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Entanglement and electron correlation in quantum chemistry calculations

Z. HUANG, H. WANG and S. KAIS*
Department of Chemistry, Purdue University,
West Lafayette, IN 47907

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Electron–electron correlation in quantum chemistry calculations can be analysed in terms of entanglement between electrons. Two exactly solvable models: two fixed spin-1/2 particles and two-electron two-site Hubbard model are used to define and discuss the entanglement as a function of the system parameters. *Ab initio* configuration interaction calculation for entanglement is presented for the H_2 molecule. Qualitatively, entanglement and electron–electron correlation have similar behaviour. Thus, entanglement might be used as an alternative measure of electron correlation in quantum chemistry calculations.

1. Introduction

Ever since the appearance of the famous Einstein, Podolsky and Rosen (EPR) paper [1], the phenomenon of entanglement [2], which features the essential difference between classical and quantum physics [3], has received wide theoretical and experimental attention [3–10]. Generally speaking, if two particles are in an entangled state, then even if the particles are physically separated by a great distance, they behave in some respect as a single entity rather than as two separate entities. There is no doubt that entanglement lies at the heart of the foundation of quantum mechanics.

Recently a desire to understand quantum entanglement has been fuelled by the development of quantum computation, which started in the 1980s with the pioneering work of Benioff [11], Bennett [12], Deutsch [13], Feynman [14] and Landauer [16] but gathered momentum and increased research interest only after Peter Shor's revolutionary discovery [15] of a quantum algorithm in 1994 that would efficiently find the prime factors of composite integers [17, 18]. Besides quantum computations, entanglement has also been the core of much other active research such as quantum teleportation [19, 20], dense coding [21, 22], quantum communication [23], quantum cryptography [24] and decohernce in quantum computers [25–27].

Generally, the strict definitions of the four most prominent entanglement measures can be summarized as follows [28]: (1) entanglement of distillation E_D;

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*Corresponding author. Email: kais@purdue.edu

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(2) entanglement of cost E_C; (3) entanglement of formation E_F; and finally (4) relative entropy of entanglement E_R. At the current time, there is no simple way to carry out calculations with all these entanglement measures. However, for the case where both subsystems A and B are spin-1/2 particles, there exists a simple formula from which the entanglement of formation can be calculated [29]. In this case the entanglement of formation is given in terms of another entanglement measure, the concurrence C [29–31]. The concurrence varies from $C=0$ for a separable state to $C=1$ for a maximally entangled state.The entanglement of formation varies monotonically with the concurrence.

Entanglement is a quantum mechanical property that describes a correlation between quantum systems that has no classical analogue [32–35]. Thus, it might be useful as an alternative measure of electron–electron correlation in quantum chemistry calculations. In quantum chemistry calculations, the correlation energy is defined as the energy error of the Hartree–Fock wave function, i.e. the difference between the Hartree–Fock limit energy and the exact solution of the nonrelativistic Schrödinger equation [36]. There also exists other measures of electron correlation in the literature such as the statistical correlation coefficients [37] and more recently the Shannon entropy as a measure of the correlation strength [38–42]. Electron correlations have a strong influence on many atomic, molecular [43], and solid properties [44]. The concept of electron correlation as defined in quantum chemistry calculations is useful but not directly observable, i.e. there is no operator in quantum mechanics such that its measurement gives the correlation energy. Moreover, there are cases where the kinetic energy dominates the Coulomb repulsion between electrons, and the electron correlation alone fails as a correlation measure [40].

In this paper, we discuss the use of the entanglement as a measure of the electron correlation for molecular systems. Besides the theoretical calculations of the entanglement, people have suggested experimental measure of many-fermion entanglement [45], a set of circuits that can measure a few qubits entanglement for pure states has also been proposed [46]. Also, people have developed ideas of observable-based distinguished subspace entanglement [47] and entanglement based on the Lie-algebraic measure of purity of a quantum state [48]. So it seems that entanglement will be a measurable physical quantity, just like energy and the other physical properties of a system. In the next section we discuss the entanglement for two-spin systems as a simple model to understand the entanglement for the H_2 molecule. In section 3, we present detailed entanglement calculations for the two-electron two-site Hubbard model. In section 4, we generalize the Hubbard model to two-site three-electrons. Finally we give *ab initio* configuration interaction calculations for entanglement of two-electron systems.

2. Entanglement for two-spin systems: a model for H_2 molecule

To understand entanglement for two-electron diatomic molecules, we start by calculating entanglement for a simpler two-spin model system. This is a model of two spin-(1/2) electrons with an exchange coupling constant J (a.u.) in an effective transverse magnetic field of strength B (a.u.). The general Hamiltonian for such a system is given by [49]

$$H = -\frac{J}{2}(1+\gamma)\sigma_1^x \otimes \sigma_2^x - \frac{J}{2}(1-\gamma)\sigma_1^y \otimes \sigma_2^y - B\sigma_1^z \otimes I_2 - BI_1 \otimes \sigma_2^z, \tag{1}$$

where σ^a are the Pauli matrices ($a = x, y, z$) and γ is the degree of anisotropy. For $\gamma = 1$ equation (1) reduces to the Ising model, whereas for $\gamma = 0$ it is the XY model.

