A critical theory of quantum entanglement for the Hydrogen molecule

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Abstract

In this paper we investigate some entanglement properties for the Hydrogen molecule considered as a two interacting spin $\frac{1}{2}$ (qubit) model. The entanglement related to the $H_2$ molecule is evaluated both using the von Neumann entropy and the Concurrence and it is compared with the corresponding quantities for the two interacting spin system. Many aspects of these functions are examined employing in part analytical and, essentially, numerical techniques. We have compared analogous results obtained by Huang and Kais a few years ago. In this respect, some possible controversial situations are presented and discussed.

1 Introduction and the model

Entanglement is a physical observable measured by the von Neumann entropy or, alternatively, by the Concurrence of the system under consideration.

The concept of entanglement gives a physical meaning to the electron correlation energy in structures of interacting electrons. The electron correlation is not directly observable, since it is defined as the difference between the exact ground state energy of the many electrons Schrödinger equation and the Hartree–Fock energy.

In this paper we discuss the Hamiltonian which describes the Hydrogen molecule regarded as a two interacting spin $\frac{1}{2}$ (qubit) model.

In [1] it was argued that the entanglement (a quantum observable) can be used in analyzing the so-called correlation energy which is not directly observable. From our point of view, the Hydrogen molecule is dealt with a bipartite system governed by the Hamiltonian

$$
\mathcal{H}_{H_2} = -\frac{J}{2}(1 + g)\sigma_1 \otimes \sigma_1 - \frac{J}{2}(1 - g)\sigma_2 \otimes \sigma_2 - B(\sigma_3 \otimes \sigma_3 + \sigma_0 \otimes \sigma_3),
$$

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where $\sigma_i$ stand for the Pauli matrices ($\sigma_0 = I$). Actually, this model was considered in [1] in order to illustrate their method. However, here we will make some interpretative changes. Indeed, from our point of view, the states of an isolated atom are strongly reduced to a system with two energy levels related to the intensity of the magnetic field $B$. Relatively to this scale, the exchange interaction constant $J$ is usually smaller than $B$, in order to represent the residual interatomic interactions. From the point of view of quantum chemistry, one may interpret the discrete spectrum as provided by the Hartree–Fock calculations, while the interaction coupling $J$ models the residual multielectronic effects, not taken into account by the mean field approximation.

For simplicity we limit ourselves to the ferromagnetic phase with $J > 0$. The parameter $g$, such that $0 \leq g \leq 1$, describes the degree of anisotropy corresponding for $g = 0$ to the completely isotropic XY spin model. Conversely, $g = 1$ provides the anisotropic XY spin model, the so-called Ising model.

We notice that when the atoms are far apart, their interaction is quite weak. This corresponds to a vanishing value of $J$. In this situation the state of the system is completely factorized in the product state of the ground states of the independent spins. The corresponding total energy, in unit of $B$, is just the sum of the two fundamental levels, $\mathcal{E}_0 = -2$, which we may consider as the Hartree–Fock approximated fundamental level in molecular structure calculations.

When $J \neq 0$, the fundamental energy eigenvalue is $\mathcal{E} = -\sqrt{4 + g^2 \lambda^2}$ in Region I defined by $0 < \lambda \leq \frac{2}{\sqrt{1 - g^2}}$, otherwise $\mathcal{E} = -\lambda$ ($\lambda$ means the coupling constant) in Region II, which is the complement of I which respect to positive real axis. The corresponding (non normalized) eigenstates are $|\Psi_I\rangle = \left\{ \frac{\sqrt{g^2 \lambda^2 + 4 + 2 g \lambda}}{g \lambda}, 0, 0, 1 \right\}$ and $|\Psi_{II}\rangle = \left\{ 0, 1, 1, 0 \right\}$, respectively. In both cases the state is entangled.

