Entanglement in helium

Giuliano Benenti\textsuperscript{1,2}, Stefano Siccardi\textsuperscript{3}, and Giuliano Strini\textsuperscript{4}

\textsuperscript{1} CNISM and Center for Nonlinear and Complex Systems, Università degli Studi dell’Insubria, via Valleggio 11, 22100 Como, Italy
\textsuperscript{2} Istituto Nazionale di Fisica Nucleare, Sezione di Milano, via Celoria 16, 20133 Milano, Italy
\textsuperscript{3} Department of Information Technologies, University of Milan, via Bramante 65, 26013 Crema, Italy
\textsuperscript{4} Department of Physics, University of Milan, via Celoria 16, 20133 Milano, Italy

Abstract. Using a configuration-interaction variational method, we accurately compute the reduced, single-electron von Neumann and linear entropy for several low-energy, singlet and triplet eigenstates of helium atom. We estimate the amount of electron-electron orbital entanglement for such eigenstates and show that it decays with energy.

PACS. 03.67.Mn Entanglement measures, witnesses, and other characterizations – 03.67.-a Quantum information – 03.65.-w Quantum mechanics

1 Introduction

The role of entanglement as a resource in quantum communication and computation\cite{1,2} has stimulated many studies trying to unveil its fundamental aspects as well as to provide quantitative entanglement measures\cite{3,4,5}. More recently, the role of entanglement attracts growing interest in systems relevant for chemistry and biology. For instance, the role of quantum coherence and entanglement in atoms and molecules is investigated in laser-induced fragmentation experiments\cite{6,7}. Moreover, entanglement is discussed in light-harvesting complexes, governing the photosynthesis mechanism in proteins\cite{8,9,10,11,12,13}. For a critical view on the role of entanglement in photosynthesis see, however, Ref.\cite{14}. In such instances, due to the complexity of the involved systems, \textit{ab initio} treatments are computationally prohibitive and one is forced to consider simplified (spin) models, with parameters introduced phenomenologically.

Besides computational problems for many-body quantum systems, one must address the problem of measuring entanglement for indistinguishable particles\cite{15,16,17,18,19,20,21,22,23,24,25,26,27}. The main difficulty in quantifying entanglement is due to the symmetrization or antisymmetrization of the wave function for bosons or fermions. That is, to discriminate entanglement from correlations simply due to statistics of indistinguishable particles. In spite of this difficulty, bipartite entanglement has been investigated in a number of systems of physical interest, including the entanglement dynamics of electron-electron scattering in low-dimensional semiconductor systems\cite{20}. The changes of the electronic entanglement during the dissociation process of diatomic molecules\cite{21}, and the entanglement of low-energy eigenstates of helium atom\cite{22}.

To evaluate entanglement in helium, Ref.\cite{22} used high-quality, state-of-the-art Kinoshita-type wavefunctions\cite{23}, expressed in terms of Hylleraas coordinates\cite{24,23,25,26,27}, and then computed the purity of the reduced, one-electron density operator by means of a twelve-dimensional Monte Carlo numerical integration. In the present paper, we compute the reduced, single-electron von Neumann and linear entropy for several low-energy eigenstates of helium by means of a simple configuration-interaction variational method. Our approach has several advantages. First of all, we do not need to evaluate multidimensional integrals: the reduced density matrix is obtained by purely algebraic methods. The reduced density matrix can then be easily diagonalized and therefore we can access not only the linear entropy but also the von Neumann entropy. Finally, we express our variational, Slater-type basis, in terms of (radial and angular) single-particle coordinates, and therefore such Fock-state basis could be easily extended to many-body systems. Despite the above mentioned, still unsolved conceptual difficulties in the definition of entanglement for indistinguishable particles, we propose a way to evaluate the orbital entanglement for states close to Fock states. From such a measure we conclude that the amount of entanglement exhibited by helium eigenstates $|1s,ns;1S\rangle$ and $|1s,ns;3S\rangle$ drops with energy.
2 Entanglement of helium eigenstates

The non-relativistic Hamiltonian of the helium atom reads, in atomic units,

\[ H = \frac{1}{2} p_i^2 + \frac{1}{2} p_j^2 - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{12}}, \]

where \( Z = 2 \) denotes the nuclear charge, \( p_i \) the momentum of electron \( i \) \((i = 1, 2)\), \( r_i \) its distance from the nucleus and \( r_{12} \) the inter-electronic separation.