This model admits an exact solution, which is simply a (4×4) matrix of the form,

$$H = \begin{pmatrix} -2B & 0 & 0 & -J\gamma \\ 0 & 0 & -J & 0 \\ 0 & -J & 0 & 0 \\ -J\gamma & 0 & 0 & 2B \end{pmatrix}, \tag{2}$$

with the following four eigenvalues

$$\lambda_1 = -J, \quad \lambda_2 = J, \quad \lambda_3 = -\sqrt{4B^2 + J^2\gamma^2}, \quad \lambda_4 = \sqrt{4B^2 + J^2\gamma^2} \tag{3}$$

and the corresponding eigenvectors in the basis set $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$, can be written as [49]

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle), \tag{4}$$

$$|\phi_2\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle), \tag{5}$$

$$|\phi_3\rangle = \sqrt{\frac{\alpha - 2B}{2\alpha}}|\downarrow\downarrow\rangle + \sqrt{\frac{\alpha + 2B}{2\alpha}}|\uparrow\uparrow\rangle, \tag{6}$$

$$|\phi_4\rangle = \sqrt{\frac{\alpha + 2B}{2\alpha}}|\downarrow\downarrow\rangle - \sqrt{\frac{\alpha - 2B}{2\alpha}}|\uparrow\uparrow\rangle, \tag{7}$$

where $\alpha = \sqrt{4B^2 + J^2\gamma^2}$.

Now we confine our interest to the calculation of the entanglement between the two spins. For simplicity we take $\gamma = 1$, equation (1) reduces to the Ising model with the ground state energy λ_3 and the corresponding eigenvector $|\phi_3\rangle$. All the information needed for quantifying the entanglement in this case is contained in the reduced density matrix $\rho(i, j)$. Wootters [29, 30] has shown, for a pair of binary qubits, that the concurrence C, which goes from 0 to 1, can be taken as a measure of entanglement. The concurrence between sites i and j is defined as [29]

$$C(\rho) = \max\{0, \epsilon_1 - \epsilon_2 - \epsilon_3 - \epsilon_4\}, \tag{8}$$

where the ϵ_i are the eigenvalues of the Hermitian matrix $R \equiv \sqrt{\sqrt{\rho}\,\tilde{\rho}\,\sqrt{\rho}}$. The spin flipped state $\tilde{\rho}$, for a general state ρ of two qubits, is given by

$$\tilde{\rho} = (\sigma_y \otimes \sigma_y)\,\rho^\star\,(\sigma_y \otimes \sigma_y), \tag{9}$$

where the $\rho^\star$ is the complex conjugate of ρ and is taken in the standard basis [29], which for a pair of spin-(1/2) particles is $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$.

For our model system in the ground state $|\phi_3\rangle$, the density matrix in the basis set$(\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow)$ is given by

$$\rho = \begin{pmatrix} \frac{\alpha + 2B}{2\alpha} & 0 & 0 & \sqrt{\frac{\alpha^2 - 4B^2}{4\alpha^2}} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \sqrt{\frac{\alpha^2 - 4B^2}{4\alpha^2}} & 0 & 0 & \frac{\alpha + 2B}{2\alpha} \end{pmatrix}. \tag{10}$$

The eigenvalues of the Hermitian matrix R can be calculated analytically. We obtained $\epsilon_2 = \epsilon_3 = \epsilon_4 = 0$ and therefore,

$$C(\rho) = \epsilon_1 = \sqrt{\frac{\lambda^2}{4 + \lambda^2}}, \tag{11}$$

where $\lambda = J/B$. Entanglement is a monotonically increasing function of the concurrence and is given by

$$E(C) = h(y) = -y\log_2 y \;-\; (1 - y)\log_2(1 - y); \quad y = \frac{1}{2} + \frac{1}{2}\sqrt{1 - C^2}. \tag{12}$$

Substituting the value of the concurrence C, equation (11), gives

$$E = -\frac{1}{2}\log_2\left(\frac{1}{4} - \frac{1}{4 + \lambda^2}\right) + \frac{1}{\sqrt{4 + \lambda^2}}\log_2\frac{\sqrt{4 + \lambda^2} - 2}{\sqrt{4 + \lambda^2} + 2}. \tag{13}$$

This result for entanglement is equivalent to the von Neumann entropy [49] of the reduced density matrix ρ_A. For our model system of the form AB in the ground state $|\phi_3\rangle$, the reduced density matrix $\rho_A = Tr_B(\rho_{AB})$ in the basis set$(\uparrow, \downarrow)$ is given by

$$\rho_A = \begin{pmatrix} \frac{\alpha + 2B}{2\alpha} & 0 \\ 0 & \frac{\alpha - 2B}{2\alpha} \end{pmatrix}. \tag{14}$$

When a bipartite quantum system AB is in a pure state there is essentially a unique measure of the entanglement between the subsystems A and B given by the von Neumann entropy $S \equiv -Tr[\rho_A \log_2 \rho_A]$. This approach gives exactly the same formula as the one given in equation (13).

This simple model can be used to examine the entanglement for two electron diatomic molecules. The value of J, the exchange coupling constant between the spins of the two electrons, can be calculated as half the energy difference between the lowest singlet and triplet states of the hydrogen molecule.

