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2015 J. Phys. B: At. Mol. Opt. Phys. 48 175002

(http://iopscience.iop.org/0953-4075/48/17/175002)

IOP Publishing Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **48** (2015) 175002 (9pp) doi:10.1088/0953-4075/48/17/175002

Quantum entanglement of helium-like systems with varying-Z: compact state-of-the-art CI wave functions

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Received 11 May 2015, revised 15 June 2015
Accepted for publication 16 June 2015
Published 17 July 2015

Abstract

In this work we have performed state-of-the-art configuration-interaction (CI) calculations to determine the linear and von Neumann entanglement entropies for the helium-like systems with varying nuclear charge Z in the range $1 \leqslant Z \leqslant 10$. The focus of the work resides on determining accurate entanglement values for 2-electron systems with the lowest computational cost through compact CI-wave functions. Our entanglement results for the helium atom fully agree with the results obtained with higher quality wave functions of the Kinoshita type (Dehesa [5]). We find that the correlation energy is linearly related to the entanglement measures associated with the linear and von Neumann entropies of the single-particle reduced density matrizes, which sheds new light on the physical implications of entanglement in helium-like systems. Moreover, we report CI-wave-function-based benchmark results for the entanglement values for all members of the helium isoelectronic series with an accuracy similar to that of Kinoshita-type wave functions. Finally, we give parametric expressions of the linear and von Neumann entanglement measures for two-electron systems as Z varies from 1 to 10.

Keywords: quantum entanglement of helium-like systems, linear entanglement entropy, von Neumann entanglement entropy, energy correlation versus entanglement

1. Introduction

Quantum entanglement is one of the most essential features of quantum physics. Its central role in quantum communication and computation technologies [1] has stimulated intense research on the qualitative and quantitative characterization of the entanglement properties of multi-partite quantum systems (see for instance the comprehensive review article [2]). Recently the study of the entanglement features exhibited by atomic and molecular systems has been the focus of considerable activity [3–8]. These developments show the relevance of entanglement for the understanding of chemical systems and processes, and in turn they suggest that entanglement may also have deep biological implications. A growing number of works indicate that this is indeed the case. In this regard we can mention studies on the biochemical compass model for avian magnetoreception [9] and on the light harvesting complexes which govern the photosynthesis mechanism in plants [10].

Within the aforementioned chemistry-related lines of research, there has been much work devoted to the study of quantum entanglement in two-electron model atoms [4, 11–17], helium and helium-like ions [3–8, 14, 16, 18–22]. For instance, investigations on model atoms such as the Moshinsky one [4, 11–13], the Crandall atom [4, 14, 15] and the Hooke atom [4, 16, 17] have been reported in the literature. In atomic systems, a great deal of studies have been performed. Osenda *et al* have calculated the von Neumann entanglement entropy in spherical helium [16]. Here, by *von Neumann entanglement entropy* we mean the von Neumann entropy of

the single-particle, reduced density matrix. A similar expression is used for the linear entropy of the single-particle reduced density matrix. These two entropies lead to useful entanglement indicators, as we shall discuss in the next Section. More recently, Coe *et al* calculated the linear entanglement entropy for the ground state of the natural helium atom by use of products of hydrogenic wave functions [14]. Manzano *et al* [4] and Dehesa *et al* [5, 6] investigated the linear entanglement entropy of the helium ground and some excited states using Kinoshita-type wave functions obtaining benchmark results for these systems. In addition, Koscik and Okopińska [19] have recently calculated the ground-state entanglement of helium-like atoms with Z = 1–5 by use of Hylleraas-type wave functions. Lin *et al* [18] employed configuration interaction wave functions by using the B-spline basis to calculate the linear entanglement entropy of the ground and excited states for the helium-like ions up to $Z = 15$. Benenti *et al* [7] calculated the linear entanglement entropy and the von Neumann entanglement entropy for the helium atom employing configuration-interaction (CI) wave functions constructed with Slater type orbitals (STOs). Some previous studies have suggested a relation of correlation energy with the von Neumann entanglement entropy. Indeed, Esquivel *et al* [23] and Ramírez *et al* [24] examined the implications of the Collins conjecture [25] to show numerically that for three-electron atoms and some selected small molecules, the von Neumann entanglement entropy behaves linearly with the correlation energy as the quality of the wave function increases. Moreover, Huang and Kais [3] and Hofer [8] have employed entanglement as an alternative measure of electron correlation for helium-like systems.

The central concept to be examined in this paper is electron entanglement in atomic systems. It is known [3, 26, 27] that a wave function composed of a single Slater determinant does not have quantum correlation usable as a resource for quantum information tasks, implying that the Hartree–Fock (HF) wave function does not represent an entangled state, whereas the multi-determinantal wave functions employed in post-HF methods are endowed with entanglement. The latter implies that the non-local effect linked to entanglement must be present in any post-HF wave function independently of its quality.

The present study was designed to explore the connection between entanglement and correlation energy measures associated with the difference of two variational bounds. We attempt to calculate accurate values for the ground-state entanglement measures by means of the linear and von Neuman entropies of the single-particle, reduced density matrix of the helium isoelectronic series with varying nuclear charge in the range $1 \leqslant Z \leqslant 10$. Our goal is three-fold: (i) to determine accurate entanglement values for helium at the lowest computational cost by use of compact CI-wave functions; (ii) to parametrize these results in terms of the nuclear charge by means of functions of the type ax^b; and (iii) to report benchmark results of entanglement values for the helium-like atoms from $Z = 1$ through $Z = 10$.