Since we are neglecting the spin-orbit interaction, we can consider global wavefunctions \( \Xi \) factorized into the product of a coordinate wavefunction \( \Psi \) and a spin wavefunction \( \chi \):

\[ \Xi_{\sigma_1, \sigma_2}(r_1, r_2) = \Psi(r_1, r_2) \chi_{\sigma_1, \sigma_2}. \]

The overall state must be antisymmetric and therefore a measure \([13]\) of the amount of entanglement \( E(|\Xi\rangle) \) of the state \( \Xi \) has been proposed in terms of the von Neumann entropy of the reduced density operator \( R_1 = Tr_2(\rho(\Xi)) \) of one particle, say particle 1, obtained after tracing the overall, two-body density operator over the other particle:

\[ E(|\Xi\rangle) = S(R_1) - 1, \]

with the von Neumann entropy

\[ S(R_1) = - \sum_i A_i \log_2 A_i, \]

where \( \{A_i\} \) are the eigenvalues of \( R_1 \).

However, with such definition a first problem arises. When considering the triplet subspace, spanned by the spin states \( \chi_{\uparrow \downarrow}, \sqrt{2} \chi_{\uparrow \uparrow}, \chi_{\downarrow \downarrow} \), it is clear that we should consider the case \( \chi_{\uparrow \downarrow} \) separately from the cases \( \chi_{\uparrow \uparrow} \) and \( \chi_{\downarrow \downarrow} \). Indeed, \( \chi_{\uparrow \downarrow} \) is a maximally entangled Bell state of the two spins while \( \chi_{\uparrow \uparrow} \) and \( \chi_{\downarrow \downarrow} \) are separable states. Therefore, the standard spectroscopic characterization in terms of triplet and singlet states is no longer useful for the purposes of computing entanglement and one should study separately the entanglement properties of the states composing the triplet. In this context, we would like to point out that, neglecting spin-spin interaction, the choice of the basis states spanning the triplet state is completely arbitrary and that the above discussed \( \chi_{\uparrow \downarrow} \) is only one in between the infinite possible choices.

To avoid this ambiguity, in this paper we compute the entanglement for the orbital part \( \Psi \) only of the wavefunction. Since \( \Psi \) is antisymmetric for spins in the triplet subspace, we can measure the amount of entanglement \( E(|\Psi\rangle) \) of \( \Psi \) as follows:

\[ E(|\Psi\rangle) = S(\rho_1) - 1, \]

where

\[ S(\rho_1) = - \sum_i \lambda_i \log_2 \lambda_i \]

is the von Neumann entropy of the reduced density operator \( \rho_1 = Tr_2(\rho(\Psi)) \), and \( \{\lambda_i\} \) are the eigenvalues of \( \rho_1 \).

