

# Dynamics of Entanglement for Two-Electron Atoms

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## Abstract

We studied the dynamics of the entanglement for two electron atoms as a "bipartite" quantum system with continuous degrees of freedom. We analyze in particular the time evolution of initial states created from a superposition of the eigenstates of the two-electron Hamiltonian with variable nuclear charge  $Z$ . We find that the pairwise entanglement for the two electrons propagate in a way that is proportional to the time evolution of the Coulombic interaction between the two electrons. Thus connecting the entanglement of the two-electron atoms to a physical quantity, the electron-electron interaction.

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## I. INTRODUCTION

The study of quantum entanglement for systems with continuous degrees of freedom possess a number of *extra* problems when they are compared with systems with discrete degrees of freedom. One particularly acute 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 [1]. Moreover, at least for two spin-1/2 distinguishable particles there is an evaluable *formula*[2] to calculate the entanglement of formation [3], 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 very reduced number of exact solution for problems involving two particles with continuous degrees of freedom. Systems with discrete levels are the likely arena for quantum computing [4] and continuous variable states can be used as a nonclassical resource for quantum computation and quantum communication [5]. In particular it would be interesting to study a "bipartite" model taking into account the interaction between the two particles subject to an external field.

There is a number of entanglement measures [6] used to quantify the nonseparability of an arbitrary quantum state. For continuous degrees of freedom the Jaynes and Shannon entropies have been used to study a two-electron artificial atom [7], and the von Neumann entropy to study the dynamics of entanglement between two trapped atoms [8]. Recently, the influence of the quantum statistics on the definition of the entanglement has begun to be noticed and discussed by several authors [9–17]. In particular Schliemann et. al. [10] characterized and classified quantum correlations in two-fermion systems having  $2K$  single-particle states. For pure states they introduced the Slater decomposition and rank i.e., they decomposed the state into a combination of elementary Slater determinants formed by pairs of mutually orthogonal single-particle states. Gittings and Fisher[13] shows that Von Neumann entropy of the reduced density matrix of one half of the system can be used as entanglement measure for the case of indistinguishable particles. More recently, Bester et. al. [18] used the Von Neumann entropy for entanglement engineering in dot molecules.

We shall study the dynamics of the entanglement for a "bipartite" quantum system with continuous degrees of freedom. The "bipartite" quantum system consists of two electrons interacting with each other and with a fixed center. The Hamiltonian for the system is given

by

$$H = h(1) + h(2) + \lambda V, \quad (1)$$

where

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

$p_i$  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. We shall concentrate 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?

We shall use the von Neumann entropy as the entanglement measure[10, 13, 14, 18] for the two-electrons system. For *pure* states the von Neumann entropy is a good entanglement measure [6] since that, under appropriate conditions, all entanglement measures coincide on pure bipartite states and are equal to the von Neumann entropy of the corresponding reduced operator. The von Neumann entropy for two-electron atoms is given by

$$S = -\text{tr}(\hat{\rho}^{\text{red}} \log \hat{\rho}^{\text{red}}), \quad (3)$$

where the reduced density operator is[19, 20]

$$\hat{\rho}^{\text{red}}(\mathbf{r}_1, \mathbf{r}'_1, t) = \text{tr}_2 |\Psi\rangle \langle \Psi|, \quad (4)$$

here the trace is taken over one electron, and  $|\Psi\rangle$  is the total two-electron wave function. This approach gives the same results for the entanglement if one take the two electron atom in  $2m$ -dimensional spin-orbital basis set and calculate entanglement based on the generalized Slater decomposition method[13] for indistinguishable particles.

The paper is organized as follows: In Section II 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 the density matrix  $|\Psi\rangle \langle \Psi|$  and the reduced density operator  $\hat{\rho}^{\text{red}}$  in Section III. Then, the eigenvalue problem for the reduced density operator is solved and the von Neumann entropy is calculated using these eigenvalues. finally, in Section IV the results and conclusions are presented.