The structure of this work is as follows. First, in section II, we define and justify the quantifiers of entanglement of a system of N identical fermions which we use throughout the work; namely, the linear and von Neumann entanglement measures. Then, in section III, various details about the CI methodology are described. In section IV the main results of our work are discussed in full detail. Finally, some conclusions and references are given.

2. Entanglement measures of fermionic systems

A pure state of a system constituted by N identical fermions can be described by a single ket vector, $|\Psi\rangle$, so that its associated density matrix is $\rho = |\Psi\rangle\langle\Psi|$. This state is non-entangled, i.e. separable, if it has Slater rank equal to one. This means that it can be expressed as a single Slater determinant constructed with N normalized and orthogonal single-particle states $\{|i\rangle,\ i = 1,...,N\}$. Otherwise, the state is called an entangled state.

Note that the minimum correlations between the particles required by the antisymmetry of the fermionic state do not contribute to the state's entanglement. In other words, the fermionic entanglement is given by the quantum correlations existing on top of these minimum correlations needed to comply with the antisymmetric constraint on the fermionic wave function [28, 29].

There are several measures to quantify the amount of entanglement for a pure state $|\Psi\rangle$ of a system with N identical fermions in the literature. In this work, we focus our attention on entanglement measures based on the linear and von Neumann entropies.

2.1. Linear entanglement measure

Let $|\Psi\rangle$ denote a pure state of N identical fermions. The single-particle reduced density matrix, obtained by taking the trace over $N - 1$ particles, is then $\rho_r = Tr_{2,3,...,N}(|\Psi\rangle\langle\Psi|)$. The linear entropy of ρ_r, given by

$$S_L[\rho_r] = 1 - Tr\left(\rho_r^2\right) \tag{1}$$

leads to a practical quantitative measure $\xi[\rho_r]$ for the amount of entanglement of the density matrix state ρ_r, namely

$$\xi_L[\rho_r] = N\left[S_L[\rho_r] - \left(\frac{N-1}{N}\right)\right] \tag{2}$$

which is normalized to the range $[0, 1]$. This quantity vanishes if and only if the state $|\Psi\rangle$ has Slater rank 1 and is therefore separable. This linear entanglement measure has been applied to several problems, particularly in connection with two-fermionic systems [15] and also to helium in its ground state and some selected singlet and triplet excited states [5, 6, 18].

Note that in the particular case of $N = 2$, this entanglement measure can be related to the Schmidt decomposition of pure states of two identical fermions. Moreover, the eigenfunctions of the first-order reduced density matrix ρ_r are usually called natural spin orbitals (Löwdin spectral decomposition) [30, 31]. Their corresponding eigenvalues are the natural spin occupation numbers $\{n_i^\gamma;\ i = 1, \ldots, M\}$, with M

standing for the number of orbitals and γ for the α or β spin majority channel ($0 \leqslant n_i^{\gamma} \leqslant 1$) and $\sum_{i,\gamma} n_i^{\gamma} = N$. Natural spin orbitals are obtained by performing symmetric (orthogonal) transformations on the density matrix so as to obtain its diagonal form characterized by a spectral decomposition [30]. When computing the amount of entanglement associated with the state of the N electrons it is convenient to normalize the single-particle reduced density matrix ρ_r to 1. In that case, the eigenvalues of ρ_r are $\lambda_i^{\gamma} = n_i^{\gamma}/N$. It is worth noting that closed-shell molecular and atomic systems are commonly represented through a $M \times M$ double occupied density matrix $\rho_r^{(DO)}$, having eigenvalues $\lambda_i^{(DO)} = (n_i^{\alpha} + n_i^{\beta})/N$, with $\sum_i^M \lambda_i^{(DO)} = 1$, where $n_i^{\alpha} = n_i^{\beta}$. In the general case for open shell molecular systems, e.g. radicals, the latter is not obeyed and a particular expression for open-shell ρ_r could be necessary, i.e. $n_i^{\alpha} \neq n_i^{\beta}$.

According to the above, the linear entropy of the single-particle reduced density matrix $\rho_r^{(DO)}$ of fermionic systems can be expressed in terms of the natural spin orbitals through Löwdin's spectral decomposition of the $\rho_r^{(DO)}$ as

$$S_L\left[\rho_r^{(DO)}\right] = 1 - \frac{1}{2}\,Tr\left[\left(\rho_r^{(DO)}\right)^2\right] = 1 - \frac{1}{2}\sum_{i=1}^{M}\left(\lambda_i^{(DO)}\right)^2 \tag{3}$$

and the linear entanglement measure can be expressed as follows:

$$\xi_L[\rho_r] = 1 - \frac{N}{2}\sum_{i=1}^{M}\left(\lambda_i^{(DO)}\right)^2 \tag{4}$$

2.2. Von Neumann entanglement measure

For a pure state of N identical fermions, $|\psi\rangle$, the von Neumann entropy of a single-particle reduced density matrix ρ_r, obtained by taking the trace over $N-1$ particles $\rho_r = Tr_{2,3,\ldots,N}(|\Psi\rangle\langle\Psi|)$, is given by [32]

$$S_{VN}[\rho_r] = -Tr\left(\rho_r \ln \rho_r\right). \tag{5}$$

This entropy allows us to quantify the amount of entanglement of the N-fermionic system's state $|\Psi\rangle$:

$$\xi_{VN}[\rho_r] = S_{VN}[\rho_r] - \ln N. \tag{6}$$

This entanglement measure constitutes a non-negative quantity that vanishes if and only if the state $|\Psi\rangle$ has Slater rank one and is therefore non-entangled. The term $-\ln N$ arises from the fact that even in the separable case, the entropy of the reduced single-particle density matrix does not vanish. Following the lines indicated in the previous case, for a double occupied density matrix $\rho_r^{(DO)}$ we obtain the expression

$$\xi_{VN}[\rho_r] = S\left[\rho_r^{(DO)}\right] - ln\,\frac{N}{2} = -\sum_{i=1}^{M}\lambda_i^{(DO)} ln\,\lambda_i^{(DO)} - ln\,\frac{N}{2} \tag{7}$$

for the von Neumann entanglement measure in terms of the natural occupation numbers.