Herring and Flicker have shown [50] that J for H_2 molecule can be approximated as a function of the interatomic distance R. In atomic units, the expression for large R is given by

$$J(R) = -0.821\ R^{5/2}e^{-2R} + O(R^2e^{-2R}). \tag{15}$$

Figure 1 shows the calculated concurrence $C(\rho)$ as a function of the distance between the two electronic spins R, using $J(R)$ of equation (15), for different values of the magnetic field strength B. At the limit $R \to \infty$ the exchange interaction J vanishes as a result the two electronic spins are up and the wave function is factorizable, i.e. the concurrence is zero. At the other limit, when $R = 0$ the concurrence or the entanglement is zero for this model because $J = 0$. As R increases, the exchange interaction increases leading to increasing concurrence between the two electronic spins. However this increase in the concurrence reaches a maximum limit as shown in the figure. For large distance, the exchange interaction decreases exponentially with R and thus the decrease of the concurrence. Figure 1 also shows that the concurrence increases with decreasing the magnetic field strength. This can be attributed to effectively increasing the exchange interaction. This behaviour of the concurrence as a function of the internuclear

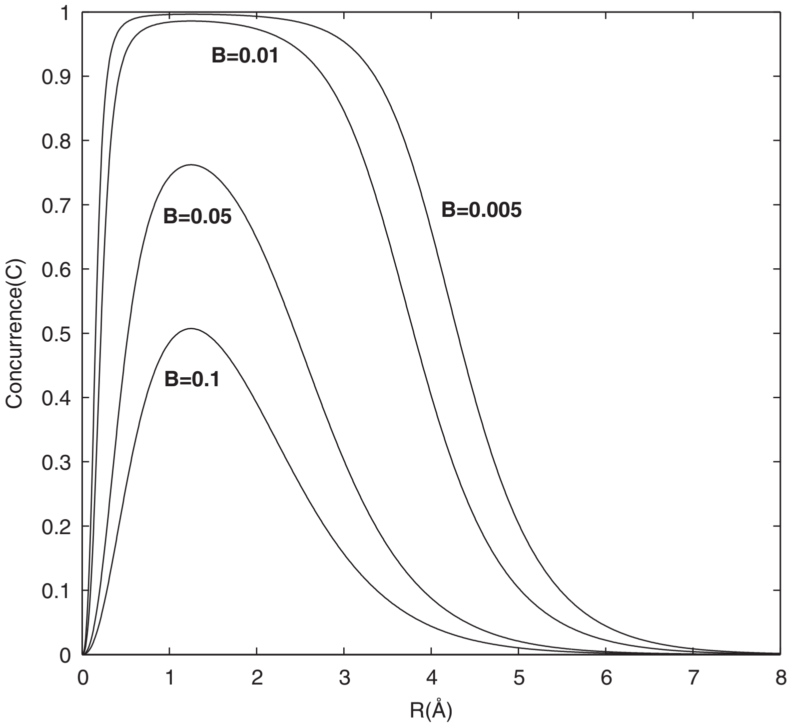

Figure 1. The concurrence (C) as a function of the distance R between the two spins for different values of the magnetic field strength B.

distance R is typical for two-electron diatomic molecules. We will show later in section 5 that by using accurate *ab initio* calculations we essentially obtained the same curve for entanglement for the H_2 molecule as a function of the internuclear distance R.

3. Two-electron two-sites Hubbard model

Many-electron systems such as molecules and quantum dots show the complex phenomena of electron correlation caused by the Coulomb interaction. This phenomena can be described to some extent by the Hubbard model [51]. This is a simple model, capture the main physics of the problem and admits an exact solution in some special cases. To calculate the entanglement for electrons described by this model we will use the Zanardi's measure, which is given in Fock space as the von Neumann entropy [52].

3.1 *Exact solution*

The Hamiltonian of the two-electron two-site Hubbard model can be written as

$$H = -\frac{t}{2}\sum_{i,\sigma} c^{\dagger}_{i\sigma} c_{\bar{i}\sigma} + 2U\sum_{i} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}, \tag{16}$$

where $c^{\dagger}_{i\sigma}$ and $c_{i\sigma}$ are the Fermi creation and annihilation operators at site i and with spin $\sigma = \uparrow, \downarrow$ and $\hat{n}_{i\sigma=c^{\dagger}_{i\sigma}c_{i\sigma}}$ is the spin-dependent occupancy operator at site i. For two-site system $i = 1$ and 2, $\bar{i} = 3 - i$, $(t/2)$ is the hopping term of different site and $2U$ is the on-site interaction($U > 0$ for repulsion in our case). The factors $t/2$ and $2U$ are chosen to make the following expressions for eigenvalues and eigenvectors as simple as possible. This Hamiltonian can be solved exactly in the basis set $|1\uparrow, 1\downarrow, 2\uparrow, 2\downarrow\rangle$, it is simply a (4×4) matrix of the form

$$H = \begin{pmatrix} 2U & -\frac{t}{2} & -\frac{t}{2} & 0 \\ -\frac{t}{2} & 0 & 0 & -\frac{t}{2} \\ -\frac{t}{2} & 0 & 0 & -\frac{t}{2} \\ 0 & -\frac{t}{2} & -\frac{t}{2} & 2U \end{pmatrix}, \tag{17}$$