## II. SOLUTION OF THE SCHRÖDINGER EQUATION

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

$$H |\Psi(1, 2)\rangle = E |\Psi(1, 2)\rangle , \quad (5)$$

where  $H$  is the Hamiltonian given in Eq. (1). This equation can be solved by using the Rayleigh-Ritz variational approximation with nonorthogonal basis functions [21]. Using a set of variational eigenfunctions  $|\psi_i(1, 2)\rangle$ , the eigenvalue problem of Eq. (5) can be recast as an algebraic generalized eigenvalue one of the form

$$H^{(N)} \mathbf{c}^{(i)} = E_i \mathcal{M} \mathbf{c}^{(i)} , \quad (6)$$

with

$$(H^{(N)})_{kj} = \langle k | H | j \rangle , \quad \mathcal{M}_{kj} = \langle k | j \rangle , \quad (7)$$

and the functions  $|\psi_i\rangle$  and the coefficients  $\mathbf{c}^{(i)}$  are related by

$$|\psi_i(1, 2)\rangle = \sum_{j=1}^M c_j^{(i)} |j\rangle , \quad c_j^{(i)} = (\mathbf{c}^{(i)})_j . \quad (8)$$

The  $E_i, i = 1, \dots, N$  are the variational eigenvalues such that  $E_i \leq 0$ , it is obvious that in most cases  $N \ll M$ . The  $M$  functions  $|j\rangle$  must be chosen in such a way that they form a complete basis for the problem. So, for any initial condition  $|\Psi_0(1, 2)\rangle$  of the two-electron problem the time dependent wave function is given by

$$|\Psi\rangle = \sum_j \alpha_j e^{-iE_j t} |\psi_j(1, 2)\rangle , \quad (9)$$

where  $\alpha_j = \langle \Psi_0(1, 2) | \psi_j(1, 2) \rangle$ . Note that the basis  $\{|j\rangle\}$  is not orthonormal, *i.e.*  $\mathcal{M}_{kj} = \langle k | j \rangle \neq \delta_{ij}$ . The approximate eigenfunctions  $|\psi_j(1, 2)\rangle$  and eigenvalues  $E_i$  can be obtained more accurately taking  $M$  as large as possible. There are some practical issues that limit the number of functions in the basis, in particular as the basis is not orthonormal  $\det \mathcal{M}$  goes to zero when the number of functions in the basis is increased, making the inversion of  $\mathcal{M}$  an ill posed problem.

Since the Hamiltonian is spin independent, for the sake of simplicity we restricted our investigation to the study of singlet states with zero total angular momentum, so the  $|j\rangle$ 's are given by

$$|j\rangle \equiv |n_1, n_2; l\rangle = (\phi_{n_1}(r_1) \phi_{n_2}(r_2))_s \mathcal{Y}_{0,0}^l(\Omega_1, \Omega_2) , \quad (10)$$

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

$$\mathcal{Y}_{0,0}^l(\Omega_1, \Omega_2) = \frac{(-1)^l}{\sqrt{2l+1}} \sum_{m=-l}^l (-1)^m Y_{lm}(\Omega_1) Y_{l-m}(\Omega_2), \quad (11)$$

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

$$(\phi_{n_1}(r_1)\phi_{n_2}(r_2))_s = \frac{\phi_{n_1}(r_1)\phi_{n_2}(r_2) + \phi_{n_1}(r_2)\phi_{n_2}(r_1)}{[2(1 + \langle n_1|n_2 \rangle^2)]^{1/2}} \quad (12)$$

where

$$\langle n_1|n_2 \rangle = \int_0^\infty r^2 \phi_{n_1}(r)\phi_{n_2}(r) dr, \quad (13)$$

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

$$\phi_n(r) = \left[ \frac{\alpha^{2n+3}}{(2n+2)!} \right]^{1/2} r^n e^{-\alpha r/2}. \quad (14)$$

It is clear that in terms of the functions defined in Eq. (10) the variational eigenfunctions reads as

$$|\psi_i(1, 2)\rangle = \sum_{n_1 n_2 l} c_{n_1 n_2 l}^{(i)} |n_1, n_2; l\rangle. \quad (15)$$

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 reference [22].