3. Configuration-interaction wave functions: Methodology

The wave function which describes the state of the helium-like atoms has been obtained by means of the CI method. In this post-HF method, the solution of the nonrelativistic Schrödinger equation for an N-electron system is given by a linear combination of Slater determinants:

$$|\Phi\rangle_{CI} = C_0|\Phi_0^{HF}\rangle + \sum_{a}^{N}\sum_{r}^{K} C_a^r|\Phi_a^r\rangle + \sum_{a<b}^{N}\sum_{r<s}^{K} C_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \ldots \tag{8}$$

where $|\Phi_i\rangle$ are successively orthonormalized L^2- and S^2- symmetric projections of two-electron Slater determinants made up of orthonormal spin orbitals. In turn, the spin orbitals are linear combinations of STO's (times a spherical harmonics and a spin function).

In the expansion given by equation (8) the first term, $|\Phi_0^{HF}\rangle$, corresponds to the HF reference-state. The other terms can be characterized by the number of spin orbitals (a, b,...) that are replaced with virtual orbitals (unoccupied orbitals r, s,...) from the HF determinant. If only one spin orbital differs, we describe this as a single excitation determinant, $|\Phi_a^r\rangle$. If two spin orbitals differ, it is a double-excitation determinant, $|\Phi_{ab}^{rs}\rangle$, and so on. The coeficients $\{C_0, C_a^r, C_{ab}^{rs},\ldots\}$ are the expansion coefficients and have been determined, as well as the exponents in the Slater determinants, by use of variational methods (minimizing the energy of the system).

If we include all possible excited state configurations where one electron is promoted from the occupied to the unoccupied orbitals, the method is called CIS; if we include all possible single and double excitations it is CISD (CISDT, CISDTQ, etc). If we include all possible excited state configurations, the method is called full CI and the result is exact.

Full CI calculations require a high computational cost, related to the binomial coefficient: $\binom{M}{N} = \frac{M!}{(M-N)!\,N!}$, where M is the total number of spin orbitals and N the number of electrons. Therefore, a full CI treatment is in most cases computationally intractable. But in helium-like atoms, only single and double excitations are possible, so we are able to implement a full CI method. The details of the wave function calculations can be found in [33, 34].

Table 1. Entanglement of the ground state of a helium atom for various HF Ansatzs. Basis orbitals are denoted as l_{n-l-1}; so that, e.g. s_0 and s_2 are the orbitals 1 s and 3 s, respectively[a].

Number of orbitals	Basis	$\xi_L(Z=2)$
3[a]	$\{s_0 s_0 s_0\}$	0.00584793
3	$\{s_0 s_2 s_2\}$	0.00915760
5	$\{s_0 s_2 s_2 s_3 s_4\}$	0.00916082
6	$\{s_0 s_2 s_2 s_3 s_3 s_4\}$	0.00915492
6	$\{s_0 s_0 s_1 s_1 s_2 s_2\}$	0.00844111

[a] Clementi-Roetti basis set [36].

4. Results

In previous works Manzano *et al* [4] and Dehesa *et al* [5, 6] reported accurate values for the linear entanglement, equation (2), of the ground state and various excited states of helium by use of high-quality Kinoshita-type wave functions. For the ground state of helium ($E = -2.903724$ a.u.), the entanglement from the linear entropy was estimated [5] to be $\xi_L = 0.015914 \pm 0.000044$. This value has been used in the present calculations as a reference-test case in order to perform a sensitivity study of the basis sets. This study is done to choose the best combination of the HF-SCF reference basis set that, along with the complementary virtual orbitals, may produce a compact CI wave function with which the entanglement value for the linear entropy matches the previous accurate result.

4.1. Choice of basis sets for compact CI wave functions

The CI wave functions necessary for the study have been calculated by use of ATMOL suite programs [33, 34] in order to construct spin adapted wave functions in a multi-determinantal space of compact basis sets for all members of the helium-like series with varying nuclear charge Z. The latter represents a formidable task in order to compute about 900 wave functions for the two-electron model systems necessary to accomplish the study. Besides, the choice of an appropriate basis set is not a trivial task because of the higher angular momentum symmetries that could be employed for the orbital configurations. Keeping that in mind, the following aspects ought to be considered: (i) to build HF reference states for each model system with a specific Z, varying from 1 to 10 in steps of 0.01; (ii) to calculate CI wave functions within a consistent basis set chosen from the HF-reference configuration reported in table 1; and (iii) to enlarge the CI configuration space within each HF initial state to keep track of convergence, either for the energy, the entanglement values, or both.

This task was achieved by tracking the value of the linear entanglement measure as the wave function is improving (see below). The convergence of this entanglement measure is studied in tables 1 and 3. Some choices employed for the construction of the HF-reference state explicitly include an s_0-STO type orbital to numerically satisfy the cusp condition exactly [35]. Finally, our last choice for the HF orbital basis is the one that best yields both the cusp condition and the ground-state energy and linear entanglement measure in helium as indicated above. Note that for all calculations full CI wave functions are used, within the single and double configuration space.