Since we are dealing with pure states, the von Neumann entropy [2]

$$S_{vN} = -\text{Tr}(\rho_1 \log_2 \rho_1)$$

is chosen to be a measurement of the entanglement, where $\rho_1$ is the 1-particle reduced density matrix. However, for general mixed states other entanglement estimators (for instance, the Concurrence [4]) have to be used. In the considered case, one has

$$S_{vN,I} = -g^2 \sqrt{g^2 \lambda^2 + 4} \log \left( \frac{1}{2} \frac{1}{\sqrt{g^2 \lambda^2 + 4}} \right) \lambda^2$$

$$-\left( g^2 \left( \sqrt{g^2 \lambda^2 + 4} + 4 \right) \lambda^2 + 8 \left( \sqrt{g^2 \lambda^2 + 4} + 2 \right) \log \left( \frac{1}{2} + \frac{1}{\sqrt{g^2 \lambda^2 + 4}} \right) \right)$$

$$= \frac{1}{\sqrt{g^2 \lambda^2 + 4} \left( g^2 \lambda^2 + 2 \sqrt{g^2 \lambda^2 + 4} + 4 \right) \log(4)}$$

$$S_{vN,II} = 1.$$
Scrutinizing Eq. (3) and Eq. (4) it emerges that the entropy is an increasing function of the coupling constant $\lambda$ in Region I, but the state is maximally entangled in Region II independently from the anisotropy parameter $g$. One sees that, as it arises graphically, for $g = 1$ the entanglement is a monotonic increasing function of the interaction coupling $\lambda$. Moreover for weak ($< 1$) coupling values it is always less than the 30%. Of course, for large coupling constants the entropy approaches 1, meaning that all levels are equiprobably visited by the considered spin.

Limiting all further considerations to the case of weak interaction, we observe that at the boundary point $\lambda_b = \sqrt{1 - g^2}$ a discontinuity occurs, signaling a crossing of the lowest eigenvalues and, in a more general context, a quantum phase transition [5].

As it was pointed out in [6], for quantifying the entanglement we can resort to the reduced density matrix. Furthermore, in [7], Wootters has shown that for a pair of binary qubits one can use the concept of Concurrence $C$ to measure the entanglement.

The Concurrence reads

$$C(\rho) = \max(0, \nu_1 - \nu_2 - \nu_3 - \nu_4),$$

(5)

where the $\nu_i$’s are the eigenvalues of the Hermitian matrix

$$R = \left( \sqrt{\tilde{\rho}} \rho \sqrt{\tilde{\rho}} \right)^{\frac{1}{2}},$$

where $\tilde{\rho} = (\sigma_y \otimes \sigma_y) \rho^* (\sigma_y \otimes \sigma_y)$, $\rho^*$ being the complex conjugate of $\rho$ taken in the standard basis [7].

Some interesting results on the simple model (1) of the Hydrogen molecule can be achieved by realizing a comparative study of the von Neumann entropy and the Concurrence.

To this aim, we compute the Concurrence $C_I$ and $C_{II}$, i.e.

$$C_I = g\lambda \sqrt{\frac{1}{g^2 \lambda^2 + 4}}, \quad C_{II} = 1.$$  

(6)

where I and II refer to Regions I and II, where $0 \leq \lambda \leq \frac{2}{1 - g^2}$, and $\mathcal{E} = -\lambda$, respectively.

In Figure 1 a comparison between the Concurrence and the von Neumann entropy for two spins system as a function of the coupling $\lambda$ for $g = 1$ is presented.

Sec. 2 contains a comparison between the entanglement and the correlation energy. In Sec. 3 the Configuration Interaction method is introduced to compare entanglement and correlation energy. In Sec. 4 some differences between the Configuration Interaction approach and the two spin Ising model are presented. Finally, our main results are summarized in Sec. 5.
2 A comparison between the entanglement and the correlation energy

Now we look for a comparison between the entanglement with the energy correlation, which as we have already recalled, it is understood as the difference of the fundamental energy level compared with respect to the corresponding value at vanishing coupling constant $\lambda$.