### III. THE REDUCED DENSITY OPERATOR

The wave function  $|\Psi\rangle$ , Eq. (9) can be used to obtain the reduced density operator defined in Eq. (4). Using the variational functions given by Eq. (15) and Eqs. (10), (11), (12), (14), the reduced density operator takes the form

$$\begin{aligned} \rho^{\text{red}}(\mathbf{r}_1, \mathbf{r}'_1, t) = & \sum_{ij} \alpha^{(i)} (\alpha^{(j)})^* e^{-i(E_i - E_j)t} \sum_{n_1, n_2, \nu_1, \nu_2} \sum_{l=0}^{\min(n_2, \nu_2)} c_{n_1 n_2 l}^{(i)} (c_{\nu_1 \nu_2 l}^{(j)})^* \mathcal{I}_{\{n_1, n_2, \nu_1, \nu_2\}}(r_1, r'_1) \times \\ & \frac{1}{(2l+1)} \sum_{m=-l}^l Y_{lm}(\Omega_1) Y_{lm}^*(\Omega'_1), \end{aligned} \quad (16)$$

where

$$\begin{aligned} \mathcal{I}_{\{n_1, n_2, \nu_1, \nu_2\}}(r_1, r'_1) = & g(n_1|n_2)g(\nu_1|\nu_2) \times [\phi_{\nu_1}(r'_1) (\langle n_2|\nu_2 \rangle \phi_{n_1}(r_1) + \langle n_1|\nu_2 \rangle \phi_{n_2}(r_1)) + \\ & \phi_{\nu_2}(r'_1) (\langle n_2|\nu_1 \rangle \phi_{n_1}(r_1) + \langle n_1|\nu_1 \rangle \phi_{n_2}(r_1))] , \end{aligned} \quad (17)$$

and

$$g(n_1|n_2) = \frac{1}{[2(1 + \langle n_1|n_2 \rangle^2)]^{1/2}}. \quad (18)$$

Diagonalizing the reduced density operator we get the eigenfunctions  $\varphi_\nu(\mathbf{r}_1, t)$  which are solutions of

$$\int_{-\infty}^{\infty} \rho^{\text{red}}(\mathbf{r}_1, \mathbf{r}'_1, t) \varphi_\nu(\mathbf{r}'_1, t) d\mathbf{r}'_1 = \lambda_\nu(t) \varphi_\nu(\mathbf{r}_1, t) \quad (19)$$

with eigenvalues  $\lambda_\nu(t)$ . In terms of the  $\lambda_\nu(t)$  the von Neumann entropy can be calculated as

$$S(t) = - \sum_{\nu=0}^{\infty} \lambda_\nu(t) \log \lambda_\nu(t). \quad (20)$$

To solve the eigenvalue problem of Eq. (19), the functions  $\varphi_\nu(\mathbf{r}_1, t)$  can be expanded as

$$\varphi_\nu(\mathbf{r}_1, t) = \sum_{nlm} \kappa_{nlm}^{(\nu)}(t) \phi_n(r_1) Y_{lm}(\Omega_1), \quad (21)$$

which reduces the integral eigenvalue problem of Eq. (19) to an algebraic one

$$\sum_{n_1 l_1 m_1} \mathcal{A}_{n_1 l_1 m_1}^{nlm} \kappa_{n_1 l_1 m_1}^{(\nu)} = \lambda_\nu(t) \sum_{n_1 l_1 m_1} \mathcal{M}_{n_1 l_1 m_1}^{nlm} \kappa_{n_1 l_1 m_1}^{(\nu)}, \quad (22)$$

where

$$\mathcal{M}_{n_1 l_1 m_1}^{nlm} = \langle n_1 | n \rangle \delta_{l_1 l} \delta_{m_1 m} \quad (23)$$

(the  $\langle n_1 | n \rangle$  are defined in Eq. (13)), and

$$\mathcal{A}_{n' l' m'}^{nlm} = \int \phi_n(r_1) Y_{lm}^*(\Omega_1) \rho^{\text{red}}(\mathbf{r}_1, \mathbf{r}'_1, t) \phi_{n'}(r'_1) Y_{l'm'}(\Omega'_1) d\mathbf{r}_1 d\mathbf{r}'_1. \quad (24)$$

The expansion of Eq. (21) has the advantage that the coefficients  $\mathcal{A}_{n' l' m'}^{nlm}$  in Eq. (24) can be obtained in terms of matrix elements already calculated to get the coefficients  $c_{n_1 n_2 l}^{(i)}$ .

