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DYNAMICS OF ENTANGLEMENT FOR TWO-ELECTRON ATOMS

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We studied the dynamics of the entanglement for two electron atoms with initial states created from a superposition of the eigenstates of the two-electron Hamiltonian. We present numerical evidence that the pairwise entanglement for the two electrons evolves in a way that is strongly related with the time evolution of the Coulombic interaction between the two electrons.

Keywords: Entanglement; two-electrons atoms; dynamics.

1. Introduction

The ability to manipulate the entanglement of physical systems is crucial to implementing quantum information processing.[1,2] Notwithstanding that the preferred physical systems for quantum information processing, particularly for quantum computers, are spin systems,[3] recent experiments[4] have raised expectations about the possibility of handling quantum information in systems with continuous degrees of freedom, which can be used as a non-classical resource for quantum computation and quantum communication.[5]

The study of quantum entanglement for systems with continuous degrees of freedom possess a number of *extra* problems when compared to systems with discrete degrees of freedom. One particularly acute difficulty is the lack of exact solutions. The existence of exact solutions has contributed enormously to the understanding of the entanglement for systems with finite degrees of freedom.[6] Moreover, at least for two spin-1/2 distinguishable particles, there is a simple *formula*[7] to calculate the entanglement of formation,[8] which is a very remarkable fact since most of the entanglement measures proposed are variational expressions, which are very difficult to evaluate. Even for highly simplified models, there are only a small number of exact solution for problems involving two particles with continuous degrees of freedom. For example, the problem of two particles in a harmonic trap interacting with some potential can be solved exactly in the case of a contact potential modeled by a regularized δ-function.[9] If the potential of interaction between the particles is Coulombic, the problem can be solved in particular cases.[10,11]

The bipartite entanglement of distinguishable spins on a chain can be studied using well-known entanglement measures such as the entanglement of formation,[12] random robustness of entanglement (or the modulus of separability),[13] which are useful for pure and mixed states. When considering systems with continuous degrees of freedom and identical particles, one is faced with subtleties that are not present in models like quantum spin chains. For a pure state $|\Psi\rangle$, the von Neumann entropy of the reduced state is a good entanglement measure,[14] although other approaches are possible, for example, Shannon entropy has been used to study the two-electron atom[15,16] and a two-electron artificial atom.[17] The von Neumann entropy has been used to study the dynamics of entanglement between two trapped atoms,[18] the entanglement between two (spin-1/2) fermions in a cylindrical harmonic trap,[19] the entanglement for one-dimensional spin systems in external time-dependent magnetic fields[20–22] and the scaling properties of entanglement shared between the two electrons of an atomic like system near the ionization threshold.[23] Gittings and Fisher[24] showed that the von Neumann entropy for the reduced density matrix of half the system can be used as an entanglement measure for the case of indistinguishable particles. Huang and Kais showed that entanglement, as measured by the von Neumann entropy, can be used as a measure of electron–electron correlation in quantum chemistry calculations.[25,26]

In a previous work, Osenda and Serra,[23] investigated the critical behavior of the von Neumann entropy near the ionization threshold of the "spherical" helium model (two electrons interacting with a fixed center and between them). They showed that the von Neumann entropy for this system is a decreasing function of the charge, i.e. at the threshold, the von Neumann entropy attains its maximum value for bounded states and it decreases to zero for the charge going to infinity. In this paper, we want to compare two ways to manipulate the entanglement between the electrons of an helium-like atom. The Hamiltonian, in atomic units, and applying the standard transformation $\vec{r} \to \vec{r}/Z$; $H \to Z^2 H$, takes the form[27]

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

where

$$h(i) = \frac{1}{2} p_i^2 - \frac{1}{r_i}, \quad \lambda = \frac{1}{Z}, \quad V = \frac{1}{r_{12}}, \tag{2}$$

p_i and r_i are the momentum operator and the position operator of the $i = 1, 2$ electron, r_{12} is the distance between them, and Z is the nuclear charge [in the spherical model, $1/r_{12}$ is replaced by $1/r_>$, where $r_> = \max(r_1, r_2)$]. We will concentrate our study on the behavior of the von Neumann entropy as a function of λ and on the dynamics of the entanglement when the system evolves from a chosen initial condition. In particular, we will address the following question: Is there a physical quantity that can be used to explain in a direct way the time evolution of the entanglement between the electrons?