For $g = 1$ and in unities of $B$ it is given by

$$\mathcal{E}_{\text{corr}} = |\mathcal{E}_0| - 2 = \sqrt{4 + \lambda^2} - 2.$$  \hspace{1cm} (7)

We observe that the entanglement measure is always bounded, while $\mathcal{E}_{\text{corr}}$ is a divergent function of $\lambda$. So it does not make much sense to look for simple relations valid on the entire $\lambda$-axes. Consequently, limiting ourselves to weak couplings, for $0 \leq \lambda \leq 1$, we minimize the mean squared deviation

$$I[\alpha] = \int_{0}^{1} \Delta S^2_{\alpha} \, d\lambda, \quad \text{with} \quad \Delta S_{\alpha} = \mathcal{E}_{\text{corr}} - \alpha S_{\text{vN}}.$$  \hspace{1cm} (8)

Thus the minimizing parameter $\alpha_{\text{min}}$ will be given by

$$\alpha_{\text{min}} = \frac{\int_{0}^{1} \mathcal{E}_{\text{corr}} S_{\text{vN}} \, d\lambda}{\int_{0}^{1} S^2_{\text{vN}} \, d\lambda} \approx -0.691217.$$  \hspace{1cm} (9)

A formula analogous to (9) can be obtained by using the Concurrence as a measure of entanglement. In this case, by minimizing the mean squared deviation we have

$$I_C[\alpha'] = \int_{0}^{1} \Delta C^2_{\alpha'} \, d\lambda, \quad \text{with} \quad \Delta C_{\alpha'} = \mathcal{E}_{\text{corr}} - \alpha' C.$$  \hspace{1cm} (10)

Now, in order to estimate the relative deviation of $S_{\text{vN}}$ with respect to $\mathcal{E}_{\text{corr}}$, let us report $|\Delta S_{\alpha_{\text{min}}}|/S_{\text{vN}}$ and $|\Delta S_{\alpha_{\text{min}}}|/\mathcal{E}_{\text{corr}}$ as functions of $\lambda$ at the optimal value $\alpha_{\text{min}}$. The graphs of these functions are shown in Figure 2.

![Figure 1: Comparison between the Concurrence and the von Neumann entropy for the two spins system as a function of the coupling constant $\lambda$ for $g = 1$.](image)
Figure 2: The relative quadratic deviation between the von Neumann entropy and the correlation energy with respect to the former and the latter, respectively, at the optimal value $\alpha_{\text{min}}$ as a function of the coupling constant $\lambda$ for $g = 1$.

In Figure 3, the relative quadratic deviation between the Concurrence and the correlation energy with respect to the former and the latter, at the optimal values $\alpha'_{\text{min}}$, is represented.

Figure 3: The relative quadratic deviation between the Concurrence and the correlation energy with respect to the former and the latter, respectively, at the optimal value $\alpha'_{\text{min}}$ as a function of the coupling constant $\lambda$ for $g = 1$.

**Remark 1**

From these graphs, one can argue that the agreement between the two functions $S_{\text{vN}}$ and $E_{\text{corr}}$ is only qualitatively good, in fact, for very small $\lambda$, it is not good at all. However, in an intermediate range of values, i.e., $0.6 \leq \lambda \leq 1$ the two functions are almost proportional within the 10%. Analogously, the same is true between energy and Concurrence. Even, the agreement becomes worst comparing the relative deviation of the Concurrence with respect to the correlation energy, since the range in which the relative deviations become smaller than 10% are narrower. Then, the question is whether the above results are i) sufficient to justify the conjecture advanced in [1], i.e., entanglement can be considered as an estimation of correlation energy; ii) if such a relation has a
more concrete physical meaning, in particular whether the minimizing parameter $\alpha_{\min}$ and the vanishing point of $\Delta S_{\alpha_{\min}}$ does possess any physical meaning (or $\alpha'_{\min}$ and the vanishing point of $\Delta C_{\alpha'_{\min}}$). Notice that in the case of the comparison for the Concurrency simpler analytical expressions appear. For instance one finds $\Delta C_{\alpha'_{\min}} = \left(0.383249 \frac{\lambda}{\sqrt{\lambda^2 + 4}} - \sqrt{\lambda^2 + 4} + 2\right)^2$.

Remark 2

We note that in an interval of values around $\alpha_{\min}$, the deviation function possesses a minimum in the interval of interest $0 \leq \lambda \leq 1$, otherwise the minimum is achieved at larger value of $\lambda$, or the function is monotonically increasing (see Figure 4).