with the following four eigenvalues and eigenvectors

$$\lambda_1 = U - \sqrt{t^2 + U^2}, \quad \lambda_2 = 0, \quad \lambda_3 = 2U, \quad \lambda_4 = U + \sqrt{t^2 + U^2} \tag{18}$$

and the corresponding eigenvectors

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ x+\sqrt{1+x^2} \\ x+\sqrt{1+x^2} \\ 1 \end{pmatrix}, \quad |\phi_2\rangle = \begin{pmatrix} 0 \\ -1 \\ 1 \\ 0 \end{pmatrix},$$
$$|\phi_3\rangle = \begin{pmatrix} -1 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \quad |\phi_4\rangle = \begin{pmatrix} 1 \\ x-\sqrt{1+x^2} \\ x-\sqrt{1+x^2} \\ 1 \end{pmatrix}, \tag{19}$$

with $x = U/t$. The eigenvalue and eigenvector for the ground state are

$$E = U - \sqrt{t^2 + U^2} \tag{20}$$

and

$$|GS\rangle = |1, x + \sqrt{1+x^2}, x + \sqrt{1+x^2}, 1\rangle. \tag{21}$$

3.2 *Hartree–Fock (HF) approximation*

In quantum chemistry, the correlation energy E_{corr} is defined as $E_{corr} = E_{exact} - E_{HF}$. In order to calculate the correlation energy of our system, we show how to calculate the ground state using the Hartree–Fock (HF) approximation. The main idea is to expand the exact wave function in the form of configuration interaction (CI) picture. The first term of this expansion corresponds to the HF wave function. As a first step we calculate the spin-traced one particle density matrix [39] (1PDM) γ

$$\gamma_{ij} = \left\langle GS \middle| \sum_{\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \middle| GS \right\rangle. \tag{22}$$

We obtain

$$\gamma = \begin{pmatrix} 1 & 2\alpha\beta \\ 2\alpha & 1 \end{pmatrix}, \tag{23}$$

where

$$\alpha = \frac{1}{\sqrt{2}}\sqrt{1 - \frac{x}{1+x^2}} \quad \text{and} \quad \beta = \frac{1}{\sqrt{2}}\sqrt{1 + \frac{x}{1+x^2}}.$$

Diagonalize this 1PDM we can get the binding (+) and unbinding (−) molecular natural orbitals (NOs)

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle), \tag{24}$$

and the corresponding eigenvalues

$$n_{\pm} = 1 \pm \frac{1}{\sqrt{1+x^2}}, \tag{25}$$

where $|1\rangle$ and $|2\rangle$ are the spatial orbitals of site 1 and 2 respectively. The NOs for different spins are defined as

$$|\pm\sigma\rangle = \frac{1}{\sqrt{2}}\left(c^{\dagger}_{1\sigma} \pm c^{\dagger}_{2\sigma}\right)|0\rangle \equiv c^{\dagger}_{\pm\sigma}|0\rangle, \tag{26}$$

where $|0\rangle$ is the vacuum state. After we define the geminals $|\pm\pm\rangle = c^{\dagger}_{\pm\uparrow}c^{\dagger}_{\pm\downarrow}|0\rangle$, we can express $|GS\rangle$ in terms of NOs as

$$|GS\rangle = \sqrt{\frac{n_+}{2}}|++\rangle - \operatorname{sgn} U\sqrt{\frac{n_-}{2}}|--\rangle. \tag{27}$$

In the HF approximation, the GS is give by $|HF\rangle = |++\rangle$ and $E_{HF} = -t + U$. Let us examine the HF results by defining the ionic and nonionic geminals, i.e. the electrons are localized on one site or delocalized on both sites, respectively:

$$\begin{aligned}|A\rangle &= \frac{1}{\sqrt{2}}\left(c^{\dagger}_{1\uparrow}c^{\dagger}_{1\downarrow} + c^{\dagger}_{2\uparrow}c^{\dagger}_{2\downarrow}\right)|0\rangle\\ |B\rangle &= \frac{1}{\sqrt{2}}\left(c^{\dagger}_{1\uparrow}c^{\dagger}_{2\downarrow} + c^{\dagger}_{2\uparrow}c^{\dagger}_{1\downarrow}\right)|0\rangle.\end{aligned} \tag{28}$$

If $x \to 0$, the system is equally mixed between ionic and nonionic germinal, $|HF\rangle = |A\rangle + |B\rangle$. When $x \to +\infty$, $|GS\rangle \to |B\rangle$, which indicate that as x becomes large, our system goes to the nonionic state. Similarly, $|GS\rangle \to |C\rangle$, as $x \to -\infty$, where $|C\rangle = (1/\sqrt{2})(c^{\dagger}_{1\uparrow}c^{\dagger}_{1\downarrow} - c^{\dagger}_{2\uparrow}c^{\dagger}_{2\downarrow})|0\rangle$. Thus, the HF results are a good approximation only when $x \to 0$. The unreasonable diverging behaviour results from not suppressing the ionic state $|A\rangle$ in $|HF\rangle$ when $|x| \to \infty$. In order to correct this shortcoming of the HF method we can consider combining different wave functions in different ranges to obtain a better wave function for our system. This can be done as follows:

Range	GS energy	correlation energy	wave function	n_+	n_-
$U > t$	0	$U - \sqrt{U^2+t^2}$	$\vert B\rangle$	1	1
$-t \geq U \leq t$	$-t + U$	$t - \sqrt{U^2+t^2}$	$\frac{1}{\sqrt{2}}(\vert A\rangle + \vert B\rangle)$	2	0
$U < -t$	2U	$-U - \sqrt{U^2+t^2}$	$\vert C\rangle$	1	1

3.3 *Correlation entropy*

The correlation entropy is a good measure of electron correlation in molecular systems [39, 41]. It is defined using the eigenvalues n_k of the one-particle density matrix 1PDM,

$$S = \sum_k n_k(-\ln n_k), \; \sum_k n_k = N. \tag{29}$$

This correlation entropy is based on the nonidempotency of the natural occupation number (NON) n_k and proves to be an appropriate measure of the correlation strength if the reference state defining correlation is a single Slater determinant. In addition to the eigenvalues n_k of the 'full' (spin-dependent) 1PDM, it seems reasonable to consider also the eigenvalues n_k of the spin-traced 1PDM. Among all the n_k there is certain number N_0 of NON n_{k_0} with values between 1 and 2 and all the other N_1 NON's n_{k_1} also have values between 0 and 1. So one possible measure of the correlation strength of spin traced 1PDM is

$$S_1 = -\sum_{k_0}(n_{k_0} - 1)\ln(n_{k_0} - 1) - \sum_{k_1} n_{k_1} \ln n_{k_1}. \tag{30}$$

Since all the $n_k/2$ have values between 0 and 1, there is another possible measurement of the correlation strength

$$S_2 = -\sum_k \frac{n_k}{2} \ln \frac{n_k}{2}. \tag{31}$$

3.4 *Entanglement*

The entanglement measure is given by von Neumann entropy [52]

$$E_j = -Tr(\rho_j \log_2 \rho_j), \qquad \rho_j = Tr_j(|\Psi\rangle\langle\Psi|) \tag{32}$$

where $T(r_j)$ denotes the trace over all but the jth site, $|\Psi\rangle$ is the antisymmetric wave function of the fermions system and ρ_j is the reduced density matrix. Hence E_j actually describes the entanglement of the jth site with the remaining sites [53].

In the Hubbard model, the electron occupation of each site has four possibilities, there are four possible local states at each site, $|\nu\rangle_j = |0\rangle_j, |\uparrow\rangle_j, |\downarrow\rangle_j, |\uparrow\downarrow\rangle_j$. The reduced density matrix of the jth site with the other sites is given by [56]

$$\rho_j = z|0\rangle\langle 0| + u^+|\uparrow\rangle\langle\uparrow| + u^-|\downarrow\rangle\langle\downarrow| + w|\uparrow\downarrow\rangle\langle\uparrow\downarrow| \tag{33}$$

with

$$w = \langle n_{j\uparrow} n_{j\downarrow}\rangle = Tr(n_{j\uparrow} n_{j\downarrow} \rho_j) \tag{34}$$

$$u^+ = \langle n_{j\uparrow}\rangle - w, \qquad u^- = \langle n_{j\downarrow}\rangle - w \tag{35}$$

$$z = 1 - u^+ - u^- - w = 1 - \langle n_{j\uparrow}\rangle - \langle n_{j\downarrow}\rangle + w. \tag{36}$$

and the entanglement between the jth site and other sites is given by

$$E_j = -z\mathrm{Log}_2 z - u^+\mathrm{Log}_2 u^+ - u^-\mathrm{Log}_2 u^- - w\mathrm{Log}_2 w. \tag{37}$$

The entanglement of the identical particles, the fermions in the system, is measured in terms of the Fock-space occupation number basis. In this measurement, the Fock-space occupation number basis we use is a convenient basis in which the tensor product structure is manifestly recovered, with the local states describing electronic modes easily accessible to an observer. The system is split into two parts, the Fock-space reduced density matrix is obtained from the full density matrix by tracing out the local states of the other part. So the entanglement measure in this

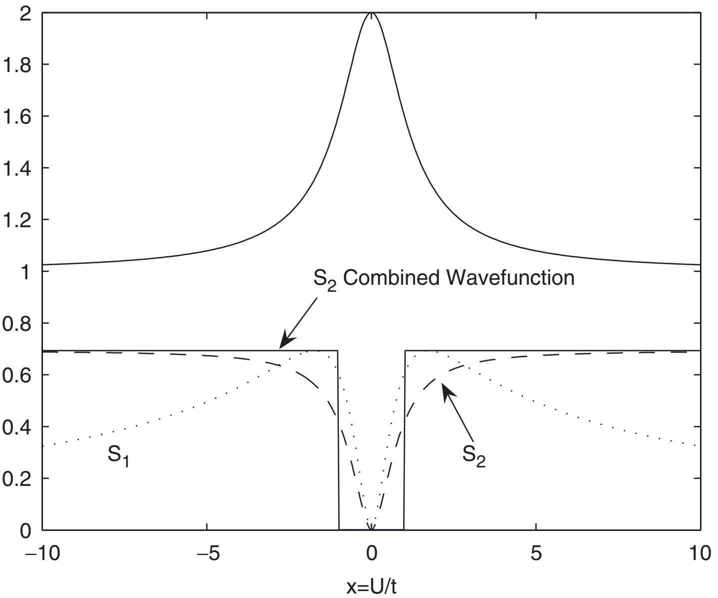

Figure 2. Two-site Hubbard model: upper curve is the entanglement calculated by von Newman entropy. The curves S_1 and S_2 are the correlation entropy of the exact wave function as defined in the text. The dashed line is the S_2 for the combined wave function based on the range of x values. S_1 for the combined wave function is zero.

system, which is defined by von Neumann entropy, is a measure of the entanglement between the electron modes of a single site and the electron modes of the other sites [45, 48, 54, 55].