The von Neumann entropy for two-electron atoms is given by

$$\mathbf{S} = -\mathrm{Tr}(\hat{\rho}^{\mathrm{red}} \log_2 \hat{\rho}^{\mathrm{red}}), \tag{3}$$

where the reduced density operator is[28,29]

$$\hat{\rho}^{\mathrm{red}}(\mathbf{r}_1, \mathbf{r}'_1, t) = \mathrm{Tr}_2 \left|\Psi\right\rangle \left\langle\Psi\right|, \tag{4}$$

here the trace is taken over one electron, and $|\Psi\rangle$ is the total two-electron wave function.

The paper is organized as follows. In Sec. 2, the time independent Schrödinger equation for the two electron problem is solved using a linear variational approach, this provides a set of approximate eigenfunctions and eigenvalues. We use this set to obtain an approximate reduced density operator $\hat{\rho}^{\mathrm{red}}$. Then, the eigenvalue problem for the approximate reduced density operator is solved and the von Neumann entropy is calculated using these eigenvalues. How we calculate the von Neumann entropy from the reduced density operator is discussed in Sec. 3. The numerical results for the von Neumann entropy are presented in Sec. 4. Finally, the conclusions are given in Sec. 5. The mathematical details about the approximate reduced density operator and its diagonalization are left to Appendix A.

2. Solution of the Schrödinger Equation

As any two identical spin-1/2 fermionic system, the total Hilbert space is the external product of the spin Hilbert space times the spatial Hilbert space. That is, the eigenfunctions of Hamiltonian equation (1) take the form

$$\Psi(1,2) \;=\; \Phi_{\substack{\mathrm{S}\\ \mathrm{A}}}(\vec{r}_1, \vec{r}_2)\; \chi_{\substack{\mathrm{sing}\\ \mathrm{trip}}}\,, \tag{5}$$

where the spatial wave function Φ_{S} (Φ_{A}) is symmetric (antisymmetric) under permutation of the particles, and χ_{sing} and χ_{trip} are the singlet and triplet spinor 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.[30] Then, as established by Ghirardi and Marinatto,[14] for values of $\lambda > 0$, the states described by bound-state eigenfunctions are entangled states, and the greater the von Neumann entropy, the larger is the amount of entanglement of the state.

In particular, the ground state eigenfunction has the form

$$\Psi_0(1,2) \;=\; \Phi_0(\vec{r}_1, \vec{r}_2)\; \chi_{\mathrm{sing}}\,, \tag{6}$$

where Φ_0 is symmetric under permutation of the particles.

The time dependent Schrödinger equation for two electron atoms is given by

$$\imath\hbar\frac{\partial\Psi(1,2;t)}{\partial t} = H\Psi(1,2;t) \qquad \Psi(1,2;t=0) = \Psi^0(1,2), \tag{7}$$

where H is the Hamiltonian defined by Eqs. (1) and (2). For a given initial condition $\Psi^0(1,2)$ of the two-electron problem, the time dependent wave function is given by

$$\Psi(1,2;t) = \sum_j \alpha_j e^{-iE_j t}\Phi_j(1,2)\chi_j, \tag{8}$$

where $\{\Phi_j(1,2)\chi_j\}$ and $\{E_j\}$ are the complete set of eigenvector and the corresponding eigenenergies of the Hamiltonian H respectively

$$H\Phi_j(1,2)\chi_j \;=\; E_j\Phi_j(1,2)\chi_j, \tag{9}$$

and $\alpha_j = \langle\Phi_j(1,2)|\Psi^0(1,2)\rangle$. We assume that only bound states are necessary in expansion Eq. (8), therefore j represents a set of discrete quantum numbers. Because the bottom of the continuum spectra is the ground state energy of the one electron atom, $E_{\text{th}} = -1/2$ and V in Eq. (2) is a positive operator we have for the discrete spectrum

$$-1 \le E_j \le -\frac{1}{2}; \quad \forall j\,. \tag{10}$$

Since the Hamiltonian is spin independent and invariant under rotations, for the sake of simplicity, we restricted our investigation to the study of singlet states with zero total angular momentum, i.e. the initial condition $\Psi^0(1,2)$ will be a s-wave singlet. Therefore only s-wave singlets in Eq. (9) contribute to the expansion Eq. (8), and the spinor $\chi_j = \chi_{\text{sing}}$, $\forall j$.

