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Collins conjecture and information entropy in dissociating diatomic molecules

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Collins conjecture is examined in the dissociating molecules of H_2 and N_2, the proportionality between the correlation energy and the entropy exists in the region close to the equilibrium bond length. Similar proportionality also exists between the kinetic energy and the entropy. On the other hand, the proportionality between the potential energy difference and the entropy expands over to a larger nuclear distance. The result suggests a new method to estimate the energy from the entropy. The entropy from the eigenvalue spectrum of 2-matrix is also discussed.

I. INTRODUCTION

In the seminal work of information theory, Shannon[1] defined the quantity called entropy as a measure of information, choice and uncertainty

$$S(p) = -k \sum_i p_i \log p_i \tag{1}$$

where p_i are the probabilities of possible events. The constant k amounts to a choice of a unit, which can be set equal to unity for most discussion. Similarly, the entropy of a continuous distribution $p(x)$ can be defined as

$$S(p) = -\int_{-\infty}^{\infty} p(x)\log p(x)dx \tag{2}$$

The entropy concept provides a type of statistical inference, which is also referred to as the maximum-entropy estimate. Jaynes [2] found that the usual computational rules in statistical mechanics, starting from the determination of the partition function, are an immediate consequence of the maximum-entropy principle. The information entropy has found many applications, including engineering optimisation, weather forecast, games theory, image reconstruction, and quantum information theory[3].

In quantum mechanics, the probability is defined with $|\Psi|^2$ from a wave function Ψ. The analog of the Shannon entropy in quantum systems is the von Neumann entropy[4],

$$S(\rho) = -\mathrm{Tr}(\rho\log\rho) \tag{3}$$

where the trace(Tr) can be summation or integration depending on the variable. ρ is the density matrix, for a pure state of an N-particle system,

$$\rho = |\Psi\rangle\langle\Psi| = \Psi(12\cdots N)\Psi(1'2'3'\cdots N') \tag{4}$$

For a mixed state which may be expressed as a sum of pure state Ψ_i with weights w_i, $\rho = \sum_i w_i|\Psi_i\rangle\langle\Psi_i|$.

The density matrix for a many-electron system is usually a multidimensional quantity. Because the electrons are identical particles, one need only the information equivalent to the reduced density matrices to calculate the energy in atomic and molecular systems. For example, for the kinetic energy and nucleus-electron Coulomb interaction, one need only the first-order reduced density matrix(1-matrix), which is defined as[5]

$$\gamma(1,1') = N\int \Psi^*(123\cdots N)\Psi(1'23\cdots N)d2\cdots dN \tag{5}$$

where N is the number of electrons. Each electron has three spatial coordinates and one spin coordinate. The integral implies integration over space coordinates and summation over spin coordinates. The diagonal element of 1-matrix, i.e. $\gamma(1,1)$, is called the density.

Similarly, one may define the second-order reduced density matrix(2-matrix),

$$\Gamma(1,2;1',2') = \frac{N(N-1)}{2} \int \Psi^*(123\cdots N)\Psi(1'2'3\cdots N)d3\cdots dN \tag{6}$$

The diagonal element $\Gamma(1,2;1,2) = \Gamma(1,2)$ is the pair density, which is responsible for the electron-electron Coulomb energy. By definition, one has the contraction relation

$$\gamma(1,1') = \frac{2}{N-1}\int \Gamma(1,2;1',2)d2 \tag{7}$$

i.e. $\gamma(1,1')$ is nested in $\Gamma(1,2;1',2')$. The 2-matrix contains all the necessary information in the wave function to calculate the energy in atomic and molecular systems.

The reduced density matrices are Hermitian by definition, so they can be diagonalized. For the 1-matrix, one has

$$\gamma(1,1') = \sum_i n_i\chi_i(1)\chi_i^*(1') \tag{8}$$

The eigenfunctions, $\chi_i(1)$, are called the natural orbitals. The eigenvalues, n_i, are their occupation numbers. The 1-matrix of the Hartree-Fock approximation is characterized by idempotence[5]: $\gamma = \gamma^2$, i.e. the eigenvalues are either 0 or 1.