Figure 4: The deviation $\Delta S_\alpha$ and its derivative with respect to $\lambda$ are computed for values of $-1.29$ (red) $\leq \alpha \leq -0.091$ (violet), for steps of $0.06$. The curve drawn thicker corresponds to $\alpha_{\min}$

This behavior suggests to consider the function $\Delta S_{\alpha_{\min}}$ as a sort of ”free energy”, where $\alpha_{\min}$ mimics the ”temperature” specific of the system. If, for some reason, we allow $\lambda$ to change, then we expect that spontaneously the interaction coupling adjusts itself to the minimum of $\Delta S_{\alpha_{\min}}$. Similar considerations can be made looking at the graphs drawn for the function $\Delta C_{\alpha'_{\min}}$ and its derivative with respect to $\lambda$ (see Figure 5).

The function $\Delta S_{\alpha_{\min}}$ or, alternatively, the minimum of $\Delta C_{\alpha'_{\min}}$ can be obtained algebraically. Such a minimum is at the value of the coupling constant $\lambda_{S_{\min}} \approx 0.485$ and $\lambda_{C_{\min}} \approx 0.371$, respectively.

The authors in [1] studied numerically the von Neumann entropy and the correlation function for a Hydrogen molecule, using an old result by Herring and Flicker [8], going back to an oldest idea by Heitler and London [9], which consists in substituting the molecular binding with a position dependent exchange coupling:

$$J(r) \approx 1.641 r^2 e^{-2r} \text{ Ry},$$

where $r$ is given in Bohr radius, see Figure 6. The maximum value taken by this function is at the point $r_{\max} = 1.25$. Assuming $B = 0.5 \text{ Ry}$, i.e. $\frac{1}{2}$ of the fundamental level of the Hydrogen atom, the maximum value $\lambda'_{\max} = J(r_{\max})/B \approx 0.618$. A more detailed analysis can be found in [10].
Figure 5: The deviation $\Delta C_{\alpha'}$ and its derivative with respect to $\lambda$ are computed for values of $-0.98(\text{red}) \leq \alpha' \leq 0.22(\text{violet})$, for steps of 0.06. The curve drawn thicker corresponds to $\alpha'_{\text{min}}$

0.470628 $< \lambda'_{\text{min}}$, i.e. the value of the effective interaction value is less than the minimum for the deviation function $\Delta S_{\alpha'_{\text{min}}}$. Then, the equilibrium balance between entanglement (as von Neumann entropy) and correlation energy predicts a length of the molecule equal to $r_{\text{max}}$ (see the first panel of Figure 7). On the other hand, if we consider the energy gap $2\mathcal{E} = 3/4$ Ry, i.e. the energy step to the first excited state, one obtains the new value $\lambda''_{\text{max}} \approx 0.628$, which goes beyond $\lambda_{\text{min}}$, even if it is always less than 1. Now, the deviation function $\Delta S_{\alpha'_{\text{min}}}$ has two minima as seen in the second panel of Figure 7, one of which is at $r''_{\text{min}} \approx 0.76$, the other one being at $r''_{\text{max}} \approx 1.91$.

These results should be compared with the experimental equilibrium length of the Hydrogen molecule, which is $r_{\text{exp}} \approx 2.0$.

We point out that although the spin–model described by the Hamiltonian (1) is characterized by features which are essentially rough, however we are induced to answer positively to the quest for a physical meaning of the deviation function $\Delta S_{\alpha'_{\text{min}}}$. Indeed, the results elucidated in Figure 7 encourage, on one part, improvement of the computation of $r$ in order to make more accurate the comparison with the experimental value $r_{\text{exp}}$. 
The first question to answer is whether this draft works also for the Concur-
rence. A statement about it is not obvious, since the von Neumann entropy is
a nonlinear function of the Concurrence in the 2-qubits case.

However, from Figure 8 one can see that the minimized deviation of the
Concurrence takes one minimum for relatively large intensity of the magnetic
field (say $B \geq 0.6$ Ry), while for weak fields two minima appear, corresponding
to the situation depicted nearby.

In correspondence of the same values considered above, for $B = 0.5$ Ry
the function $\Delta C_{\alpha_{\min}}(r)$ has two minima at $r = 0.79$ and $r = 1.88$, while for
$B = 0.375$ Ry they are located at $r = 0.60$ and $r = 2.25$. So one sees that the
resulting equilibrium configurations are not much very close to the experimental
one. The equilibrium configuration more closest to the experimental one is the
minimum occurring at $r = 1.88$ ($B = \frac{1}{2}$ Ry) for the function $\Delta C_{\alpha_{\min}}(r)$.