According to the linear entanglement values for the CI-wave functions shown in table 1, we realize that the use of bigger basis sets do not necessarily guarantee more accurate results for this kind of entanglement measure with respect to smaller basis sets. For instance, the choice of 6 orbitals for the HF reference wave function produces a worst linear entanglement value than the smaller basis set with 5 orbitals. Since the entanglement depends on the one-density matrix, it is much more sensitive to changes in the wave function than from the energy itself. Hence, we decided to follow the convergence of the linear entanglement values instead of the energy as a criterion to choose the best basis set. Although, of course, keeping track of the energy requires much larger basis sets, this is not the goal of our study.

In addition, we note from table 1 that the Clementi-Roetti basis set [36] produces a linear entanglement value that is far from the reference one. Moreover, we have observed that compliance of the exact cusp condition conducts to much faster convergence for the linear entanglement values and higher accuracy. This is because we have chosen different Ansatzs as initial HF-reference states obeying the cusp requirement. Accordingly, in table 2 we have reported results for the following HF– reference basis sets: $\{s_0 s_2 s_2\}$, $\{s_0 s_2 s_2 s_3 s_4\}$ and $\{s_0 s_2 s_2 s_3 s_3 s_4\}$, which take into account the cusp. Note that at this stage of the calculation, virtual orbitals had not been included; then, enlarging the basis set would improve linear entanglement values towards convergence through new virtual orbitals. It is interesting to mention that this observation also applies to the von Neumann entanglement measure. The selection of the virtual orbitals is reflected in table 2, where we have reported the final basis sets for the CI wave functions that obey all requirements mentioned above. Note that some CI wave functions reported in this table were constructed from SCF orbitals only without any virtual orbitals.

In table 3, we have reported the ground-state values for the energy and for both entanglement measures (linear and von Neumann) of helium for various choices of basis sets. Our results show that the most appropriate basis set for this analysis is represented by the [322] basis set, which satisfies all requirements mentioned above. It is remarkable to observe that although these compact basis sets were not constructed to produce exact values for the energy of helium, they account for 99.91% of the correlation energy in the smallest basis set. More importantly, these basis sets do produce linear entanglement values that are very close to the exact one reported by [4] (see table 3). This is supported by the fact that from the CI methodology it is possible to control the size and the convergence of the calculation which is advantageous with respect to other strategies. Therefore we would like to emphasize that according to our results it is not indispensable

Table 2. Slater type orbital sets for various compact CI wave function. Basis orbitals are denoted as l_{n-l-1}; so that e.g., s_0 and s_2 are the orbitals 1 s and 3 s, respectively[a].

Number of orbitals (spdf...)	Initial HF term	Virtual orbitals
[3[a]]	$\{s_0 s_0 s_0\}$	—
[3]	$\{s_0 s_2 s_2\}$	—
[32]		$\{p_0 p_0\}$
[322]		$\{p_0 p_0 d_0 d_0\}$
[3222]		$\{p_0 p_0 d_0 d_0 f_0 f_0\}$
[34]		$\{p_0 p_0 p_1 p_1\}$
[342]		$\{p_0 p_0 p_1 p_1 d_0 d_0\}$
[632]		$\{s_3 s_4 s_5 p_0 p_1 p_2 d_0 d_1\}$
[88642]		$\{s_3 s_4 s_5 s_6 s_7 p_0 p_0 p_1 p_1 p_2 p_2 p_3 p_3 d_0 d_0 d_1 d_1 d_2 d_2 f_0 f_0 f_1 f_1 g_0 g_1\}$
[5]	$\{s_0 s_2 s_2 s_3 s_4\}$	—
[632]		$\{s_5 p_0 p_1 p_2 d_0 d_1\}$

[a] Clementi-Roetti basis set [36].

Table 3. Ground-state entanglement and energy of helium for various bases[a,b].

Basis	$\xi_L(Z=2)$	$\xi_{VN}(Z=2)$	Energy (a.u.)
	Initial HF term $\{s_0 s_0 s_0\}$		
[3[a]]	0.0058479310	0.0404132691	−2.87680937
	Initial HF term $\{s_0 s_2 s_2\}$		
[3]	0.0091576	0.0301553873	−2.87747769
[32]	0.016570343	0.0597554046	−2.89857401
[322]	0.0164727801	0.0603217554	−2.90071387
[3222]	0.0164423655	0.060378164	−2.90121732
	Initial HF term $\{s_0 s_2 s_2\}$		
[3]	0.0091576	0.0301553873	−2.87747769
[34]	0.0166231319	0.0601039078	−2.89895165
[342]	0.0165272316	0.0606673288	−2.90107225
	Initial HF term $\{s_0 s_2 s_2\}$		
[632]	0.0161354407	0.0592281104	−2.90217862
	Initial HF term $\{s_0 s_2 s_2\}$		
[88642]	0.0163666527	0.0604637346	−2.90237025
	Initial HF term $\{s_0 s_2 s_2 s_3 s_4\}$		
[5]	0.00916082	0.0602693554	−2.87801774
	Initial HF term $\{s_0 s_2 s_2 s_3 s_4\}$		
[632]	0.0164213083	0.0601239465	−2.90132275
	Reference value		
Manzano *et al.*[b]	0.015914 ± 0.000044	Not available	−2.90372

[a] Clementi-Roetti basis set [36].
[b] Manzano *et al* [4]; see also [5, 6].