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Similarly, the 2-matrix has an eigenvalue expansion[6].

$$\Gamma(1,2;1',2') = \sum_k \lambda_k g_k(1,2) g_k^*(1',2') \tag{9}$$

where the eigenfunction $g_k(1,2)$, called the natural geminals, are antisymmetric: $g_k(1,2) = -g_k(2,1)$. The eigenvalue λ_k may be interpreted as the occupation number of electron-pair described by g_k. For the Hartree-Fock approximation, the geminals are just 2×2 Slater determinant of Hartree-Fock spin orbitals $g_k(1,2) = 1/\sqrt{2}[\psi_i(1)\psi_j(2) - \psi_j(1)\psi_i(2)]$. The occupation number $\lambda_k = 1$, if both ψ_i and ψ_j are occupied, and 0 otherwise.

Using either the wave function or the density matrices, one can define an entropy to measure our knowledge of the system. Jaynes[7] once proposed an entropy defined from the eigenvalue spectrum of a reduced density matrix.

$$S = -\sum_i n_i \log n_i \tag{10}$$

Here n_i are not necessary summed to 1, as the probabilities in Shannon's definition would. However, one can always define renormalized quantity p_i, such as

$$p_i = \frac{n_i}{N} \tag{11}$$

which will result in a shift of zero point by $\log N$. In the discussion where only the difference of two entropies matters, the shift of zero point can be neglected. The advantage with the definition Eq. (10) is that the entropy for the Hartree-Fock approximation vanishes uniformly because the eigenvalues n_i=1 or 0. Beyond Hartree-Fock(HF) approximation, for example, in popular configuration interaction(CI) method, the eigenvalues of 1-matrix are between 0 and 1, so the entropy is positive. The entropy based on the 1-matrix thus provide a measure for the strength of " electron correlation" [8, 9].

The correlation energy has long been defined as the difference between the true energy (E) and that of the Hartree-Fock approximation(E_0)[10],

$$E_c = E - E_0 \tag{12}$$

Since the true energy is usually lower than the Hartree-Fock energy, the correlation energy is a negative number. In practice, the true energy is often approximated with a sophisticated CI calculation. Collins[11] once conjectured that the correlation energy(with a sign change) is proportional to the Jaynes entropy,

$$E_c \sim \sum_i n_i \log n_i \tag{13}$$

Numerical evidences for the conjecture have since been reported. For example, Esquivel *et al*[12, 13] found evidence of the conjecture in the lithium isoelectronic series and small molecules using sequences of increasingly large basis sets. Ziesche *et al* [14] noticed that there are cases where E_c fails as a correlation measure, such as the He(Z) isoelectronic series as Z→ ∞. In this case, the wave function becomes a single Slater determinant with the hydrogen-like $1s$ state occupied twice, corresponds to "no correlation", while the correlation energy does not vanish, instead E_c^∞=-46.66mH. They attributed it to the dominance of kinetic energy over the Coulomb repulsion and suggested a modification to Collins conjecture.

Correlation energy has been discussed differently depending on the context. Kutzelnigg[15–17] once proposed to define the correlation energy as the electron-electron Coulomb repulsion energy from the cumulant,

$$\Delta(1,2) = \Gamma(1,2) - \gamma(1,1)\gamma(2,2) + \gamma(1,2)\gamma(2,1) \tag{14}$$

where $\gamma(1,1')$ is intrinsically from the same CI wave function as $\Gamma(1,2)$. Correlation obviously manifests in both 1-matrix and 2-matrix, so correlation energy may also contain contribution from the kinetic energy, for example.

In the density-functional theory(DFT), the correlation energy is defined as[18]

$$E_c[n] = \langle \Psi^{\lambda=1} | T + V_{ee} | \Psi^{\lambda=1} \rangle - \langle \Psi^{\lambda=0} | T + V_{ee} | \Psi^{\lambda=0} \rangle \tag{15}$$

where Ψ^λ is the antisymmetric wave function yielding the electron density n and minimizing the expectation value $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$, $\hat{T}$, and $\hat{V}_{ee}$ being the operators for the kinetic and electron-electron interaction, respectively. Although it has been proved to be a universal function of density[19], it is still a subject of extensive modelling in practice [20–26]. A monotonic relation to Jaynes entropy has been proposed by Smith *et al* [27].

In the reduced density matrix functional theory(RDMFT), the key variable is the 1-matrix[28, 29]. In principle, the functional should be a function of both the natural orbitals and their occupation numbers(viz. the eigenvalues and eigenfunctions of 1-matrix). However, in practice, the search is often simplified to a functional of the occupation numbers only[30–38], i.e.

$$E = \sum_i h_{ii} n_i + \frac{1}{2} \sum_{ijkl} f_{ijkl} \langle ij|kl \rangle \tag{16}$$

where h_{ii} and $\langle ij|kl \rangle$ are the usual one- and two-electron integrals in the natural orbital basis, f_{ijkl} is a functional of only the occupation numbers. Possible pitfall of such functionals is the non-uniqueness in the mapping between the 1-matrix and the many-electron wave function[39–43].