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

$$\left\langle \frac{1}{r_{12}} \right\rangle = \left\langle \Psi \left| \frac{1}{r_{12}} \right| \Psi \right\rangle. \quad (25)$$

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

$$\left\langle \frac{1}{r_{12}} \right\rangle = \sum_{ij} \alpha^{(i)} (\alpha^{(j)})^* e^{-i(E_i - E_j)t} \sum_{n_1, n_2, \nu_1, \nu_2, l, l'} c_{n_1 n_2 l}^{(i)} (c_{\nu_1 \nu_2 l'}^{(j)})^* \left\langle n'_1, n'_2; l' \left| \frac{1}{r_{12}} \right| n_1, n_2; l \right\rangle \quad (26)$$

The relation between the entanglement, measured by von Neumann entropy, and the Coulombic repulsion between the two electrons can be qualitatively shown to be linear. Using Hellmann-Feynman theorem for the two-electron Hamiltonian, Eq. (1),

$$\frac{dE}{d\lambda} = \left\langle \Psi \left| \frac{1}{r_{12}} \right| \Psi \right\rangle. \quad (27)$$

Recently, in analogy with first order phase transition in classical statistical mechanics[23], we have shown that the ground state energy for two electron atoms  $E$  bends sharply at the transition point  $\lambda_c = \frac{1}{Z_c} = 1.0971$ , this leads to discontinuity of the first derivative of the energy with respect to  $\lambda$ . Thus the behavior of ground state energy as a function of  $\lambda$  resemble a "first-order phase transition" [24]. At the critical point, the ground state energy becomes degenerate with the hydrogenic threshold. The Shannon-information entropy develops a step-like discontinuity at  $\lambda_c$ . Further analysis indicate that the entropy as a function of  $\lambda$  is proportional to the first derivative of the energy with respect to  $\lambda$ [25, 26]. Since  $\frac{dE}{d\lambda}$  is proportional to "negative entropy", we expect a linear relation between the entanglement and the Coulombic repulsion between the two electrons.

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 momentum, *i.e* to singlet states. A rather natural choice are the eigenstates of the Hamiltonian in Eq. (5) with a *charge different to the one used during the time evolution of the system*. As we shall see the "collisions" between the electrons allows a direct interpretation of the time evolution of the entanglement. The collisions are signaled by local maxima of the Coulombic repulsion.

#### IV. RESULTS AND CONCLUSIONS

In this section we present the numerical results showing the time evolution of the entanglement for different initial conditions, in all cases the time evolution corresponds to the two-electron atom with the nuclear charge  $Z = 2$ .

Figure (1) 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

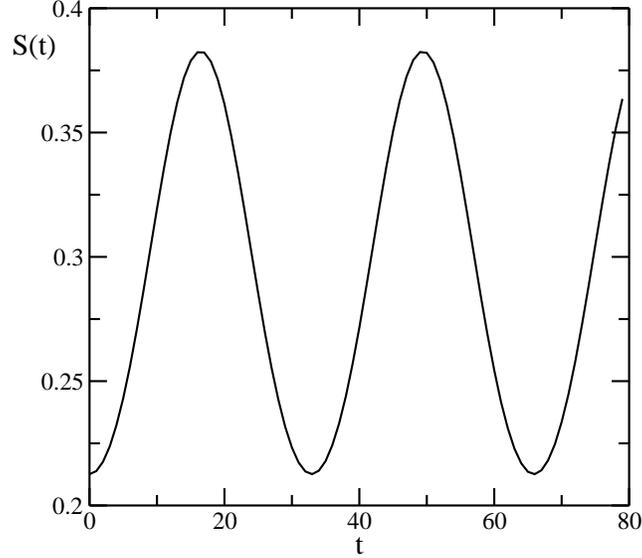


FIG. 1: Time evolution of the von Neumann entropy as a function of time. The initial condition for the wave function is the ground state wave function corresponding to the nuclear charge  $Z = 2$ .