When the spin part of the wavefunction is in the singlet state \( \chi_S = \chi_{\uparrow \downarrow} \), the orbital part is necessarily symmetric and this causes an additional, open problem in the quantification of entanglement. Indeed in this case the reduced von Neumann entropy alone is not sufficient to discriminate between entangled and separable states \([13]\). The core of the problem is the fact that we can have separable states with either \( S(\rho_1) = 0 \) or \( S(\rho_1) = 1 \). The first instance corresponds to basis states of the kind \( \psi_{\alpha}(r_1, r_2) = \phi_1(r_1) \phi_2(r_2) \), the second to basis states like \( \psi_{\beta}(r_1, r_2) = \sqrt{2} \phi_1(r_1) \phi_2(r_2) + \phi_2(r_1) \phi_1(r_2) \), with \( i \neq j \). On the other hand, even the quantification of entanglement of the global, antisymmetric wavefunction by means of Eq. \([3]\) poses a problem. Indeed, as the von Neumann entropy is additive for tensor products, for the state \( \Xi = \psi_{\alpha} \chi_S \), Eq. \([3]\) gives \( E(|\Xi\rangle) = 0 \), while for the state \( \Xi = \psi_{\beta} \chi_S \) \((i \neq j)\) we have \( E(|\Xi\rangle) = 1 \). Even though measure \([3]\) gives different results, the amount of entanglement in both cases is the same, since the orbital wavefunctions \( \psi_{\beta} \) are both separable: the reduced density matrices for these two states have different entropies only due to the symmetrization of the state \( \psi_{\beta} \).

We will not address in this paper the unsolved problem of quantification of entanglement for a generic state \( \Psi \). On the other hand, since from our calculations it turns out that for each low-energy helium eigenstate the reduced density operator for the orbital part is rather weakly perturbed with respect to one of the two above non-entangled cases, we expect that an approximate quantification of entanglement is provided by the distance between the von Neumann entropy \( S(\rho_1) \) of \( \rho_1 \) and the von Neumann entropy \( S(\rho_1^{(0)}) \) (\( S(\rho_1^{(0)}) = 0 \) or \( S(\rho_1^{(0)}) = 1 \)) of the reduced density operator \( \rho_1^{(0)} \) for the corresponding non-interacting, non-entangled state:

\[ E(|\Psi\rangle) = |S(\rho_1) - S(\rho_1^{(0)})|. \]

We do not intend to propose an entanglement measure in a rigorous sense; that is not one satisfying all the requirements listed e.g. in \([3]\); in particular we are not going to show that it is not increasing under Local General Measurements and Classical Communication. Our aim is just to have some provisional heuristics that could put some order in the data. We expect such quantification to be in general meaningful only in the regime of weak interactions, such that \( |S(\rho_1) - S(\rho_1^{(0)})| \ll 1 \). Note, however, that for antisymmetric orbital wave functions this definition reduces to \([3]\) and therefore could be applied in this case also for strong interactions.

3 Method

We compute with high accuracy the lowest energy eigenstates of helium by means of a variational method, the
configuration-interaction method (see, for instance, Ref. 28) 4 Numerical results

In the following, we will present data only for total orbital momentum quantum number \( L = 0 \), thus implying \( l_1 = l_2 \equiv l \) and \( m_1 = m_2 \).

We first discuss convergence of our method, as a function of the number \( n_{\text{max}}(l) \) of radial wavefunctions for a given \( l \) and as a function of the cut-off \( l_{\text{max}} \) on \( l \). For the low-energy states discussed below, we found that \( l_{\text{max}} = 2 \) (S, P, and D shells) and \( n_{\text{max}} \approx 10 - 20 \) (from \( n_{\text{max}} = 10 \) for the ground state up to \( n_{\text{max}} = 20 \) for the highest excited states reported below) are sufficient to reproduce helium eigenenergies with at least four significant digits (as deduced from comparison of our results with those of Refs. 23, 25, 26, 27) and reduced von Neumann entropy \( S(\rho_1) \), estimating at least two-three significant digits. To illustrate the convergence of our method, we provide in Table 1 the obtained values of \( S(\rho_1) \) of the ground state of helium for different values of the cut-offs \( l_{\text{max}} \) and \( n_{\text{max}} \) (we take the same \( n_{\text{max}} \) for all values of \( l \)). We also show in Fig. 1 the spectrum of the reduced density matrix \( \rho_1 \), that is, the eigenvalues \( \lambda_k \) versus \( k \), for a few exemplary cases: the ground state \((|1s\rangle^2,|1S\rangle \) and the lowest energy excited states \([1s,2s;|1S\rangle \) and \([1s,2s;|3S\rangle \). We note that in the case of the ground state there is a single dominant eigenvalue, \( \lambda_1 \approx 0.992 \), while for the singlet excited state we have two dominant eigenvalues, \( \lambda_1 \approx 0.577 \) and \( \lambda_2 \approx 0.422 \). Finally, for the triplet states the orbital wave function is antisymmetric and therefore the eigenvalues are doubly degenerate. For the states \([1s,2s;|3S\rangle \) we have \( \lambda_1 = \lambda_2 \approx 0.4998 \). The different features of the spectrum in the above described cases are consistent with the different values of the reduced von Neumann and linear entropies, in spite of the fact that we are always close to the non-interacting limit where the eigenstates are single Slater permanents or determinants.