In Collins' conjecture, the correlation energy is expressed as the entropy function of the eigenvalue spectrum of 1-matrix, which obviously inherits the non-uniqueness problem of above mentioned RDMFT functionals. In principle, the 2-matrix is responsible to the energy, so an immediate question is any difference if the spectrum of 1-matrix is replaced by that of 2-matrix?

We have seen results that Collins' conjecture performs well in atoms and molecules under certain circumstances [12, 13], will it also perform well along the dissociating line of diatomic molecules? Another motivation is to check any possibility to turn Collins' conjecture into a computational method for the correlation energy, with all its simplicity and limitation.

II. ENTROPY IN H_2 MOLECULE

The electronic structure of H_2 molecule has been extensively studied in history[44–47]. The simple molecule is ideal for test and development of a new theory or computational method. Previous entropy analysis for the H_2 molecule have been reported[48, 49]. Gersdorf *et al*[48] defined spin entropy and spatial entropy separately in view of the specific form of the wave function $\Psi(x_1, x_2) = X(\sigma_1, \sigma_2)\Phi(\mathbf{r}_1, \mathbf{r}_2)$. The entropy curves are thus different from Huang and Kais'[49].

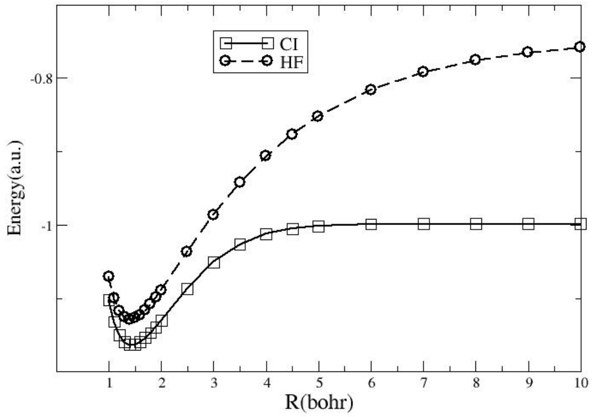

FIG. 1. Total energy(in atomic unit) of H_2 as a function of internuclear separation R for the Hartree-Fock approximation(HF) and a full CI calculation.

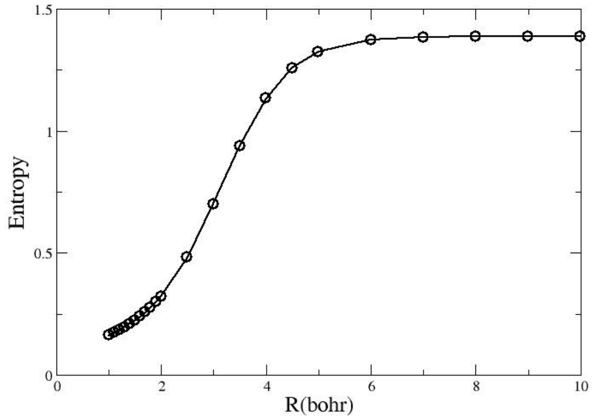

FIG. 2. Jaynes entropy of H_2 is given as a function of internuclear separation R.

Fig. 1 shows typical total energy curves of H_2 in its singlet ground state ($X^1\Sigma_g^+$). The data was calculated with the Molpro code[50] using the augmented correlation consistent basis set aug-cc-pV6Z, which gives a cohesive energy -0.15485 a.u. at 1.4 bohr. At short nuclear distance, the CI wave function is dominated by a single determinant, the Hartree-Fock method is then a good approximation. As the nuclear distance R increases, the wave function becomes a linear combination of several determinants. In terms of the natural orbitals, the wave function can be expanded as[51]

$$\Psi(1,2) = \frac{\alpha_1\beta_2 - \alpha_2\beta_1}{\sqrt{2}} \sum_i c_i\chi_i(\mathbf{r}_1)\chi_i(\mathbf{r}_2) \qquad (17)$$

where α and β are the spin functions, and χ_i are the real spatial orbitals. The occupation numbers are related to the expansion coefficients as $n_i = c_i^2$.

