i^{(N)}(r_1') = \Lambda_i^{(N)}\varphi_i^{(N)}(r_1), \tag{27}$$

where $i = 1, \ldots, N$. The exact eigenfunctions $\varphi_i^{(N)}$ of this integral equation can be written as a linear combination of the functions ϕ_m, $m = 1, \ldots, N$ [29]. Then equation (27) can be recast as an algebraic eigenvalue problem for a $N \times N$ matrix. The conservation of the probability

$$\sum_{i=1}^{N} \Lambda_i^{(N)} = 1 \tag{28}$$

is satisfied for all values of N. In consequence, the Nth-order approximation to the entropy is

$$S^{(N)} = -\sum_{i=1}^{N} \Lambda_i^{(N)} \log_2\left(\Lambda_i^{(N)}\right). \tag{29}$$

Now we study the scaling of $S^{(N)}(\lambda)$ with the size of the basis-set N applying the FSS methods described in the previous section. So, replacing $\langle\mathcal{O}\rangle$ in equation (12) by $S(\lambda_c) - S(\lambda)$ we get

$$\Delta_S(\lambda, N, N') = \frac{\ln(S_c - S^{(N)}(\lambda)) - \ln(S_c - S^{(N')}(\lambda))}{\ln(N') - \ln(N)}, \tag{30}$$

where $S_c = \log_2 2 = 1$ is the limit value of $S^{(N)}(\lambda)$ for $N \to \infty$ and $\lambda > \lambda_c$. At the critical point we have

$$\Delta_S(\lambda_c, N, N') = \frac{\mu}{\nu} \tag{31}$$

independent of the values of N and N'. As in the previous case, we choose $N' = N - 2$ and $N'' = N + 2$ [25].

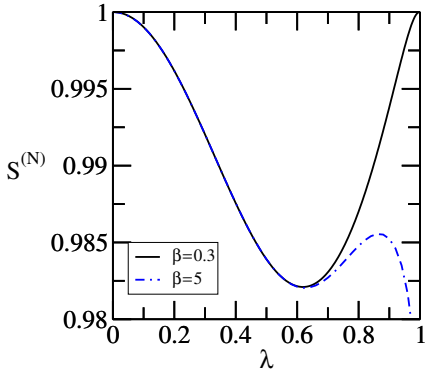

Figure 4. Comparison of $S^{(N)}$ versus λ for $N = 50$ and $\beta = 0.3$ and $\beta = 5$.

For the ground state [16] the nonlinear-variational parameter β in the basis-set equation (8) that gives better results for the energy is $\beta = 1.3$ [16], but there is a smooth dependence of the physical magnitudes with β as a consequence of the electrons being exponentially localized even at $\lambda = \lambda_c$. It is clear that, as long as the lowest triplet state is less localized than the ground state, smaller values of β should be considered in order to obtain accurate results. But in this case, physical magnitudes, such as the von Neumann entropy, depend dramatically on β in the critical region. Figure 4 shows the behaviour of the von Neumann entropy $S^{(N)}$ versus λ, for two different values of the nonlinear-variational parameter β as a function of λ calculated with for $\beta = 0.3$, optimal parameter for the energy, and $\beta = 5$, both curves give similar results near the non-interacting limit $\lambda = 0$, but for $\beta = 5$ it can be seen that near $\lambda = \lambda_c = 1$ the approximation fails. This can be better understood in terms of the characteristic lengths involved; $1/\beta$ is the scale length associated with the variational functions equation (8); the other length scale is the radius of the external orbit, which goes to infinity when λ goes to its critical value.

From now on, we will concentrate on the results found with $\beta = 0.3$. The critical parameter $\lambda_c^{(N)}$ versus $1/N$ is shown in figure 5. As the FSS analysis can be performed for the energy and the von Neumann entropy, there are two sets of curves (energy and entropy), with two curves per set, corresponding to even and odd values of N. All these data support the value $\lambda_c = 1$.