| \( n_{\text{max}} \) | \( l_{\text{max}} = 0 \) | \( l_{\text{max}} = 1 \) | \( l_{\text{max}} = 2 \) | \( l_{\text{max}} = 3 \) |
|---------|---------|---------|---------|---------|
| 5       | 0.04131 | 0.07772 | 0.07844 | 0.07853 |
| 6       | 0.04133 | 0.07776 | 0.07848 | 0.07837 |
| 10      | 0.04134 | 0.07777 | 0.07849 | 0.07839 |
| 11      | 0.04134 | 0.07777 | 0.07849 | 0.07839 |

Table 1. Reduced von Neumann entropy of the ground state of helium, computed with different cut-off values in the basis of Slater-type orbitals.

The reduced von Neumann entropy \( S(\rho_1) \), as well as the linearized entropy \( S_\ell(\rho_1) = 1 - \text{Tr}(\rho_1^2) \) often used in the literature, are shown in Table 2 and in Table 3 for several low-energy singlet and triplet eigenstates, respectively.

Since the obtained values of the von Neumann entropy are very close to those expected for Fock states, which are separable, the entanglement content is weak and can be estimated by means of Eq. (4). The obtained results are shown in Fig. 2 as a function of the state number \( n \), for both singlet states \(|1s,ns;|1S\rangle \) and triplet states

Orthonormal basis functions are provided by

\[
\Phi_{n_1,l_1,m_1,n_2,l_2,m_2}(r_1,r_2) = F_{n_1,l_1;n_2,l_2}(r_1,r_2)Y_{l_1,m_1}(\Omega_1)Y_{l_2,m_2}(\Omega_2),
\]

where \( Y_{l,m} \) are spherical harmonics, with \( \Omega \) solid angle for particle \( i \) and the radial functions \( F_{n_1,l_1;n_2,l_2}(r_1,r_2) \) are obtained after orthonormalizing the Slater-type orbitals

\[
R_{nl}(r) = r^{n+l-1} \exp(-\xi_{nl}r),
\]

with \( \xi_{nl} \) variational parameters, and properly symmetrizing the products of the obtained one-particle radial wavefunctions \( f_{nl}(r) \). That is, if the spin wavefunction is symmetric, \( F \) must be antisymmetric,

\[
F_{n_1,l_1;n_2,l_2}(r_1,r_2) = \frac{1}{\sqrt{2}} [f_{n_1,l_1}(r_1)f_{n_2,l_2}(r_2) - f_{n_2,l_2}(r_1)f_{n_1,l_1}(r_2)];
\]

if the spin wavefunction is antisymmetric, \( F \) must be symmetric:

\[
F_{n_1,l_1;n_2,l_2}(r_1,r_2) = \frac{1}{\sqrt{2}} [f_{n_1,l_1}(r_1)f_{n_2,l_2}(r_2) + f_{n_2,l_2}(r_1)f_{n_1,l_1}(r_2)]
\]

if \( (n_1,l_1) \neq (n_2,l_2) \),

\[
F_{n_1,l_1,n_2,l_2}(r_1,r_2) = f_{n_1,l_1}(r_1)f_{n_2,l_2}(r_2)
\]

otherwise.