Figure (2) 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  $\langle \frac{1}{r_{12}} \rangle$ .

It is clear that the local maxima of the entanglement corresponds to the local minima of the Coulombic repulsion and vice versa. Since for the initial condition 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 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 figure (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 evolution of the entanglement shown in Figure (3) which correspond to the time evolution of the ground state of an atom with initial condition corresponds to  $Z = 3$ . As in Figure (2) 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  $\langle \frac{1}{r_{12}} \rangle$ . In Figure (4) we show the time evolution of the entanglement for the second excited state with zero total angular momentum.

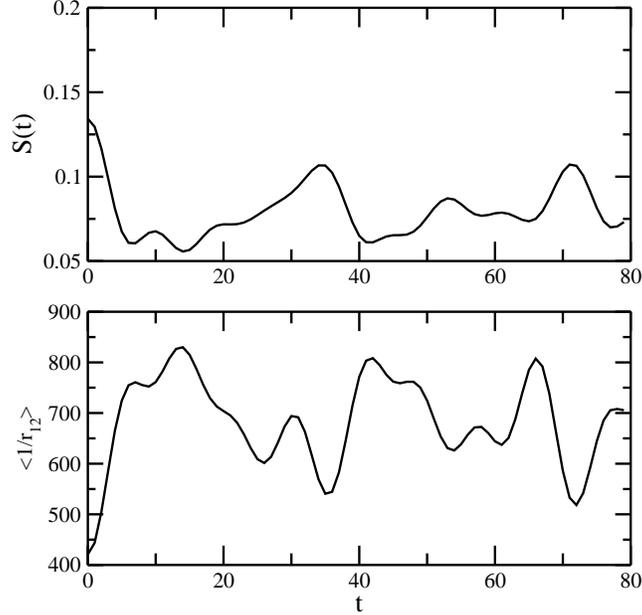


FIG. 2: Time evolution of the von Neumann entropy (upper graph) and the Coulombic repulsion between the electrons (lower graph). The initial condition for the wave function is the ground state wave function corresponding to the nuclear charge  $Z = 1.2$

Figures (1)-(4), obtained by using  $M = 165$  functions  $|n_1, n_2; l\rangle$ . The value of  $M$  is obtained by performing the following sum

$$\sum_{n_1=0}^8 \sum_{n_2 \leq n_1} \sum_{l \leq n_2} 1 = 165.$$

Since our solution is only an approximate one, it is necessary to check its validity. In Figure (5) we show the time evolution of the ground state corresponding to  $Z = 1.2$  for  $M = 165$  and  $M = 286$  (which corresponds to  $n_1 = 10$ ). 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.

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

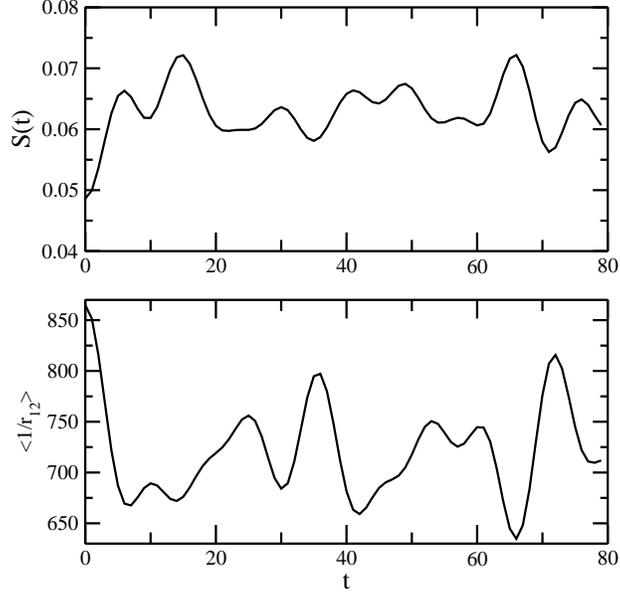


FIG. 3: Time evolution of the von Neumann entropy (upper graph) and the Coulombic repulsion between the electrons (lower graph) . The initial condition for the wave function is the ground state function corresponding to the nuclear charge  $Z = 3$

precise relationship between the entanglement and the bounds of the Coulombic will be the subject of future study.