Table 4. STO set for the compact CI wave function of helium ($Z=2$). The radial functions for the STO are given by $R_{il}(r) = \sum_j S_{jl}(r) a_{jli}$ where $S_{jl}(r) = N_{jl} r^{n-l-2} e^{-Z_{jl} r}$. The table is divided into HF-SCF orbitals and the virtual ones.

j	Orbital	Z_{jl}	Type
1	s_0	2.00000	SCF
2	s_2	1.88711	SCF
3	s_2	2.69410	SCF
1	p_0	2.39230	V
2	p_0	3.55016	V
1	d_0	3.34622	V
2	d_0	4.89000	V

to construct higher quality wave functions in order to account for a precise value of the entanglement of helium; in other words, the non-local character of the wave function seems to be accounted for with compact basis sets. Perhaps a higher degree of non-locality might be required for other properties of the systems as they interact at larger distances, but this is beyond the scope of the present study.

4.2. Linear and von Neumann entanglement measures for helium-like atoms

4.2.1. Entanglement measures versus energy correlation. In the previous section we have shown that within our present numerical framework, the set [322] is the best choice for the CI basis set. Linear entanglement values computed on the concomitant helium states reproduce the results reported in Manzano *et al* [4]. In this section we use this basis set to calculate the linear and von Neumann entanglement measures for all members of the helium isoelectronic series with

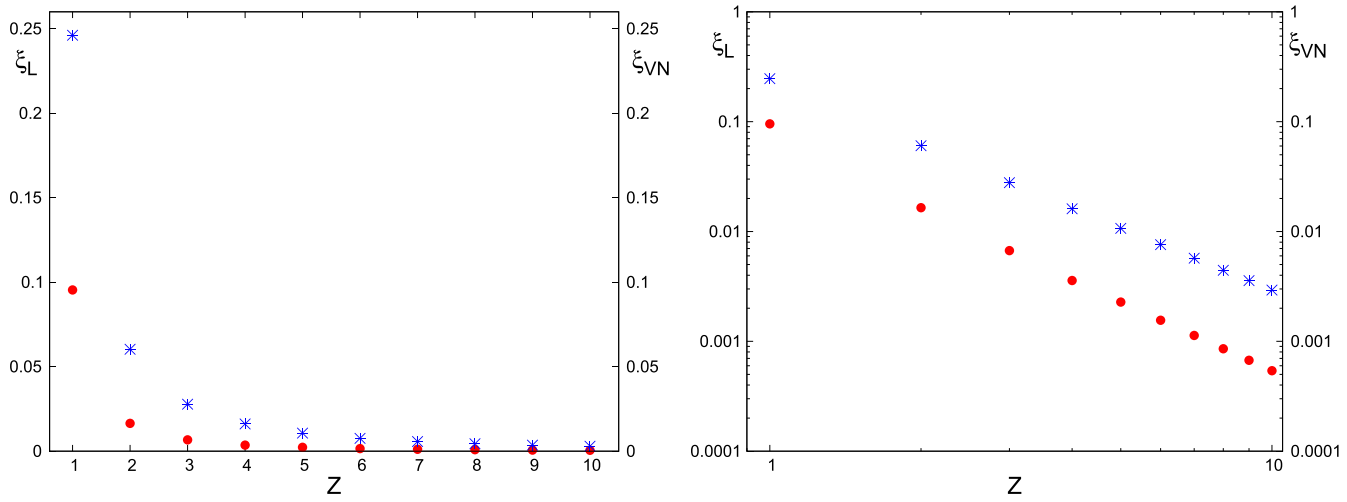

Figure 1. Variation of the linear entanglement, ξ_L(dots), and von Neumann entanglement, ξ_{VN}(stars), of ground-state helium-like atoms with the nuclear charge $Z \in [1, 10]$.