We then compute the reduced (single-electron) density matrix

\[
\rho_1(r_1,r_2) = \int dr_3 \Psi^*(r_1,r_2)\Psi(r_1',r_2'),
\]

with

\[
\Psi(r_1,r_2) = \sum_{l_1,l_2} c_{l_1,l_2} F_{l_1,l_2}(r_1,r_2),
\]

with the multi-indexes \( L \equiv (n_1,l_1,m_1) \) and \( \hat{L} \equiv (n_2,l_2,m_2) \). Since the expansion is done over an orthonormal basis the reduced density matrix on that basis is simply given by a partial trace over the second particle of the overall density matrix: \( \rho_1(l_1,l_2) = \int dr_2 \rho_{l_1,l_2,l'_1,l'_2} \), where \( \rho_{l_1,l_2,l'_1,l'_2} = c_{l_1,l_2}^* c_{l'_1,l'_2}^* \). We point out a major advantage of the configuration-interaction method and the use of orthonormal orbitals: the reduced density matrix is obtained by purely algebraic methods, without numerical computation of the multi-dimensional integrals of Eq. (13). The reduced density matrix can then be easily diagonalized and in this paper we will study the entanglement properties of helium by means of the eigenvalues \( \lambda_k \) of \( \rho_1 \). We will limit our investigation to the ground state and singly excited eigenstates of helium. While doubly excited states can also be addressed by our method, their investigation requires, as well known in the literature, much larger basis dimensions.

G. Benenti, Si. Siccardi and G. Strini: Entanglement in helium 3
approach differs from the one in Ref. [22] because we focus exclusively on the entanglement associated with the spatial part of the two-electron wave function, while Ref. [22] considers the entanglement associated with the global two-electron state, taking spin explicitly into account. In that paper, the amount of entanglement of state $|\Xi\rangle = |\Psi_X\rangle$ is defined as $E(\Xi) = 2 |S_L(\rho_1) - \frac{1}{2}| = 1 - 2\text{Tr}(R^2_1)$, where $\text{Tr}(R^2_1) = \text{Tr}(\rho_1^0)\text{Tr}(\rho_1^0)$, with $\rho_1^0$ reduced density operator for the spin wavefunction. Such definition causes problems. For instance, for the singlet eigenstates we have $\text{Tr}(\rho_1^0) = \frac{1}{2}$, and therefore $E(\Xi) = 1 - \text{Tr}(\rho_1^0) = S_L(\rho_1)$, which is a growing function of energy (see Table 2). On the other hand, this definition does not take into account the fact that $S_L(\rho_1)$ for the state $|\langle 1s^2;1S\rangle\rangle$ is much smaller than for the states $|\langle 1s,ns;1S\rangle\rangle$, with $n > 1$, not due to a smaller entanglement content but as a consequence of the symmetrization of the orbital part of the wavefunction. Indeed, as discussed at the end of the Sec. 2, for the state $|\langle 1s^2;1S\rangle\rangle$ we have $S_L(\rho_1^0) = 0$ and $S_L(\rho_1^0)$, while for the states $|\langle 1s,ns;1S\rangle\rangle$ we have $S_L(\rho_1^0) = 1$ and $S_L(\rho_1^0) = \frac{1}{2}$, with $\rho_1^0$ orbital density operator when electron-electron interaction is neglected. Since state $\rho_1^0$ is not entangled and $S_L(\rho_1) \approx S_L(\rho_1^0)$, the entanglement content of state $|\Psi\rangle$ cannot be properly estimated by $S_L(\rho_1)$, but one should rather consider the difference $|S_L(\rho_1) - S_L(\rho_1^0)|$ or, as we have proposed in this paper, $|S(\rho_1) - S(\rho_1^0)|$. We also point out that a measure of the degree of quantum correlations in multipartite systems was proposed in Ref. [24]. In that paper, the degree of correlations of a $N$-particle bosonic of fermionic system was estimated by means of the inverse participation ratio of the eigenvalues $\lambda_k$ of the reduced single-particle density operator, multiplied by a factor $N$ in the case of fermions to take into account the $N$-fold degeneracy of eigenvalues. However, such definition does not take into account the fact that,