For a given complete λ-independent basis set for s-waves singlets $\{\phi_i(1,2)\}$, the eigenvectors have the following expansion:

$$\Phi_j(1,2) \;=\; \sum_i a_i^{(j)}(\lambda)\phi_i(1,2), \tag{11}$$

where i represents the adequate set of quantum numbers and $a_i^{(j)}(\lambda) = \langle\phi_i(1,2)|\Phi_j(1,2)\rangle$. The equation of eigenvalues (9) cannot be solved exactly, or equivalently, we cannot calculate the coefficients $\{a_i^{(j)}(\lambda)\}$ in the expansion equation (11). An approximate solution could be obtained using the Rayleigh-Ritz variational method.[31] This method is applicable to the discrete spectrum of the Hamiltonian, and consists of truncation of the series equation (11) at order M. Then, as usual, the eigenvalue problem equation (9) is recast as an algebraic generalized eigenvalue one of the form

$$H^{(M)}\mathbf{c}^{(i)} \;=\; E_i^{\text{var}}\mathcal{M}\,\mathbf{c}^{(i)}, \tag{12}$$

where

$$(H^{(M)})_{kj} = \langle\phi_k|H|\phi_j\rangle, \quad \mathcal{M}_{kj} = \langle\phi_k|\phi_j\rangle. \tag{13}$$

For an orthonormal basis set, the overlap matrix $\mathcal{M}$ is equal to the identity matrix. In our case, the basis set is not orthogonal (see below), but Eq. (12) is mapped to a usual eigenvalue problem applying a Cholesky decomposition to the overlap matrix.[32] In general, only $K \leq M$ eigenvalues of Eq. (12) will be less than the threshold energy for bound states $E_{\mathrm{th}} = -1/2$. In fact, $K \ll M$ for large values of M. The variational approach establish that these K eigenvalues E_i^{var} are optimal upper bounds for the first K exact eigenenergies: $E_1 \leq E_1^{\mathrm{var}}$; $E_2 \leq E_2^{\mathrm{var}}, \ldots, E_K \leq E_K^{\mathrm{var}}$ and the corresponding eigenvectors give the optimal approximation for the coefficients $a_i^{(j)}$:

$$\Phi_j(1,2) \simeq \Phi_j^{\mathrm{var}}(1,2) = \sum_{i=1}^{M} c_i^{(j)} \phi_i, \quad c_i^{(j)} = (\mathbf{c}^{(j)})_i; \quad j = 1, \ldots, K. \tag{14}$$

As a basis set, we used s-wave singlets characterized by the quantum numbers n_1, n_2, l given by

$$\phi_{n_1,n_2;l} = (f_{n_1}(r_1)\, f_{n_2}(r_2))_s \mathcal{Y}_{0,0}^{l}(\Omega_1, \Omega_2), \tag{15}$$

where $n_2 \leq n_1$, $l \leq n_2$, and the $\mathcal{Y}_{0,0}^{l}(\Omega_1, \Omega_2)$ are given by

$$\mathcal{Y}_{0,0}^{l}(\Omega_1, \Omega_2) = \frac{(-1)^l}{\sqrt{2l+1}} \sum_{m=-l}^{l} (-1)^m Y_{l\,m}(\Omega_1) Y_{l\,-m}(\Omega_2), \tag{16}$$

i.e. they are eigenfunctions of the total angular momentum with zero eigenvalue, and the $Y_{l\,m}$ are the spherical harmonics. The radial term $(f_{n_1}(r_1) f_{n_2}(r_2))_s$ has the appropriated symmetry for a singlet state,

$$(f_{n_1}(r_1) f_{n_2}(r_2))_s = \frac{f_{n_1}(r_1) f_{n_2}(r_2) + f_{n_1}(r_2) f_{n_2}(r_1)}{[2\,(1 + \langle n_1 | n_2 \rangle^2)]^{1/2}} \tag{17}$$

where

$$\langle n_1 | n_2 \rangle = \int_0^\infty r^2 f_{n_1}(r) f_{n_2}(r)\, dr, \tag{18}$$

the f's are chosen to satisfy $\langle n_1 | n_1 \rangle = 1$. The numerical results in Sec. 4 are obtained by taking the Slater type forms for the orbitals

$$f_n(r) = \left[\frac{\alpha^{2n+3}}{(2n+2)!} \right]^{1/2} r^n e^{-\alpha r/2}. \tag{19}$$