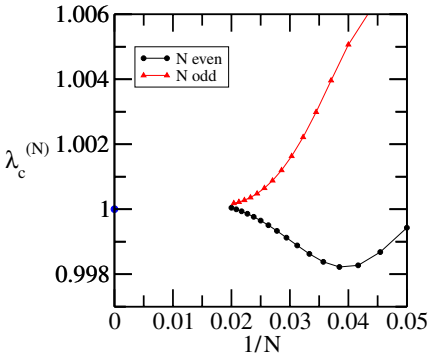

Figure 5. Critical parameter obtained with FSS from the von Neumann entropy $\lambda_c^{(N)}$ versus $1/N$. The curves corresponds to odd or even values of N, as in figure 2; the data strongly support the hypothesis $\lambda_c = 1$.

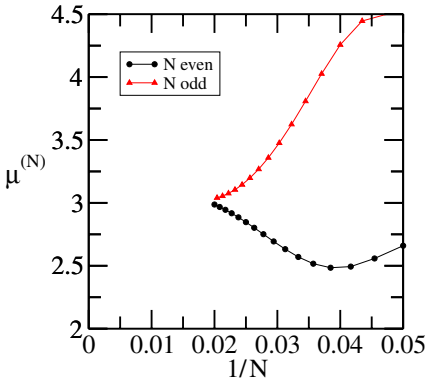

Figure 6. Critical exponent for the entropy $\mu^{(N)}$ versus $1/N$. The curves corresponds to odd or even values of N; the data suggest $\mu \simeq 3$.

Finally, figure 6 shows the critical parameter $\mu^{(N)}$ versus $1/N$. The curves correspond to odd or even values of N, and both curves seem to converge to $\mu_c \cong 3$. Again this result is compatible with the picture drawn in the introduction.

4. Conclusions

In this work, we studied the lowest-energy triplet state for the spherical helium atom. In particular, we show that the near-threshold properties for this state are qualitatively different from the ground state critical behaviour. For $\lambda = 0$ the spatial wavefunction of the ground state is a simple product, so $S = 0$. In the case of the triplet state, because the spin contribution is symmetric, for $\lambda = 0$ the spatial wavefunction can be written as $(\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2))/\sqrt{2}$ which gives $S = 1$. The same form for the spatial wavefunction corresponds to the ionized system, so $S \to 1$ when $\lambda \to \lambda_c$. So, in contradistinction with the ground state case, the von Neumann entropy is a continuous function at $\lambda = \lambda_c$ with a critical exponent $\mu = 3$. It is interesting that for $0 < \lambda < \lambda_c$ the spatial contribution of the von Neumann entropy $S < 1$, i.e. the superposition of more terms of the form $(\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2))/\sqrt{2}$ actually decreases the entanglement. Moreover, we want to remark that the sum of the spatial contribution of the von Neumann entropy S with the spin contribution, c, is always bigger than 1, $c + S > 1$, i.e. the two electrons are entangled for $0 \leqslant \lambda \leqslant \lambda_c$.

In the triplet state the electrons are in different atomic shells, and in the near-threshold region the state could be described as one electron in a 1s hydrogenic state plus a weakly bounded electron whose mean distance to the nucleus goes to infinity at the critical charge.

In quantum spin chains it is well known that the order of a quantum phase transition (QPT) is related to the kind of singularity of the entanglement measure [30], for a first- (second-) order QPT corresponds a discontinuity (discontinuity or divergence of the first derivative) of the entanglement measure. In this sense, the results presented in this paper for the critical behaviour of the von Neumann entropy as an entanglement measure for two-electron systems, together with results already presented [5], cover the different behaviours observed near the ionization threshold: continuous or discontinuous ionization.

As we claim in the study of the ground state [5, 16], it is expected that the spherical model has the same critical behaviour as the helium model, that is, the same critical exponents. In this sense, our approximate model describes the correct critical behaviour of many atomic systems. In particular, we argue that the critical behaviour of the ground state of a lithium-like atom is similar to the critical behaviour of the lowest triplet state of a helium-like atom. In both cases, a continuous ionization process takes place when the nuclear charge goes to its critical value, as has been described above. Work to corroborate these ideas is in progress.

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