Since the seminal paper of Osterloh *et al* [1] there has been increasing interest in studying the scaling properties of the entanglement of system near a critical point. The two-electron atom exhibit a critical point for the ground state energy and a another for the second excited state. In this context critical means the value of the nuclear charge  $Z$  where a bound state becomes absorbed or degenerates with the continuum[23]. Finite size scaling method has been used to calculate critical parameters for atomic and molecular systems [27] and scaling of entanglement at quantum phase transition for two-dimensional array of quantum dots[15, 16]. Work is in progress using the finite size scaling method to examine the scaling of entanglement for two-electron systems in the neighborhood of the critical nuclear charges.

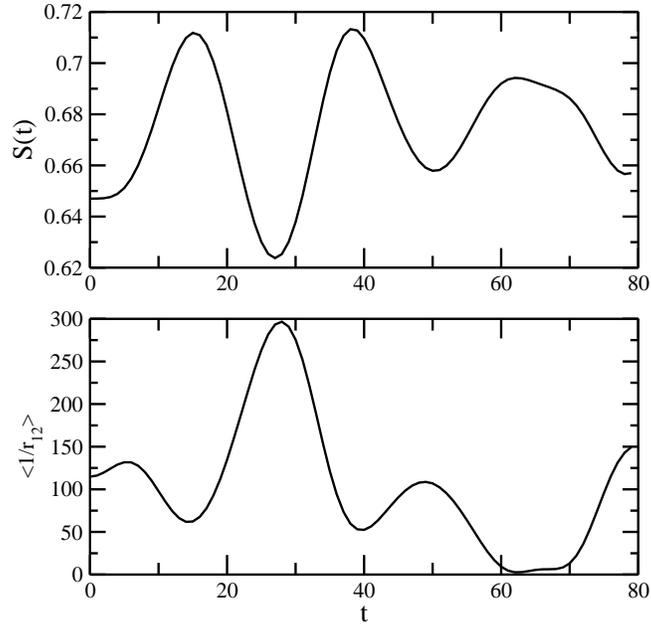


FIG. 4: Time evolution of the von Neumann entropy (upper graph and the Coulombic repulsion between the electrons (lower graph) . The initial condition for the wave function is the second excited state function  $c$

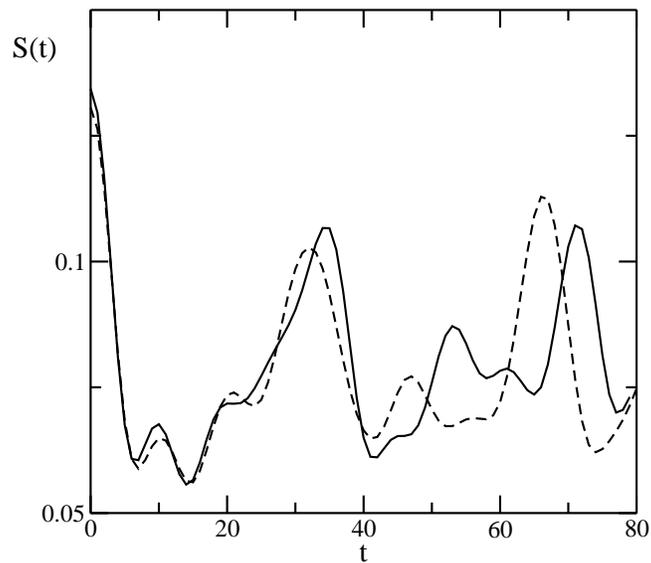


FIG. 5: Time evolution of the von Neumann entropy. The initial condition for the wave function is the ground state function corresponding to the nuclear charge  $Z = 1.2$ . The solid line corresponds to 165 basis set functions and the dashed line to 286 basis set functions, respectively

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