It is clear that in terms of the functions defined in Eq. (15), the variational eigenfunctions read as

$$\Phi_j^{\mathrm{var}}(1,2) = \sum_{n_1=0}^{N} \sum_{n_2=0}^{n_1} \sum_{l=0}^{n_2} c_{n_1 n_2 l}^{(j)}\, \phi_{n_1,n_2;l}, \tag{20}$$

where N is the higher power of r on the radial function (19) that is included in the variational expansion. Then, M, the number of variational functions $\{\phi_{n_1,n_2;l}\}$, can be obtained as

$$\sum_{n_1=0}^{N} \sum_{n_2=0}^{n_1} \sum_{l=0}^{n_2} 1 = M. \tag{21}$$

Since there is a bijection between M and N, from now on we will use the superscript N to denote those quantities obtained using M variational functions, for example, the variational function in Eq. (20) can be denoted by $\Phi_j^{(N)}(1,2)$.

The matrix elements of the kinetic energy, the Coulombic repulsion between the electrons and other mathematical details involving the functions $|n_1, n_2; l\rangle$ are given in Ref. 33.

3. The von Neumann Entropy

The wave function $|\Psi\rangle$, Eq. (8) can be used to obtain the reduced density operator defined in Eq. (4). Since the state $|\Psi\rangle$ has spatial and spin degrees of freedom, both remain factorized, the von Neumann entropy of the reduced density operator becomes[19,23]

$$\mathbf{S} = S + \log_2(2), \tag{22}$$

where $\log_2(2)$ is the contribution of the factorized spin part. From here, we will refer to the spatial contribution S in Eq. (22) as the von Neumann entropy.

The von Neumann entropy S could be written as

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

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

$$\int_{-\infty}^{\infty} \rho_s^{\mathrm{red}}(\mathbf{r}_1, \mathbf{r}_1', t)\varphi_\nu(\mathbf{r}_1', t)\, d\mathbf{r}_1' = \Lambda_\nu(t)\varphi_\nu(\mathbf{r}_1, t). \tag{24}$$

For example, for an eigenfunction $\Phi_i(1,2)\chi_i$ of the Hamiltonian, the spatial part of the reduced density operator is given by

$$\rho_s^{\mathrm{red}}(\mathbf{r}_1, \mathbf{r}_1') = \int \Phi_i(\mathbf{r}_1, \mathbf{r}_2)\Phi_i(\mathbf{r}_1', \mathbf{r}_2)\, d\mathbf{r}_2. \tag{25}$$

Starting from an approximate solution of the Schrödinger equation of Nth order $\Psi^{(N)}(1,2,t)$, it is possible to calculate approximations of Nth order for the eigenvalues of the spatial part of the reduced density operator $\Lambda^{(N)}$ and for the von Neumann entropy $S^{(N)}$. The mathematical details are left to Appendix A.

We want to address the problem of the time evolution of the entanglement from specified initial conditions. As a result of the restrictions imposed on the variational functions used in our approach, we have to confine our study to initial conditions with zero total angular moment, i.e. to singlet states. A rather natural choice are the eigenstates of the Hamiltonian in Eq. (7) with a *charge different to the one used during the time evolution of the system.* As we shall see, the "collisions" between the electrons allow a direct interpretation of the time evolution of the entanglement. The collisions are signaled by local maxima of the Coulombic repulsion.

4. Numerical Results

In this section, we present the numerical results showing the behavior of the von Neumann entropy as a function of $\lambda = 1/Z$ for the ground state, and the time evolution of the entanglement for different initial conditions. The time evolution corresponds to the Hamiltonian of a two-electron atom with nuclear charge $Z = 2$.

Figure 1 shows the behavior of the von Neumann entropy $S^{(N)}$ versus λ, for different values of N. For $Z < Z_c \simeq 0.911$ ($\lambda > \lambda_c$), the system consists of one electron bounded to the central charge, and one unbounded electron.[27] The behavior of the von Neumann entropy can be understood as follows, for $\lambda \to 0$, the two electrons become independent since the Coulomb repulsion between electrons goes to zero (see Eq. (1)). In that situation, the spatial wave function can be written as a simple product, giving $S^{(N)} = 0$. For $\lambda > \lambda_c$, the spatial wave function can be written as a symmetrized product of one electron wave functions so $S = S_c = 1$.

Figure 2 shows the periodic behavior of the von Neumann entropy $S(t)$ as a function of time when the initial condition is given by a linear combination of the ground and first excited states with zero total angular momentum, $(|0\rangle + |1\rangle)/\sqrt(2)$ and nuclear charge $Z = 2$.