In Hartree-Fock approximation, the spatial part has the form

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}[\psi_A(\mathbf{r}_1) + \psi_B(\mathbf{r}_1)][\psi_A(\mathbf{r}_2) + \psi_B(\mathbf{r}_2)] \qquad (18)$$

the products $\psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_2)$ and $\psi_B(\mathbf{r}_1)\psi_B(\mathbf{r}_2)$ are ionic configurations (H^+H^-), which contributes a R^{-1} dependence in the energy curve. In the CI method, with additional determinant from anti-bonding orbitals, the ionic configurations cancel each other, which leaves only the covalent configurations (i.e. the Heitler-London ansatz) at $R \to \infty$. The two electrons then split themselves to different H atoms, which can be confirmed from the convergence of CI energy to -1 a.u. which is just the sum of the ground state energy of two H atoms (-0.5 a.u. for each H atom).

Fig. 2 displays the information entropy using Eq. (10). Following the CI energy curve in Fig. 1, the entropy flattens as $R \geq 6$ bohr. The wave function switches from a single configuration dominant form at short nuclear distance to two-configuration dominant form in the critical windows of R=4 to 5 bohr. At larger distance(such as $R \geq 10$), the wave function is dominated by two determinants with coefficients $c_i = \sqrt{2}/2$. The 1-matrix converges to 4 degenerate spin-orbitals each with occupation 0.5. So the entropy saturates at 2ln2=1.386. One may expect the entropy from two separated hydrogen atoms be 0. This is not the case here because the spin state of whole system is fixed as a singlet, there is uncertainty to specify the spin state of the individual electron even at large distance R.

However, the saturation behaviour of the entropy as R≥6 does not follow the trend of the correlation energy at the large nuclear distance. The spacing between the CI and HF curves, E_0-E, continuously increases with R as is clearly shown in Fig. 3. Also shown are the kinetic energy difference T-T_0 and the potential energy difference V_0/2-V/2, the plot is such that all three curves fit into the same window. T and V are the CI values, while T_0 and V_0 are the Hartree-Fock counterparts. The T-T_0 rises sharply as R increases from small distance, reaches a maximum around R=6 bohr and then drops slowly as R increases further. The evolution of the kinetic energy as a function of the internuclear distance is a complicated variational process involving the displacement of charge from regions near the nuclei towards the center of the bond or vice

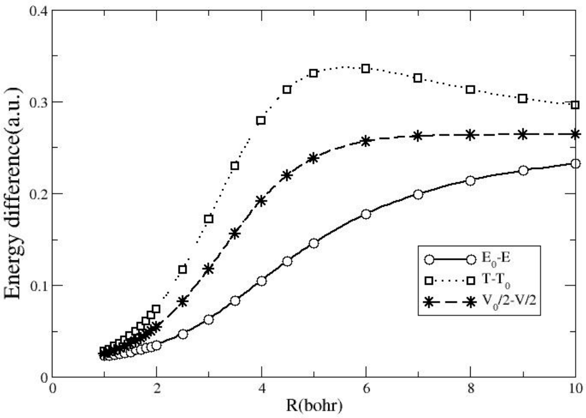

FIG. 3. Kinetic energy, potential energy, and total energy differences between the Hartree-Fock approximation and a full CI calculation are given as a function of internuclear separation R in H_2. Note the kinetic energy in Hartree-Fock approximation is less than that in the CI calculation, while the potential energy and total energy in Hartree-Fock approximation are higher than that in the CI calculation.

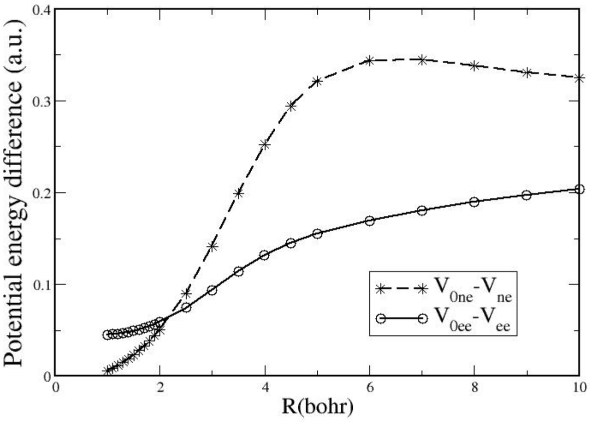

FIG. 4. Nucleus-electron and electron-electron contributions to potential energy difference between the Hartree-Fock approximation and a full CI calculation are given as a function of internuclear separation R in H_2.

versa[52]. Comparing with Fig. 2, the V_0/2-V/2 curve has an overall shape closer to the entropy than the other two curves.