For the one-dimensional Hubbard model with half-filling electrons, we have $\langle n_\uparrow\rangle = \langle n_\downarrow\rangle = (1/2)$, $u^+ = u^- = (1/2) - w$, and the entanglement is given by

$$E_j = -2w\log_2 w - 2\left(\frac{1}{2} - w\right)\log_2\left(\frac{1}{2} - w\right). \tag{38}$$

Consider the particle-hole symmetry of the one-dimensional Hubbard model, one can obtain $w(-U) = (1/2) - w(U)$, so the entanglement is an even function of U, $E_j(-U) = E_j(U)$.

For our case of a two-sites two-electrons system $w = (1/(2 + 2[x + \sqrt{1 + x^2}]^2))$. Thus the entanglement is readily calculated from equation (38). In figure 2, we show the entanglement between the two sites, top curve, and the correlation entropy S_1 and S_2 as function of $x = U/t$. The entanglement measure is given by the von Neumann entropy in which the density matrix of the system is traced over the other site to get the reduced density matrix; the reduced density matrix describes the four possible occupations on the site: $|0>$, $|\uparrow\rangle$, $|\downarrow\rangle$, $|\uparrow\downarrow\rangle$. The minimum of the entanglement is 1 as $x \to \pm\infty$. It can be understood as when $U \to +\infty$ all the sites are singly occupied, the only difference is the spin of the electrons on each site, which can be referred to as spin entanglement. As $U \to -\infty$, all the sites are either doubly occupied or empty, which is referred to as space entanglement. The maximum of the entanglement is 2 at $U=0$, all four occupations are evenly weighted, which is the sum of the spin and space entanglement of the system. The correlation entropy S_1 vanishes for $x \to 0$ and $x \to \pm\infty$ and has a maximum near $|x| = 1$, the correlation entropy S_2 vanishes for $x \to 0$ and increases monotonically and approaches ln2 for $x \to \pm\infty$. For $x \to +\infty$ can be viewed as $t \to 0$ for fixed $U > 0$ or as $U \to +\infty$ for fixed t. The first case can be understood to indicate the sites are decoupled and the electrons are well described by the Heitler–London model. This can be described reasonably by S_1. In the second case, the electron correlation between electrons increase as the Hubbard repulsion U increases. This is described by S_2.

4. Hubbard model with two sites and three electrons

The general Hamiltonian for the Hubbard model can be written as

$$H = -\sum_{<i,j>\sigma} t_{i\sigma,j\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{i} U_{i\uparrow,i\downarrow} \hat{n}_{i\uparrow} \hat{n}_{j\downarrow}, \tag{39}$$

where $t_{i\sigma,j\sigma}$ is the hopping term describes the hopping between site i and j with spin σ and $U_{i\uparrow,i\downarrow}$ is the on-site interaction between the two electrons with the spin-dependent site occupancy operator $\hat{n}_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$, with $c^{\dagger}_{i\sigma}$, $c_{i\sigma}$ the Fermi creation and annihilation operators (at site i and with spin $\sigma =\uparrow, \downarrow$). In order to describe the H_2^- molecule, we introduce two energy levels for each site and express the Hamiltonian as

$$\begin{aligned} H = {} & -t_A\left(c^{\dagger}_{A1\uparrow} c_{A2\uparrow} + c^{\dagger}_{A1\downarrow} c_{A2\downarrow}\right) - t_B\left(c^{\dagger}_{B1\uparrow} c_{B2\uparrow} + c^{\dagger}_{B1\downarrow} c_{B2\downarrow}\right) \\ & - t_{AB}\left(c^{\dagger}_{A1\uparrow} c_{B1\uparrow} + c^{\dagger}_{A1\downarrow} c_{B1\downarrow} + c^{\dagger}_{A2\uparrow} c_{B2\uparrow} + c^{\dagger}_{A2\downarrow} c_{B2\downarrow}\right) \\ & - t_{AB}\left(c^{\dagger}_{A1\uparrow} c_{B2\uparrow} + c^{\dagger}_{A1\downarrow} c_{B2\downarrow} + c^{\dagger}_{A2\uparrow} c_{B1\uparrow} + c^{\dagger}_{A2\downarrow} c_{B1\downarrow}\right) \\ & + U_{A1}\left(\hat{n}_{A1\uparrow} + \hat{n}_{A1\downarrow}\right) + U_{A2}\left(\hat{n}_{A2\uparrow} + \hat{n}_{A2\downarrow}\right) + U_{B1}\left(\hat{n}_{B1\uparrow} + \hat{n}_{B1\downarrow}\right) + U_{B2}\left(\hat{n}_{B2\uparrow} + \hat{n}_{B2\downarrow}\right) \\ & + U_A\left(\hat{n}_{A1\uparrow}\hat{n}_{A1\downarrow} + \hat{n}_{A2\uparrow}\hat{n}_{A2\downarrow}\right) + U_B\left(\hat{n}_{B1\uparrow}\hat{n}_{B1\downarrow} + \hat{n}_{B2\uparrow}\hat{n}_{B2\downarrow}\right) \end{aligned} \tag{40}$$