Figure 3 shows the time evolution of the entanglement when the initial condition is the ground state of Hamiltonian (1) with $Z = 1.2$. Also shown is the evolution of the Coulombic repulsion between the electrons $\langle 1/r_{12} \rangle$.

It is clear that the local maxima of the entanglement corresponds to the local minima of the Coulombic repulsion and vice versa. Since the initial condition of the mean (square) distance between the electrons, corresponding to an atom with $Z = 1.2$, is larger than the mean distance in an atom with $Z = 2$, it is reasonable

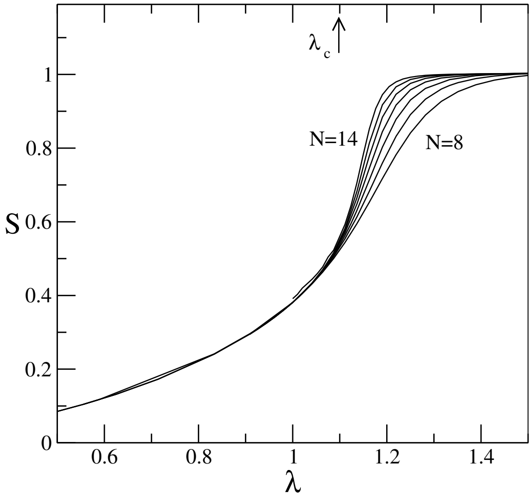

Fig. 1. $S^{(N)}$ versus λ for $N = 8, 9, 10, 11, 12, 13$ and 14. The convergence of the data for values of λ up to $\lambda_c \simeq 1.098$ is excellent.

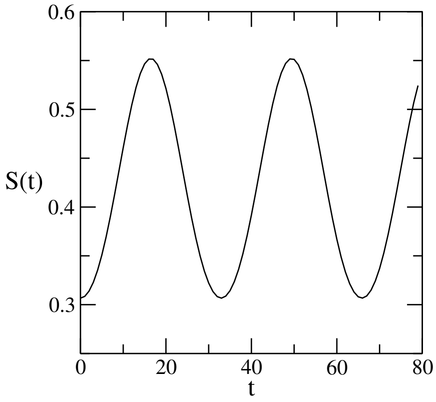

Fig. 2. Time evolution of the von Neumann entropy as a function of time. The initial condition for the wave function is given by a linear combination of the ground and first exited states with zero total angular momentum and nuclear charge $Z = 2$.

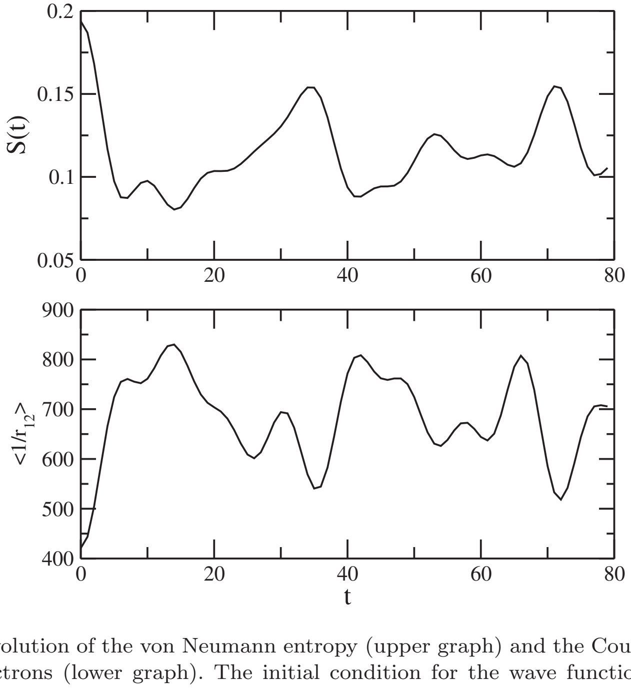

Fig. 3. Time evolution of the von Neumann entropy (upper graph) and the Coulombic repulsion between the electrons (lower graph). The initial condition for the wave function is the ground state wave function corresponding to the nuclear charge $Z = 1.2$.

that a stronger potential will diminish this distance and, after expending some time approaching, the electrons will bounce back. The time evolution is not periodic as shown in Fig. 1, since there are a number of levels which are mixed by the time evolution of the system. The scenario described above is consistent with the time