![Fig. 1. Eigenvalue spectrum of the reduced density matrix $\rho_1$, for the states $|\langle 1s^2;1S\rangle\rangle$ (squares), $|\langle 1s,2s;1S\rangle\rangle$ (diamonds), and $|\langle 1s,2s;3S\rangle\rangle$ (stars). In these computations $n_{\text{max}} = 10$ and $l_{\text{max}} = 2$.](image1)

![Fig. 2. Entanglement of the singlet states $|\langle 1s,ns;1S\rangle\rangle$ (circles) and of the triplet states $|\langle 1s,ns;3S\rangle\rangle$ (triangles) as a function of $n$ (main plot, with logarithmic scale for both axes) and of the energy $E$ of the eigenstates, measured in hartrees (inset, logarithmic scale only for the $E$-axis).](image2)

| State       | $S(\rho_1)$ | $S_L(\rho_1)$ |
|-------------|-------------|---------------|
| $|\langle 1s^2;1S\rangle\rangle$ | 0.0785 | 0.01606 |
| $|\langle 1s,2s;1S\rangle\rangle$ | 0.991099 | 0.48871 |
| $|\langle 1s,3s;1S\rangle\rangle$ | 0.998513 | 0.49724 |
| $|\langle 1s,4s;1S\rangle\rangle$ | 0.999577 | 0.49892 |
| $|\langle 1s,5s;1S\rangle\rangle$ | 0.999838 | 0.499465 |
| $|\langle 1s,6s;1S\rangle\rangle$ | 0.999923 | 0.499665 |
| $|\langle 1s,7s;1S\rangle\rangle$ | 0.999961 | 0.499777 |

| Table 3. Same as in Table 2 but for the lowest energy triplet eigenstates of helium. |

| State       | $S(\rho_1)$ | $S_L(\rho_1)$ |
|-------------|-------------|---------------|
| $|\langle 1s^2;3S\rangle\rangle$ | 1.00494 | 0.500378 |
| $|\langle 1s,3s;3S\rangle\rangle$ | 1.00114 | 0.5000736 |
| $|\langle 1s,4s;3S\rangle\rangle$ | 1.000453 | 0.5000267 |
| $|\langle 1s,5s;3S\rangle\rangle$ | 1.000229 | 0.5000127 |
| $|\langle 1s,6s;3S\rangle\rangle$ | 1.000133 | 0.5000070 |
| $|\langle 1s,7s;3S\rangle\rangle$ | 1.000091 | 0.5000047 |

Note that data, with the exception of the ground state value of entanglement, are consistent with a power law decay of entanglement with $n$. From a power-law fit we obtained $E(n) = 0.19 n^{-4.41}$ for singlet states at $n \geq 2$ and $E(n) = 0.040 n^{-3.19}$ for triplet states. The same entanglement data are shown as a function of energy in the inset of Fig. 2. It can be clearly seen that the entanglement content drops with energy. This result is rather intuitive in that for states $|\langle 1s,ns;1S\rangle\rangle$ and $|\langle 1s,ns;3S\rangle\rangle$ the wave functions corresponding to the states $1s$ and $ns$ are localized farther apart for larger $n$. Therefore, electron-electron interactions become weaker (and entanglement smaller) when $n$ increases.