For simplicity, we set the inner hopping term $t_A = t_B = 1.0$, the energy level corresponding to the first state of site 1 and site 2, $U_{A1} = U_{B1} = 0$ and the onsite electron electron repulsion term $U_A = U_B = U$. After expanding this Hamiltonian in the basis set $|A1\uparrow, A1\downarrow, A2\uparrow, A2\downarrow, B1\uparrow, B1\downarrow, B2\uparrow, B2\downarrow\rangle$, we diagonalize the Hamiltonian matrix to get the ground state energy and wave function. In figure 3 we show the entanglement of this system as a function of $x = U/t_{AB}$, where t_{AB} is the hopping term between two sites and U_{A2} and U_{B2} are the energies of the second state of site 1 and site 2. As we observed in the figure 2, the entanglement for the three-electron system increases as x increases and reaches a maximum value at $x=0$. The different curves in figure 3 correspond to different onsite energy gaps.

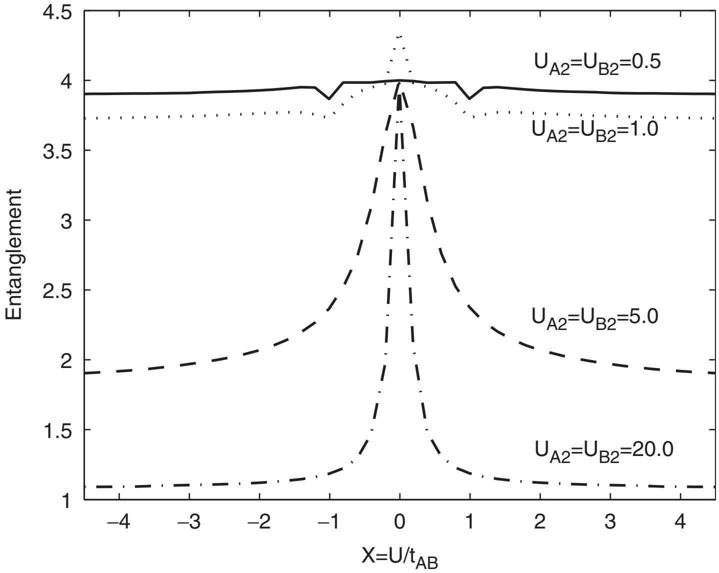

Figure 3. Two-site three-electron Hubbard model: the entanglement as a function of $x = U/t_{AB}$ for different values of U_{A2} and U_{B2} as defined in the text.

The entanglement increases as the energy gap decreases. When the energy gap is large, electrons tend to stay at the lowest energy level and reduces the entanglement of the total system.

5. Ab initio calculations and entanglement

For the two-electron system in a $2m$-dimensional spin-space orbital with c_a and $c_a^\dagger$ denoting the fermionic annihilation and creation operators of single-particle states and $|0\rangle$ representing the vacuum state, a pure two-electron state $|\Phi>$ can be written as

$$|\Phi\rangle = \sum_{a,b\in\{1,2,3,4,\ldots 2m\}} \omega_{a,b} c_a^\dagger c_b^\dagger |0\rangle \tag{41}$$

where a, b run over the orthonormlized single particle states, and Pauli exclusion requires that the $2m \times 2m$ expansion coefficient matrix ω is antisymmetric: $\omega_{a,b} = -\omega_{b,a}$, and $\omega_{i,i} = 0$.

In the occupation number representation $(n_1\uparrow, n_1\downarrow, n_2\uparrow, n_2\downarrow, \ldots, n_m\uparrow, n_m\downarrow)$, where ↑ and ↓ mean α and β electrons respectively, the subscripts denote the spatial orbital index and m is the total spatial orbital number. By tracing out all other spatial orbitals except n_1, we can obtain a (4×4) reduced density matrix for the spatial orbital n_1

$$\rho_{n_1} = Tr_{n_1}|\Phi\rangle\langle\Phi| = \begin{pmatrix} 4\sum_{i=1}^{m-1}\sum_{j=1}^{m-1}|\omega_{2i+1,2j+2}|^2 & 0 & 0 & 0 \\ 0 & 4\sum_{i=1}^{m-1}|\omega_{2,2i+1}|^2 & 0 & 0 \\ 0 & 0 & 4\sum_{i=2}^{m}|\omega_{1,2i}|^2 & 0 \\ 0 & 0 & 0 & 4|\omega_{1,2}|^2 \end{pmatrix}. \tag{42}$$

The matrix elements of ω can be calculated from the expansion coefficient of the *ab initio* CI method. The CI wave function with single and double excitation can be written as