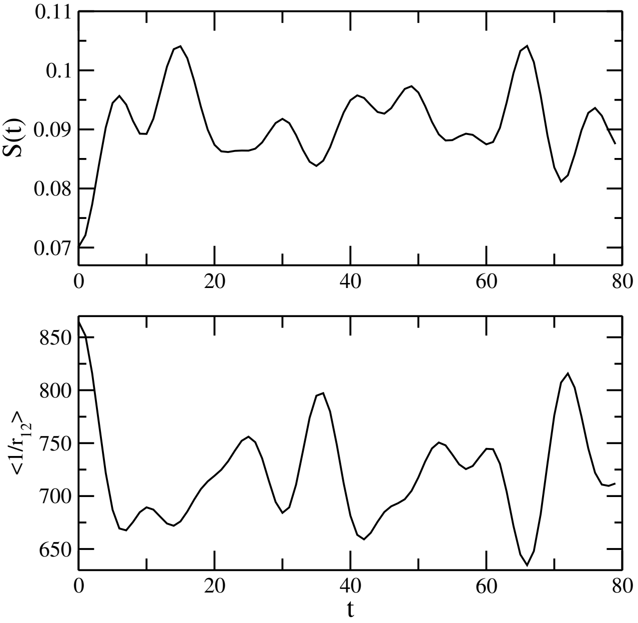

Fig. 4. Time evolution of the von Neumann entropy (upper graph) and the Coulombic repulsion between the electrons (lower graph). The initial condition for the wave function is the ground state function corresponding to the nuclear charge $Z = 3$.

evolution of the entanglement shown in Fig. 4, which corresponds to the time evolution of the ground state of an atom with initial condition corresponding to $Z = 3$. As in Fig. 3, the upper part shows the time evolution of the entanglement $S(t)$, and the lower one shows the time evolution of the Coulombic repulsion interaction between electrons $\langle 1/r_{12}\rangle$. In Fig. 5, we show the time evolution of the entanglement for the second excited state with zero total angular momentum.

Figures 2–5 are obtained by using $M = 165$ basis functions $\phi_{n_1,n_2;l}$. The value 165 is obtained from Eq. (21) for $N = 8$.

Since our solution is only an approximate one, it is necessary to check its validity. In Fig. 6, we show the time evolution of the ground state corresponding to $Z = 1.2$ for $M = 165$ and $M = 286$ (which corresponds to $N = 10$ in Eq. (21)). The agreement is very good, especially for short times. This reinforces the idea that the time evolution of the entanglement is qualitatively well-described, in particular, its relationship with the Coulombic repulsion between the two electrons.

5. Conclusion

In the model studied, since the increase (or decrease) of the entanglement from that of the initial state is determined somehow by the excess (or lack) of Coulombic repulsion between the two electrons (compared with the Coulombic repulsion that

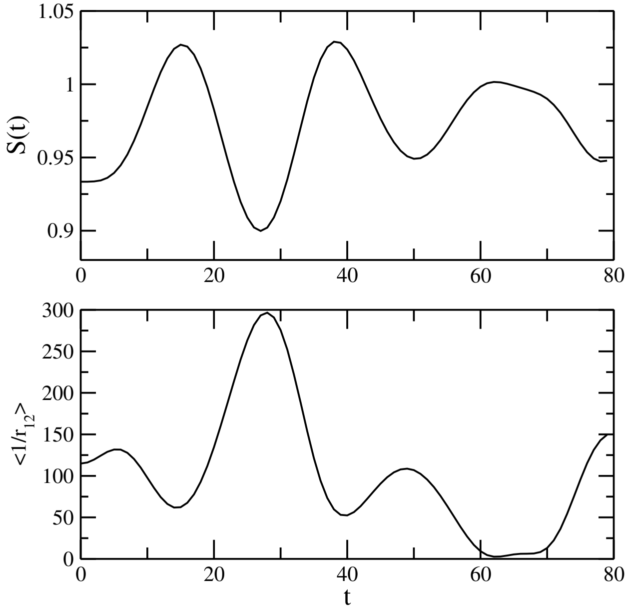

Fig. 5. Time evolution of the von Neumann entropy (upper graph) and the Coulombic repulsion between the electrons (lower graph). The initial condition for the wave function is the second excited state function corresponding to the nuclear charge $Z = 1.2$.