Figure 7: The von Neumann entropy for the 2-spin model for $B = .5$ Ry (left
panel) and for $B = .375$ Ry (right panel) and the position depending interaction
given by (11).

Figure 8: Two contour plots of the minimized deviation of the Concurrence as a
function of the magnetic field $B$ (Ry) and of the internuclear distance $r$, as given
by (11). The range of values divided by the contour lines is $[-0.038, 0.04]$ for
the left panel and $[-0.03705, -0.03000]$ for the right one that approximatively
corresponding to the black area in the left panel.
One sees that one of the resulting equilibrium configurations is only roughly close to the experimental one.

In other words, to conclude monitoring numerically $B$ the equilibrium configuration more closest to experimental one in the minimum occurring at $r = 1.88$ for $B = \frac{1}{2} \text{Ry}$ and at $r = 2.25$ for $B = 0.375 \text{Ry}$ for the function $\Delta C_{\alpha \alpha'}(r)$.

3 A quantum chemical framework to compare entanglement and correlation energy

In this Section we represent the results produced in [1], where the electron entanglement in the Hydrogen molecule, calculated by the von Neumann entropy of the reduced density matrix $\rho_1$, is obtained starting by the excitation coefficients of the wave function expanded by a configuration interaction method:

$$S(\rho_1^{\text{CISD}}) = -\text{Tr}(\rho_1^{\text{CISD}} \log_2 \rho_1^{\text{CISD}}) =$$

$$- \left( \sum_{i} |c_1^{2i+1}|^2 + \sum_{i=1}^{m-1} |c_{1,2}^{2i+1,2i+2}|^2 \right) \log_2 \left( \sum_{i} |c_1^{2i+1}|^2 + \sum_{i=1}^{m-1} |c_{1,2}^{2i+1,2i+2}|^2 \right) +$$

$$- \left( |c_0|^2 + \sum_{i=1}^{m-1} |c_{2}^{2i+2}|^2 \right) \log_2 \left( |c_0|^2 + \sum_{i=1}^{m-1} |c_{2}^{2i+2}|^2 \right), \quad (12)$$

where $c_1$ is the coefficient for a single excitation, and $c_{1,2}$ is the double excitation (in Appendix A of [10] more details are shown).

In this framework, entanglement ($S$) and correlation energy ($E_{\text{corr}}$), as functions of nucleus – nucleus separation are those in Figure 9.

![Figure 9: Comparison between the entanglement, calculated by the von Neumann entropy of the reduced density matrix, and the electron correlation energy in the Hydrogen molecule.](image)

By the results given by this model, we want to discuss and to suggest some answers to the questions i) and ii) presented in Remark 1. Even if, in order
to represent correlation energy and entanglement, we use two different scales, in Figure 9 we can see that entanglement has a small value in the united atom limit after it is growing for small distances till it arrives at a maximum value then it decrease till it assumes zero value at the separated atom limit and it is exactly the progress of the correlation curve.

In order to compare the entropy $S$ with the electron correlation energy $E_{\text{corr}}$, we rescale $S$ with the parameter $\alpha_{\text{min}}$ calculated with some procedure illustrated in Eq. (8) and Eq. (9) replacing the integration variable $\lambda$ with $R$; in this way we extract

$$\alpha = \frac{\int E_{\text{corr}}S_{\text{vN}}dR}{\int S_{\text{vN}}dR} \approx 0.009. \quad (13)$$

The corresponding $\Delta S_{\alpha_{\text{min}}} = E_{\text{corr}} - \alpha S$ allows us to answer to the question ii); in fact, as it is shown in Figure 10 the vanishing point of $\Delta S_{\alpha_{\text{min}}}$ is, according to the two–spin Ising model, nearby $R \approx 2 \text{ Å}$ that corresponds to the equilibrium configuration of the Hydrogen molecule.