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ar} c_a^r|\Psi_a^r\rangle + \sum_{a<b,\, r<s} c_{a,b}^{r,s}|\Psi_{a,b}^{r,s}\rangle, \tag{43}$$

where $|\Psi_0\rangle$ is the ground state Hartree–Fock wave function, c_a^r is the coefficient for single excitation from orbital a to r, and $c_{a,b}^{r,s}$ is the double excitation from orbital a and b to r and s. Now the matrix elements of ω can be written in terms of the CI expansion coefficients. In this general approach, the ground state entanglement is given by von Neumann entropy of the reduced density matrix ρ_{n1} [49]

$$S(\rho_{n_1}) = -Tr(\rho_{n_1} log_2 \rho_{n_1}). \tag{44}$$

We are now ready to evaluate the entanglement for the H_2 molecule as a function of R using a two-electron density matrix calculated from the CI wave function with single and double electronic excitations [57]. Figure 4 shows the calculated entanglement S for H_2 molecule, as a function of the internuclear distance R using a minimal Gaussian basis set STO-3G (each Slater-Type-Orbital fitted by 3 Gaussian functions) and a split valence Gaussian basis set 3-21G[57]. For comparison we included the usual electron correlation ($E_c = |E^{Exact} - E^{UHF}|$) and spin-unrestricted Hartree–Fock (UHF) calculations [57] using the same basis set in the figure. At the limit $R = 0$, the electron correlation for the He atom, $E_c = 0.0149(a.u.)$ using 3-21G basis set compared with the entanglement for the He atom $S = 0.0313$. With a larger basis set, $cc - pV5Z$ [58], we obtain numerically $E_c = 0.0415(a.u.)$ and $S = 0.0675$. Thus, qualitatively entanglement and absolute correlation have similar behaviour. At the united atom limit, $R \to 0$, both have small values, then rise to a maximum value and finally vanishes at the separated atom limit, $R \to \infty$. However, note that for $R > 3$Å the correlation between the two electrons is almost zero but the entanglement is maximal until around $R \sim 4$Å, the entanglement vanishes for $R > 4$Å.

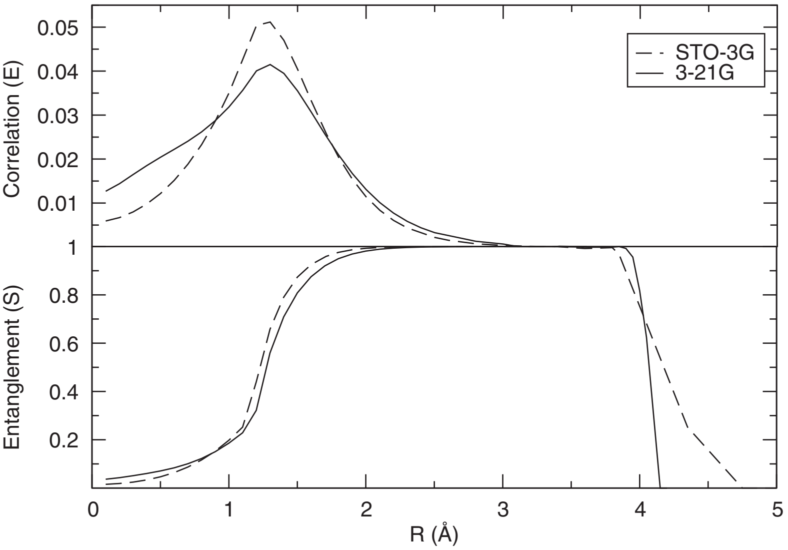

Figure 4. Comparison between the absolute value of the electron correlation $E_c = |E^{Exact} - E^{UHF}|$ and the von Neumann Entanglement (S) as a function of the internuclear distance R for the H_2 molecule using two Gaussian basis sets STO-3G and 3-21G.

6. Summary and outlook

We have studied the relation between electron–electron correlation, correlation entropy and entanglement for two exactly solvable models: the Ising model and the Hubbard model for two sites. The *ab initio* calculation of the entanglement for the H_2 system is also discussed. Our results show that there is a qualitatively similar behaviour between the entanglement and absolute standard correlation of electrons for the Ising model. Thus, entanglement might be used as an alternative measure of electron correlation in quantum chemistry calculations. For the Hubbard model there is a similar pattern between the entanglement and the correlation entropy S_2; both reach an extremum at $x = U/t = 0$ and tend to 1 at $x \to \infty$.

Dimensional scaling theory pioneered by Herschbach [59] provides a natural means to examine electron–electron correlation and entanglement. At the large-dimension limit (D→∞), in a suitably scaled space electrons become fixed in position but their geometrical configuration typically undergoes marked changes for certain ranges of the nuclear charges. As the large-D limit is pseudoclassical, the analysis deals with a point charge representation rather than a differential equation; thus, energies are obtained simply by finding the minimum of a scalar effective potential. The primary effect of electron correlation in the $D \to \infty$ limit is to open up the dihedral angles from their Hartree–Fock values [59] of exactly 90°. Angles in the correlated solution are determined by the balance between centrifugal effects which always favour 90° and interelectron repulsions which always favour 180°. Since the electrons are localized at the $D \to \infty$ limit one might need to add the first harmonic correction in the $1/D$ expansion to obtain a useful density matrix for the whole system, and thus the von Neumann entropy. The relation between entanglement and electron–electron correlation at the large-dimensional limit for the dimensional scaling model of the H_2 molecule [60] will be the subject of future studies.

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