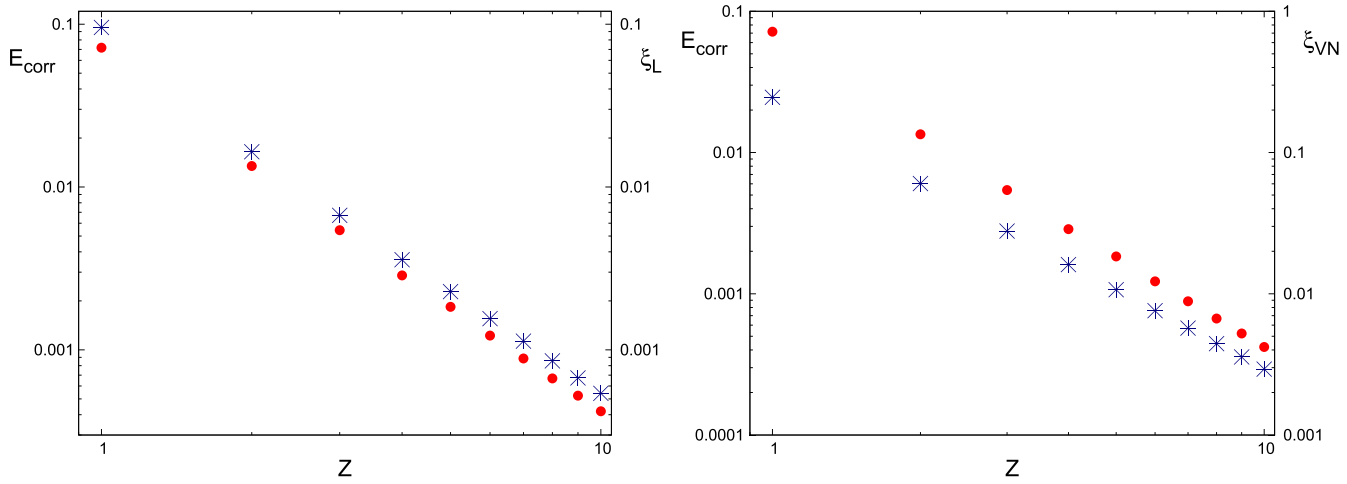

Figure 2. Dependence of the correlation energy, E_{corr} (dots), and entanglement (stars) of the ground-state helium-like atoms on the nuclear charge $Z \in [1, 10]$. The linear entanglement measure, ξ_L, and the von Neumann entanglement measure, ξ_{VN}, are given on the left and right pictures, respectively.

Z = 1–10 by use of the corresponding HF-reference state for each system. In figure 1 we study the dependence of these two entanglement measures on the nuclear charge Z. Therein, we observe that both quantities show: (i) a qualitatively similar decreasing behavior as the nuclear charge is increasing, which corroborates and extends previous works [4, 19]; and (ii) for a given Z the von Neumann value is bigger than the linear entanglement value in all cases considered in this work. Moreover, these two entanglement measures are linear logarithmic functions of Z.

Let us now explore the relationship of the linear and von Neumann entanglement measures with the correlation energy defined as

$$E_{corr} = \frac{E_{CI} - E_{HF}}{E_{CI}} \tag{9}$$

where E_{CI} is the true state energy given by the post-HF method, and E_{HF} is the (monoconfigurational) HF energy. Note that this quantity has been renormalized in order to be always less than one for entangled states and strictly equal to zero for the pure state (i.e. a single determinant Slater). The behavior of the correlation energy and the entanglement measures in terms of the nuclear charge is shown in figure 2. The correlation energies computed using different basis sets are compared in figure 3.

The results summarized in figure 2 indicate that the correlation energy and two entanglement measures show (within the range of Z-values here considered) a linear behavior when plotted against Z in a log-log scale. In other words, these three quantities exhibit a power law dependence on the nuclear charge Z. This is in agreement with previous works which numerically support Collins' conjecture [23–25]. Since this observation has been considered a strong proof of the quality of the wave functions to represent correlation energy, we have tested the methodology employed in the last section to double check the reliability of our basis set choice. This is shown in figure 3, where we have plotted the correlation energy *versus* Z for three different basis sets.

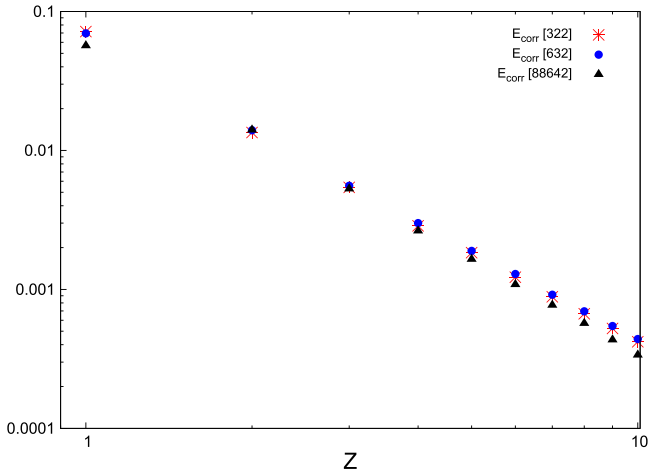

Figure 3. Correlation energy, E_{corr}, of the ground-state helium-like atoms as a function of the nuclear charge $Z \in [1, 10]$ for the following basis sets: [322] (stars), [632] (dots), and [88642] (triangles).

4.2.2. Z-parametrization of entanglement: $\xi(Z)$. In this subsection we provide a parametrization for the dependence of the entropic measures on the nuclear charge Z. We have found it useful to present benchmark results for the behavior of entanglement as Z varies continuously from $Z = 1$ to $Z = 10$. They are given in figure 4 by means of the following parametric expression

$$\xi(Z) = aZ^b, \qquad Z \in [1, 10] \tag{10}$$

where the fitting parameters a and b are given in table 5 for both entanglement measures. Also reported in the table is the value of the residual sum of squares, *RSS*, as an indicator of the goodness of the parametrization [37].

In figure 4 we observe again the monotonic decreasing behavior of the two entanglement measures as a function of Z, showing that the entanglement phenomenon is more important for lower values of Z, i.e. for smaller atoms.

To end this section, let us consider the determination of the minimum (critical) nuclear charge Z_c required to bind N electrons (and, therefore, to give rise to an N-electrons atom), which has been the subject of intense theoretical work since the 1960 s [38–43]. For helium-like atoms, this value has been found to be $Z_c \approx 0.911246$, which was obtained by use of perturbation theory and it should be considered the exact one for the helium series [38, 39, 42]. Although the calculation of this value is not one of the goals of our study we have found that, by use of compact CI wave functions, a value of $Z_c \approx 0.84$ was obtained. Of course, this result is not very accurate because we did not employ very large basis sets, a goal that is beyond the scope of this study.

Table 5. Entanglement parameters for $\xi_L(Z)$ and $\xi_{VN}(Z)$ in equation (10) for helium-like atoms.