![Figure 10: $\Delta S_{\alpha_{\text{min}}}$ for the $H_2$ molecule as a function of nucleus–nucleus distance.](image)

**4 Differences between the Configuration Interaction approach and the two–spin Ising model**

The model proposed in Sec. 1 provides us with a measurement of entanglement: indeed, Eq. (3) describes the von Neumann entropy as a function of coupling constant $\lambda$, for small $\lambda$. By using Eq. (7), we can express $\lambda$ in terms of correlation energy and substituting it in Eq. (3) we can obtain the variation of $S_{\text{vN}}$ in terms of $E_{\text{corr}}$.

$$S_{\text{vN}} = -\frac{\{E_{\text{corr}}\log\left(\frac{E_{\text{corr}}}{2(E_{\text{corr}}+2)}\right) + (E_{\text{corr}}+4)\log\left(\frac{E_{\text{corr}}+4}{2(E_{\text{corr}}+2)}\right)\}}{(E_{\text{corr}}+2)\log 4}. \quad (14)$$
In order to calculate the coefficient of proportionality among $S_{vN}$ and $E_{\text{corr}}$, we make an expansion of $S_{vN}$ for $E_{\text{corr}} \to 0$ (or equivalently for $\lambda \to 0$) at the first order, obtaining a straight line characterized by an angular coefficient given by $m_{S_{vN}(E_{\text{corr}})} = \left(\frac{1}{2}\right)(1 + \frac{1}{\text{Log}2})$. Since this behavior is incorrect to represent the logarithmic singularity of $S_{vN}$ in the origin, we make an expansion of Eq. (14), preserving the logarithmic deviation, and we obtain an expression of the form

$$S_{vN} = A E_{\text{corr}} + B E_{\text{corr}} \text{Log}(E_{\text{corr}}),$$

(15)

where $A = 1/2$ and $B = -1/(4 \text{Log}2)$.

![Figure 11: A comparison among the behavior of Eq. (14) and its linear approximation and the logarithmic one, for the Ising model.](image)

![Figure 12: A correspondence of $E_{\text{corr}}$ and $S_{vN}$ calculated by the numerical procedure suggested by [1].](image)

Of particular significance is the fact that, in the range where $S$ is monotonically increasing, the correlation energy has its maximum, consequently $S$ seems to be not a function. Moreover, it is important to note that $E_{\text{corr}}$ begins to decrease for $R > 1 \; \text{Å}$, region where the states become mixed, i.e., $\text{Tr} \rho \neq \text{Tr} \rho^2$; as depicted in Figure [13].
Figure 13: The increasing of the degree of mixing in the two electron state: in black we depict the trace of $\rho$, in red the trace of $\rho^2$.

Probably, for this reason, the procedure adopted in [1] seems to be not correct: the density matrix, in fact, is calculated starting by the excitation coefficient of a wave function obtained developping with the Configuration Interaction Single Double method a pure two electrons state.

However, even if we consider only the first branch of the plot in Figure 12, i.e., the numerical values of $S_{vN}$ corresponding with increasing values of $E_{corr}$, and we fit the values around $E_{corr} \to 0$ with a $F = A E_{corr} + B E_{corr} \log(E_{corr})$ we draw out numerical values of the coefficient different from the ones used in Eq. (15). This result is shown in Figure 14.

Figure 14: A fit of $S_{vN}$ as a function of $E_{corr}$, around the origin, with a function of the form $F = A E_{corr} + B E_{corr} \log(E_{corr})$ whose coefficients $A$ and $B$ assume the numerical values in Figure.

In particular the arithmetic sign of the coefficient $B$ in the two models are opposite and this implies the opposite concavity of the curve.

This fact, clearly demonstrates a not satisfactory agreement between the Ising model and the one proposed in [1].
5 Concluding remarks

We have explored the role of entanglement in the model of two qubits describing the Hydrogen molecule \( \text{H}_2 \), considered as a bipartite system. In our discussion we have limited to the ferromagnetic case governed by the interaction coupling parameter \( J > 0 \).

The concept of entanglement gives a physical meaning to the electron correlation energy in structures of interacting electrons. The entanglement can be measured by using the von Neumann entropy or, alternatively, the notion of Concurrence \[7\]. To compute the entanglement it is convenient to consider two Regions, say \( I \) and \( II \), which provide two different reduced density matrices. The entropy turns out to be an increasing function of the coupling constant \( \lambda \) in Region \( I \), but the state under consideration is maximally entangled in Region \( II \) independently from the anisotropy parameter \( g \).