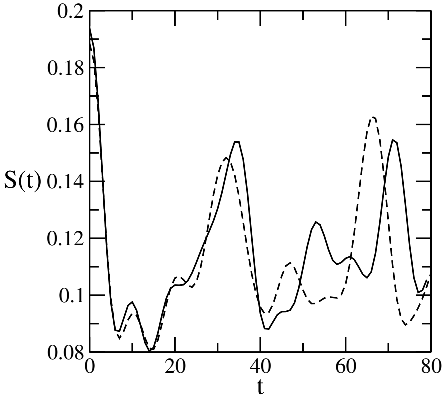

Fig. 6. Time evolution of the von Neumann entropy. The initial condition for the wave function is the ground state function corresponding to the nuclear charge $Z = 1.2$. The solid line corresponds to 165 basis set functions and the dashed line to 286 basis set functions, respectively.

the electrons would have if they were in an eigenstate of the atom with $Z = 2$), and this being excess (or lack) bounded, it is clear that the entanglement will not increase (or decrease) beyond some limits.

An atomic like system is not a good model for a trap, but some of the conclusions that can be extracted from our study could be applicable to the behavior of trapped identical particles. In traps, ground states are considered because they can be prepared faithfully (for example, by cooling off the system enough) as many times as necessary. In this sense, an initial condition of two separate particles heading for collision-like that considered on Ref. 18 is, at some extent, unrealistic if it must be prepared repeatedly with some reliability.

From our study, it is clear that the time evolution of an initial condition given by a ground state Ψ_{λ_0} (corresponding to a value of λ_0) produces more entanglement if the ground state of the Hamiltonian driving the time evolution Ψ_λ (with $\lambda < \lambda_0$) has greater entanglement, that is

$$S(\Psi_{\lambda_0}) < S(\Psi_\lambda), \tag{26}$$

anyway the amount of entanglement produced is similar to $S(\Psi_\lambda)$, so at least in our case, the time evolution does not seem like a good method to substantially increase the entanglement shared by the electrons.

In the atomic like model considered in this paper, the entanglement is an increasing function of the intensity of the interaction between the electrons. This behavior is opposite to that observed by Sun *et al.*,[19] they observed that there is an optimal intensity of the interaction between the trapped particles, for which the entanglement is maximum, increasing the interaction strength from this value diminishes the entanglement. Since in the model considered by Sun *et al.*, the length of interaction is very short compared with the length scale characteristic of the trap, it could be interesting to analyze a model in which both variables, the intensity and length scale of the interaction can be varied.

Another important issue is the control and manipulation of the dynamics of entanglement between electrons in atomic and molecular systems by external interactions. Recently, we propose a new scheme to control the level of entanglement between two fixed spin 1/2 systems by interaction with a third particle.[34] For specific designs, entanglement is shown to be "pumped" into the system from the surroundings even when the spin–spin interaction within the system is small or nonexistent. The effect of the external particle on the dynamics of entanglement for the two-electron atoms will be presented in a future study.

Appendix A. Some Mathematical Details

We start from the definition for the reduced density operator

$$\rho^{\mathrm{red}} = \mathrm{Tr}_2 |\Psi\rangle\langle\Psi|, \tag{A.1}$$

so, introducing the expansion in Eq. (8), and keeping only the spatial part, we get

$$\rho_s^{\mathrm{red}}(\mathbf{r}_1, \mathbf{r}_1', t) = \sum_{ij} \alpha^{(i)} (\alpha^{(j)})^\star e^{-i(E_i - E_j)t} \int \Phi_j^\star(1,2) \Phi_i^\star(1',2)\, d\mathbf{r}_2. \tag{A.2}$$

Using the variational functions given by Eq. (20) and Eqs. (15)–(17) and (19), the reduced density operator takes the form

$$\rho_s^{\mathrm{red}}(\mathbf{r}_1,\mathbf{r}_1',t) = \sum_{ij} \alpha^{(i)}(\alpha^{(j)})^\star e^{-i(E_i^{\mathrm{var}}-E_j^{\mathrm{var}})t} \sum_{n_1,n_2,\nu_1,\nu_2} \sum_{l=0}^{\min(n_2,\nu_2)} c^{(i)}_{n_1 n_2 l}\,(c^{(j)}_{\nu_1\nu_2 L})^\star$$

$$\times \mathcal{I}_{\{n_1,n_2,\nu_1,\nu_2\}}(r_1,r_1')\frac{1}{(2l+1)}\sum_{m=-l}^{l} Y_{l\,m}(\Omega_1)Y^\star_{lm}(\Omega_1'), \tag{A.3}$$