We note that, due to a different definition of entanglement, the energy-dependence obtained in our results contrasts the one obtained in Ref. [22]. Our present approach differs from the one in Ref. [22] because we focus exclusively on the entanglement associated with the spatial part of the two-electron wave function, while Ref. [22] considers the entanglement associated with the global two-electron state, taking spin explicitly into account. In that paper, the amount of entanglement of state $|\Xi\rangle = |\Psi_X\rangle$ is defined as $E(\Xi) = 2 |S_L(\rho_1) - \frac{1}{2}| = 1 - 2\text{Tr}(R^2_1)$, where $\text{Tr}(R^2_1) = \text{Tr}(\rho_1^0)\text{Tr}(\rho_1^0)$, with $\rho_1^0$ reduced density operator for the spin wavefunction. Such definition causes problems. For instance, for the singlet eigenstates we have $\text{Tr}(\rho_1^0) = \frac{1}{2}$, and therefore $E(\Xi) = 1 - \text{Tr}(\rho_1^0) = S_L(\rho_1)$, which is a growing function of energy (see Table 2). On the other hand, this definition does not take into account the fact that $S_L(\rho_1)$ for the state $|\langle 1s^2;1S\rangle\rangle$ is much smaller than for the states $|\langle 1s,ns;1S\rangle\rangle$, with $n > 1$, not due to a smaller entanglement content but as a consequence of the symmetrization of the orbital part of the wavefunction. Indeed, as discussed at the end of the Sec. 2, for the state $|\langle 1s^2;1S\rangle\rangle$ we have $S_L(\rho_1^0) = 0$ and $S_L(\rho_1^0)$, while for the states $|\langle 1s,ns;1S\rangle\rangle$ we have $S_L(\rho_1^0) = 1$ and $S_L(\rho_1^0) = \frac{1}{2}$, with $\rho_1^0$ orbital density operator when electron-electron interaction is neglected. Since state $\rho_1^0$ is not entangled and $S_L(\rho_1) \approx S_L(\rho_1^0)$, the entanglement content of state $|\Psi\rangle$ cannot be properly estimated by $S_L(\rho_1)$, but one should rather consider the difference $|S_L(\rho_1) - S_L(\rho_1^0)|$ or, as we have proposed in this paper, $|S(\rho_1) - S(\rho_1^0)|$. We also point out that a measure of the degree of quantum correlations in multipartite systems was proposed in Ref. [24]. In that paper, the degree of correlations of a $N$-particle bosonic of fermionic system was estimated by means of the inverse participation ratio of the eigenvalues $\lambda_k$ of the reduced single-particle density operator, multiplied by a factor $N$ in the case of fermions to take into account the $N$-fold degeneracy of eigenvalues. However, such definition does not take into account the fact that,
for symmetric wave functions, the degree of degeneracy of the eigenvalues $\lambda_k$ is not unique, see the above described difference between the states $|1s, ns; 1S\rangle$ and $|1s, ns; 1S\rangle$.

5 Conclusions

In this paper, we have computed the reduced von Neumann entropy for several low-energy (singlet and triplet) eigenstates of helium. The von Neumann entropy has then been used to estimate the amount of entanglement of such states, showing that the entanglement of the states $|1s, ns; 1S\rangle$ and $|1s, ns; 1S\rangle$ decays with $n$, that is, with energy. This result is in agreement with the intuition, suggesting that when the electronic wavefunctions are localized far apart, electron-electron interactions are weak and therefore the entanglement is expected to be small. Our results can be seen as one of the first steps towards a “spectroscopy of entanglement” for atomic and molecular systems. While electron-electron interactions are weak and therefore the entanglement is expected to be small. Our results can be extended to more complex systems, and the obtained numerical results could be used to test the validity, with respect to the calculation of the reduced von Neumann or linear entropy, of perturbative approaches or of simplified phenomenological models. Finally, we point out that, while our bipartite entanglement measure can be applied to wavefunctions close to separable Fock states, quantification of entanglement for generic states of indistinguishable particles remains an interesting open problem.

Acknowledgements

We thank Jesús Dehesa for very useful discussions.