An interesting result is that for large coupling constants the entropy approach 1, meaning that all levels are equiprobably visited by the considered spin.

For weak interactions, at the boundary point \( \lambda_b = \frac{2}{\sqrt{1-g^2}} \) the von Neumann entropy admits a discontinuity, indicating a crossing of the lowest eigenvalues and, in a more general context, a quantum phase transition \[5\].

In Sec. 2 a comparison between the entanglement and the correlation energy is performed.

To quantifying the entanglement we resort to the reduced density matrix. The entanglement can also be measured by exploiting the concept of Concurrence.

The entanglement measure is always bounded, while the energy correlation, \( E_{\text{corr}} = |\mathcal{E}_0| - 2 = \sqrt{4 + \lambda^2} - 2 \), is a divergent function of \( \lambda \). This fact tells us that to look for simple relations valid on the whole \( \lambda \)-axes has no sense.

Thus, by limiting ourselves to weak couplings, we have minimized the mean square deviation given by Eq. \( \text{S} \). This procedure leads to the value \( \alpha_{\text{min}} \approx -0.691217 \) for the minimizing parameter (see Eq. \( \text{B} \)).

Sec. 4 contains a comparison between the von Neumann entropy and the Concurrence.

Such a comparison is illustrated in Figure 11 for two spin system as a function of the coupling \( \lambda \) for \( g = 1 \).

Some important points are commented in Remark 1 and Remark 2.

In Figure 4 the deviation \( \Delta S_\alpha \) and its derivatives with respect to \( \lambda \) are computed and \( \alpha_{\text{min}} \) is evaluated for \( \alpha \) ranging in the interval \( -1.29 \leq \alpha \leq -0.091 \).

In Figure 5 the minimized Concurrence deviation \( \Delta C_{\alpha_{\text{min}}} \) for the four eigenstates of the 2-spin model is shown.

We point out the existence of a perfect symmetry among the Concurrence deviations for pairs of eigenstates of opposite eigenvalues.

Formula \( \text{I1} \), due to Heitler–London \[9\], is reported, where the position dependent exchange coupling \( J(r) \) is expressed in term of the length \( r \) of the
nucleus–nucleus separation in the Hydrogen molecule.

To conclude, the magnetic field $B$ has been monitored such that the equilibrium configuration more closest to the experimental one, $r \approx 2.00$, is the minimum occurring at $r = 1.88$ for $B = \frac{1}{2} \text{Ry}$ and $r = 2.25$ for $B = 0.375 \text{Ry}$ for the function $\Delta C_{\alpha \alpha'}(r)$.

We observe also that in the intermediate range of values, i.e., for $0.6 \leq \lambda \leq 1$, the two functions $S_{vN}$ and the correlation energy are almost proportional within the 10%.

However, when we organized the pairs of points $(E_{corr}, S_{vN})$ calculated by following the procedure described by [1], it is clear that the von Neumann entropy cannot be considered a function of correlation energy. The principle cause is that the function $E_{corr}$ presents a maximum in the region where $S_{vN}$ is monotonically increasing.

The reversing behavior of correlation energy occurs in correspondence with an increase of the mixing degree of the two electrons state. The function $E_{corr}$ in terms of the nucleus–nucleus distance $R$, increases till the state is pure, on the contrary, when $\text{Tr}(\rho^2)$ becomes discordant from $\text{Tr}(\rho)$, the function $E_{corr}$ decreases.

This fact suggests us that the numerical model based on the calculation of $S_{vN}$ starting by the excitation coefficients $c_i$, isn’t completely correct because the density matrix is obtained as a product of two electron pure states. However, even if we consider only a branch of the plot in Figure 12, the function obtained by the two spin Ising model, i.e., Eq. 12, is unsuitable for fitting these numerical data.

On the basis of our results, essentially grounded on numerical considerations, in the near feature we would explore more complicated systems of molecules, such as for example the ethylene or other hydrocarbons, and compare these studies with the goals obtained for the Hydrogen molecule.

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