where

$$\mathcal{I}_{\{n_1,n_2,\nu_1,\nu_2\}}(r_1,r_1') = g(n_1|n_2)g(\nu_1|\nu_2) \times [f_{\nu_1}(r_1')(\langle n_2|\nu_2\rangle f_{n_1}(r_1) + \langle n_1|\nu_2\rangle f_{n_2}(r_1))$$

$$+ f_{\nu_2}(r_1')(\langle n_2|\nu_1\rangle f_{n_1}(r_1) + \langle n_1|\nu_1\rangle f_{n_2}(r_1))], \tag{A.4}$$

$$g(n_1|n_2) = \frac{1}{[2(1+\langle n_1|n_2\rangle^2)]^{1/2}}. \tag{A.5}$$

Diagonalizing the reduced density operator, we get the eigenfunctions $\varphi_\nu(\mathbf{r}_1,t)$, i.e. the φ's are the solutions of

$$\int_{-\infty}^{\infty} \rho_s^{\mathrm{red}}(\mathbf{r}_1,\mathbf{r}_1',t)\varphi_\nu(\mathbf{r}_1',t)\,d\mathbf{r}_1' = \Lambda_\nu(t)\varphi_\nu(\mathbf{r}_1,t) \tag{A.6}$$

with eigenvalues $\Lambda_\nu(t)$.

To solve the eigenvalue problem of Eq. (A.6), the functions $\varphi_\nu(\mathbf{r}_1,t)$ can be expanded as

$$\varphi_\nu(\mathbf{r}_1,t) = \sum_{nlm} \kappa^{(\nu)}_{nlm}(t) f_n(r_1) Y_{lm}(\Omega_1), \tag{A.7}$$

where the functions f_n are defined in Eq. (19). Introducing the expansion (A.7) in the Eq. (A.6) transforms the integral eigenvalue problem of Eq. (24) to an algebraic one

$$\sum_{n_1 l_1 m_1} \mathcal{A}^{nlm}_{n_1 l_1 m_1}\;\kappa^{(\nu)}_{n_1 l_1 m_1} = \lambda_\nu(t) \sum_{n_1 l_1 m_1} \mathcal{M}^{nlm}_{n_1 l_1 m_1}\;\kappa^{(\nu)}_{n_1 l_1 m_1}, \tag{A.8}$$

where

$$\mathcal{M}^{nlm}_{n_1 l_1 m_1} = \langle n_1|n\rangle \delta_{ll_1}\delta_{mm_1} \tag{A.9}$$

(the $\langle n_1|n\rangle$ are defined in Eq. (18)), and

$$\mathcal{A}^{nlm}_{n'l'm'} = \int f_n(r_1) Y^\star_{lm}(\Omega_1)\,\rho^{\mathrm{red}}(\mathbf{r}_1,\mathbf{r}_1',t) f_{n'}(r_1') Y_{l'm'}(\Omega_1')\,d\mathbf{r}_1\,d\mathbf{r}_1'. \tag{A.10}$$

The expansion of Eq. (A.7) has the advantage that the coefficients $\mathcal{A}^{nlm}_{n'l'm'}$ in Eq. (A.10) can be obtained in terms of matrix elements already calculated to obtain the coefficients $c^{(i)}_{n_1 n_2 l}$.

A useful quantity, which will help us understand the behavior of the entanglement, is the Coulombic repulsion between the two electrons

$$\left\langle \frac{1}{r_{12}} \right\rangle = \left\langle \Psi \left| \frac{1}{r_{12}} \right| \Psi \right\rangle . \tag{A.11}$$

In terms of the quantities introduced above, the Coulombic repulsion can be written as

$$\begin{aligned} \left\langle \frac{1}{r_{12}} \right\rangle &= \sum_{ij} \alpha^{(i)} (\alpha^{(j)})^{\star} e^{-i(E_i - E_j)t} \\ &\quad \times \sum_{n_1, n_2, \nu_1, \nu_2, l, l'} c^{(i)}_{n_1 n_2 l} \, (c^{(j)}_{\nu_1 \nu_2 l'})^{\star} \left\langle n_1', n_2'; l' \left| \frac{1}{r_{12}} \right| n_1, n_2; l \right\rangle . \end{aligned} \tag{A.12}$$

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