The nucleus-electron potential energy and the electron-electron potential energy are often calculated separately. As shown in Fig. 4, the nucleus-electron potential energy difference V_{0ne} -V_{ne} has a similar behaviour as the kinetic energy, first increases with the nuclear distance, then decreases at even large nuclear distance. On the other hand, the electron-electron potential energy difference V_{0ee} -V_{ee} increases continuously to large nuclear distance. Since these two potentials undergo opposite change as $R \geq 6$, the total potential energy line V_0/2-V/2 becomes flat as shown in Fig. 3.

Fig. 5 plots the energy differences with respect to the entropy. The curves for both the kinetic energy difference T-T_0 and the total energy difference E_0-E are far from a straight line, especially from the saturation part of the entropy as $R \geq 6$ bohr. However, the potential energy difference V_0/2-V/2 shows a much extended proportionality with the entropy, with a slope approximately around 0.18. The results suggest a possible modification of Collins' conjecture with the potential energy difference

$$V - V_0 = \kappa \sum_i n_i \log n_i \tag{19}$$

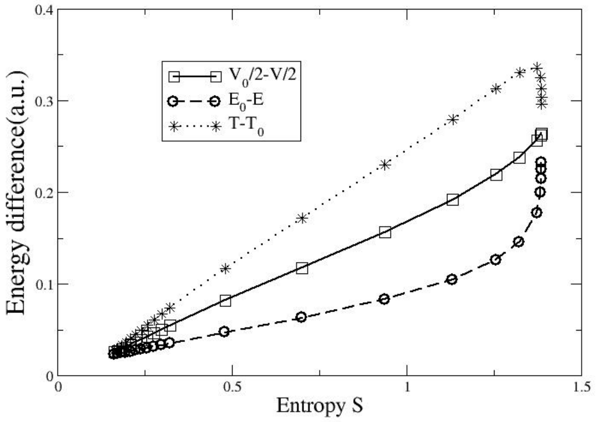

FIG. 5. Kinetic energy, potential energy, and total energy differences between the Hartree-Fock approximation and a full CI calculation are given as a function of Jaynes entropy S in H_2.

III. ENTROPY IN N_2 MOLECULE

To check Collins' conjecture in a many-electron molecule, we choose N_2, which has a highly correlated electronic structures [53–56]. Using the multiconfiguration self-consistent field method(MCSCF), the wave function consists of 512088 determinants constructed from 6 electrons in 24 active orbitals with Dunning's correlation-consistent set cc-pvDz[57]. An energy of -109.15 a.u. is reached at the equilibriurm bond length R=2.1 a.u., which is in agreement with previous report [55]. The molecule has D_{2h} symmetry. At the equilibrium geometry, the wave function is dominated by a single determinant doubly occupying the s, x, y symmetry orbitals (atoms are on the z axis). As R increases, the wave function is dominated by multi-configuration character.

Fig. 6 displays the kinetic energy, potential energy, and total energy differences with respect to the nuclear separation R in N_2. Fig. 7 compares the energy differences with respect to the entropy, Again we see a closer proportionality between the potential energy difference and the entropy(with a slope around 0.26). The kinetic energy difference and the the correlation energy are proportional to the entropy only at short nuclear distances up to $R = 4$ bohr.

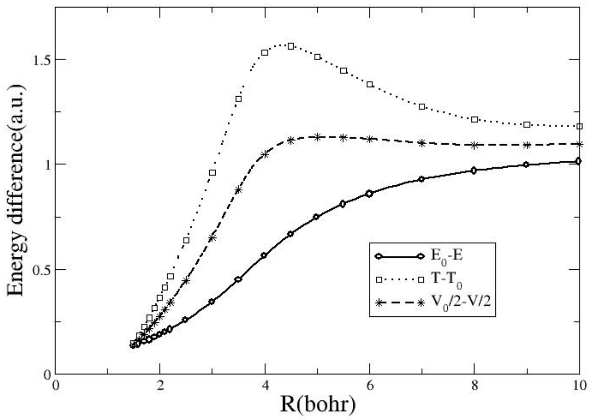

FIG. 6. Kinetic energy, potential energy, and total energy differences between the Hartree-Fock approximation and a MCSCF calculation are given as a function of internuclear separation R in N_2.