Parameters	ξ_L	ξ_{VN}
a	0.0922141 ± 0.0001389	0.241959 ± 0.0001762
b	−2.45654 ± 0.004226	−1.98125 ± 0.001565
RSS	0.000229126	0.000475027

5. Conclusions

In this work we have shown that entanglement for ground-state helium-like atoms can be accounted for by wave functions obtained with a compact CI basis. In this way we are able to match the very accurate ground state value calculated for helium through a more demanding computational methodology (high-quality Kinoshita-type wave functions). The CI wave functions obtained in this work are more tractable from a convergence point of view which allows for the evaluation of reliable wave function properties.

On the other hand, we have shown that energy correlation is linearly related to the entanglement measures associated with the linear and the von Neumann entropies. In this way we obtained a strightforward connection between an information-related kinematic property of the atomic states

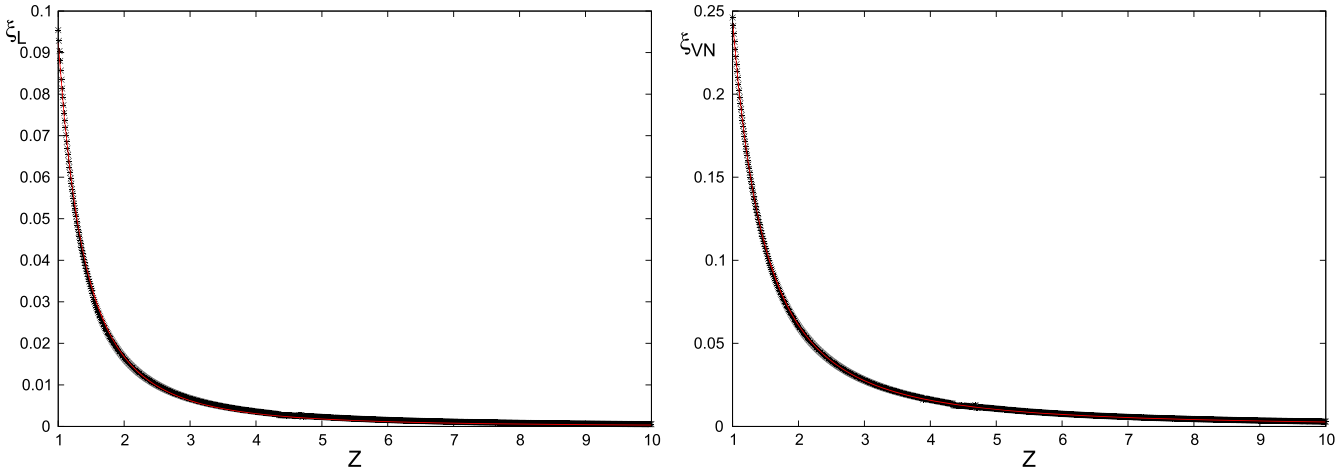

Figure 4. Entanglement fitting of the linear, $\xi_L(Z)$, and von Neumann, $\xi_{VN}(Z)$, measures in terms of the nuclear charge, Z, for helium-like atoms. The red line represents the parametrization given by equation (10).

(i.e. entanglement) and an energy-related quantity determined by the atomic Hamiltonian. Moreover, we have reported benchmark results for the entanglement values for all members of the helium isoelectronic series with an accuracy similar to that of Kinoshita-type wave functions.

Finally, we have given parametric expressions of the linear and von Neumann entanglement measures as Z varies from $Z = 1$ to $Z = 10$, demonstrating numerically that entanglement is an atomic physical feature directly related to the size of the atom which behaves in a decreasing monotonic manner.

We hope that this work will promote the calculations of accurate quantum entanglement values by FCI methods for atoms with three and more electrons, specially taking into account that current *ab initio* quantum chemical packages are able to solve very large secular equations.

Acknowledgments

We acknowledge financial support through Mexican grants from CONACyT (grant number CB-2009-01/132224) and Spanish grants FIS2014-54497P, FIS2014-59311-P, FIS2011-24540, FQM-7276, FQM-207, FQM-020 and FQM-239. Sheila López Rosa wishes to thank Fellowship Program 'Estancias de movilidad José Castillejo para jóvenes doctores (MECD)' for the finantial support of her research stay at UAM (Universidad Autónoma Metropolitana) de Iztapalapa (México), as well as Rodolfo O Esquivel for their kind hospitality during this stay. We thank Moyocoyani Molina-Espíritu for fruitful discussions.