References

1. G. Benenti, G. Casati, and G. Strini, Principles of Quantum Computation and Information, Vol. I: Basic concepts (World Scientific, Singapore, 2004); Vol. II: Basic tools and special topics (World Scientific, Singapore, 2007).
2. M. A. Nielsen and I. L. Chuang, Quantum computation and quantum information (Cambridge University Press, Cambridge, 2000).
3. M. B. Plenio and S. Virmani, Quant. Inf. Comput. 7, 1 (2007).
4. R. Horodecki, P. Horodecki, M. Horodecki, and K. Horodecki, Rev. Mod. Phys. 81, 865 (2009).
5. L. Amico, R. Fazio, A. Osterloh, and V. Vedral, Rev. Mod. Phys. 80, 517 (2008).
6. D. Akoury et al. Science 318, 949 (2007).
7. U. Becker U. and B. Langer B., Nucl. Instrum. Methods A 601, 78 (2009).
8. G. S. Engel et al., Nature 446, 782 (2007).
9. H. Lee, Y.-C. Cheng, and G. R. Fleming, Science 316, 1462 (2007).
10. M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik, J. Chem. Phys. 129, 174106 (2008).
11. M. Sarovar, A. Ishizaki, G. R. Fleming, and K. B. Whaley, Nature Phys. 6, 462 (2010).
12. A. W. Chin, A. Datta, F. Caruso, S. F. Huelga, and M. B. Plenio, New J. Phys. 12, 065002 (2010).
13. T. Scholak, F. de Melo, T. Wellens, F. Mintert, and A. Buchleitner, Phys. Rev. E 83, 021912 (2011).
14. M. Tiersch, S. Popescu and H. J. Briegel, Phil. Trans. R. Soc. A 370, 3771 (2012).
15. J. Schliemann, J. I. Cirac, M. Kuś, M. Lewenstein, and D. Loss, Phys. Rev. A 64, 022303 (2001); J. Schliemann, D. Loss, and A. H. MacDonald, Phys. Rev. B 63, 085311 (2001).
16. P. Zanardi, Phys. Rev. A 65, 042101(R) (2002).
17. H. M. Wiseman and J. A. Vaccaro, Phys. Rev. Lett. 91, 097902 (2003).
18. G. C. Ghirardi and L. Marinatto, Phys. Rev. A 70, 012109 (2004).
19. M. C. Tichy, F. Mintert and A. Buchleitner, J. Phys. B 44, 192001 (2011).
20. F. Buscemi, P. Bordone, and A. Bertoni, Phys. Rev. A 73, 052312 (2006).
21. R. O. Esquivel et al., J. Phys. B 44, 175101 (2011).
22. D. Manzano, A. R. Plastino, J. S. Dehesa, and T. Koga, J. Phys. A 43, 275301 (2011); J. S. Dehesa, T. Koga, R. J. Jáñez, A. R. Plastino, and R. O. Esquivel, J. Phys. B 45, 015504 (2012).
23. T. Koga, J. Chem. Phys. 104, 6308 (1996).
24. E. A. Hylleraas, Adv. Quant. Chem. 1, 1 (1964).
25. C. L. Pekeris, Phys. Rev. 115, 1216 (1959).
26. A. Kono and S. Hattori, Phys. Rev. A 31, 1199 (1985); ibid., 34 1727 (1986); ibid., 37 2241 (1988).
27. G. W. F. Drake, Phys. Scr. T83, 83 (1999).
28. P. Fulde, Electron correlations in molecules and solids, Third Edition (Springer, 2002).
29. E. Cormier and P. Lambropoulos, J. Phys. B 28, 5043 (1995).
30. B. Grémaud and D. Delande, Europhys. Lett. 40, 363 (1997).
31. A. Scrinzi and B. Piraux, Phys. Rev. A 56, 13 1997.
32. J. Madroñero J. and A. Buchleitner, Phys. Rev. A 77, 052312 (2008).
33. J. Eiglsperger, J. Madroñero and B. Piraux, Phys. Rev. A 81, 042527 (2010); Phys. Rev. A 81, 042528 (2010).
34. R. Grobe, K. Rzażewski and J. H. Eberly, J. Phys. B 27, L503 (1994).