References

[1] Nielsen M A and Chuang I L 2000 *Quantum Computation and Quantum Information* (Cambridge: Cambridge University Press)
[2] Amico L, Fazio R, Osterloh A and Vedral V 2008 Entanglement in many-body systems *Rev. Mod. Phys.* **80** 517
[3] Kais S 2007 Entanglement, electron correlation and density matrices *Adv. Chem. Phys.* **134** 493
[4] Manzano D, Plastino A R, Dehesa J S and Koga T 2010 Quantum entanglement in two-electron atomic models *J. Phys.* A **43** 275301
[5] Dehesa J S, Koga T, Yáñez R J, Plastino A R and Esquivel R O 2012 Quantum entanglement in helium *J. Phys.* B **45** 015504
[6] Dehesa J S, Koga T, Yáñez R J, Plastino A R and Esquivel R O 2012 Corrigendum: Quantum entanglement in helium *J. Phys.* B **45** 239501
[7] Benenti G, Siccardi S and Strini G 2013 Entanglement in helium *Eur. Phys. J.* D **67** 1
[8] Hofer T S 2013 On the basis set convergence of electron-electron entanglement measures: helium-like systems *Front. Chem.* **1** 24
[9] Gauger E M, Rieper E, Morton J J L, Benjamin S C and Vedral V 2011 Sustained quantum coherence and entanglement in the avian compass *Phys. Rev. Lett.* **106** 040503
[10] Sarovar M, Ishizaki A, Fleming G R and Whaley K B 2010 Quantum entanglement in photosynthetic light-harvesting complexes *Nature Phys.* **6** 462
[11] Amovilli C and March N H 2004 Quantum information: Jaynes and Shannon entropies in a two-electron entangled artificial atom *Phys. Rev.* A **69** 054302
[12] Amovilli C and March N H 2003 Exact density matrix for a two-electron model atom and approximate proposals for realistic two-electron systems *Phys. Rev.* A **67** 022509
[13] Nagy A and Pipek J 2010 Approximations for the interparticle interaction energy in an exactly solvable two-electron model atom *Phys. Rev.* A **81** 014501
[14] Coe J P and D'Amico I K 2010 The entanglement of few-particle systems when using the local-density approximation *J. Phys. Conf. Ser* **254** 012010
[15] Yáñez R J, Plastino A R and Dehesa J S 2010 Quantum entanglement in a soluble two-electron model atom *Eur. Phys. J.* D **56** 141
[16] Osenda O and Serra P 2012 Entanglement in Hooks law atoms: an effect of the dimensionality of the space *Few-Body Syst.* **52** 189
[17] Kościk P and Hassanabadi H 2012 *Few-Body Syst.* **52** 189
[18] Lin Y C, Lin C Y and Ho Y K 2013 Spatial entanglement in two-electron atomic systems *Phys. Rev.* A **87** 022316
[19] Koscik P and Okopińska A 2014 Entanglement Entropies in the Ground States of Helium-Like Atoms *Few-Body Syst.* **55** 1151
[20] Kościk P and Okopińska A 2010 Two-electron entanglement in elliptically deformed quantum dots *Phys. Lett.* A **374** 3841
[21] Kościk P 2011 Two-electron entanglement in a two-dimensional isotropic harmonic trap: radial correlation effects in the low density limit *Phys. Lett.* A **375** 458
[22] Kościk P and Okopińska A 2013 Correlation effects in the N-particle Moshinsky model *Few-Body Syst.* **54** 1637
[23] Esquivel R O, Rodriguez A L, Sagar R P, Ho M and Smith V H Jr 1996 Physical interpretation of information entropy: numerical evidence of the Collins conjecture *Phys. Rev.* A **54** 259
[24] Ramírez J C, Soriano C, Esquivel R O, Sagar R P, Ho M and Smith V H Jr 1997 Jaynes information entropy of small molecules: numerical evidence of the Collins conjecture *Phys. Rev.* A **56** 4477
[25] Collins D M 1993 Entropy maximations on electron-density *Z. Naturforsch.* **48** 68
[26] Ghirardi G and Marinatto L 2004 General criterion for the entanglement of two indistinguishable particles *Phys. Rev.* A **70** 012109
[27] Wang H and Kais S 2007 Quantum entanglement and electron correlation in molecular systems *Isr. J. Chem.* **47** 59
[28] Naudts J and Verhulst T 2007 Ensemble-averaged entanglement of two-particle states in Fock space *Phys. Rev.* A **75** 062104
[29] Ghirardi G 2002 Entanglement and properties of composite quantum systems: a conceptual and mathematical analysis *J. Stat. Phys.* **108** 40
[30] Löwdin P O 1955 Quantum theory of many-particle systems: I. Physical interpretations by means of density matrices, natural spin-orbitals, and convergence problems in the method of configurational interaction *Phys. Rev.* **97** 1474
[31] Löwdin P O 1970 On the nonorthogonality problem *Adv. Quantum Chem.* **5** 185
[32] von Neumann J 1955 *Mathematical Foundations of Quantum Mechanics* (Princeton: Princeton University)
[33] Bunge C F 2006 Selected configuration interaction with truncation energy error and application to the Ne atom *J. Chem. Phys.* **125** 014107

[34] Almora-Diaz C X and Bunge C F 2010 Nonrelativistic CI calculations for B^+, B, and B^- ground states *Int. J. Quant. Chem.* **110** 2982
[35] Steiner E 1963 Charge densities in atoms *J. Chem. Phys.* **39** 2365
[36] Clementi E and Roetti C 1974 Roothaan-Hartree–Fock atomic wavefuntions *At. Data Nucl. Data Tables* **14** 177
[37] For a set of data $\{x_i, y_i\}$ and its fitting function $f(x)$, the *RSS* is given by $RRS = \sum_i^n [y_i - f(x_i)]^2$
[38] Brändas E and Goscinski O 1970 Critical point, singularities and extrapolations in the helium iso-electronic sequence *Int. J. Quant. Chem.* **4** 574
[39] Stillinger F H 1966 Ground-state energy of two-electron atoms *J. Chem. Phys.* **45** 3623
[40] Stillinger F H and Stillinger D K 1974 Nonlinear variational study of perturbation theory for atoms and ions *Phys. Rev.* A **10** 1109
[41] Baker J D, Freund D E, Hill R N and Morgan J D III 1990 Radius of convergence and analytic behavior of the $1/Z$ expansion *Phys. Rev.* A **41** 1247
[42] Sergeev A V and Kais S 1999 Critical nuclear charges for N-electron atoms *Int. J. Quant. Chem.* **75** 533
[43] Lin Y C and Ho Y K 2013 Quantum entanglement for two electrons in the excited states of helium-like systems arXiv:1307.5532