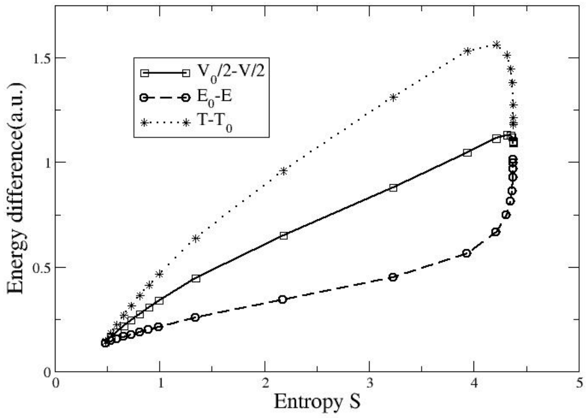

FIG. 7. Kinetic energy, potential energy, and total energy differences between the Hartree-Fock approximation and a MCSCF calculation are given as a function of Jaynes entropy S in N_2.

For the electron-electron Coulomb energy, one need the pair density of 2-matrix. The entropy based on the eigenvalues of 1-matrix may be not enough to predict correctly the correlation energy in the electron-electron Coulomb energy. So we analysed the entropy from the eigenvalue spectrum of the 2-matrix using Eq. (10). The 2-matrix elements have spins indicies as $\alpha\alpha\alpha\alpha$, $\alpha\beta\alpha\beta$, $\beta\alpha\beta\alpha$ and $\beta\beta\beta\beta$. In the singlet state, the block $\alpha\alpha\alpha\alpha$ is the same as $\beta\beta\beta\beta$, while the block $\alpha\beta\alpha\beta$ is the same as $\beta\alpha\beta\alpha$. Remove the zero elements between the same spin orbitals due to the Pauli principle, we have a 2-matrix with 24*48-24=1128 eigenvalues. By our definition of (6), the 2-matrix is normalized to N(N-1)/2=15. The 1-matrix has only 48 eigenvalues(normalized to N=6). To compare them at the same scale, we divide the entropy from the 1-matrix by 6 and that from the 2-matrix by 15. As shown in Fig. 8, the overall features such as the monotonicity and the saturation at large nuclear distance are similar, that is understandable because the 1-matrix by definition is contracted from the 2-matrix (see Eq.(7)). Even though the 2-matrix have much more eigenvalues than the 1-matrix, but the superposition in the definition of entropy smoothes out much of the detail. The difference may still be useful in differentiate systems with the same spectrum of 1-matrix but different spectrum of 2-matrix.

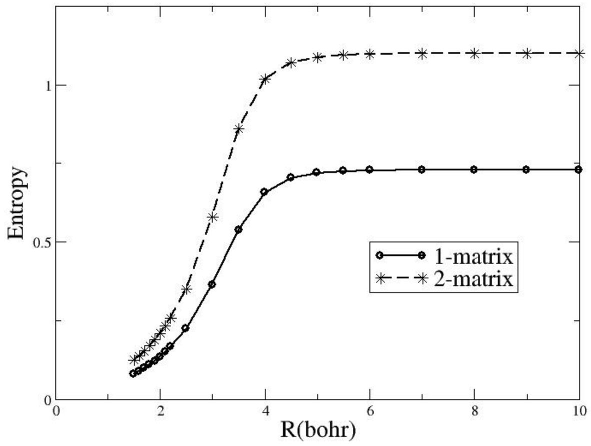

FIG. 8. Entropies based on the eigenvalue spectra of 1-matrix and 2-matrix are given as a function of internuclear separation R in N_2. For comparison on the same scale, the entropies from the 1-matrix have been divided by 6 while those from the 2-matrix divided by 15.

IV. DISCUSSION AND CONCLUSION

In recent years, several other measures of electron correlation have been proposed in the literature. Gottlieb and Mauser [58] proposed an interesting measure taking into account both the CI coefficients of the wave function expansion and the eigenvalues of 1-matrix. Juhász and Mazziotti[59] proposed the squared Frobenius norm of the cumulant as a measure of correlation and entanglement. Of course, these measures can avoid the non-uniqueness of the 1-matrix. Only the function form for the measure deviates from the entropy, which requires a consistent probability distribution as the von Neumann density matrix. In this respect, the entropy measure based on the density distribution is close to Jaynes entropy [60–62].

As Jaynes noted[7], the entropy represents the best estimates on the basis of the information available and is justified independently of any physical argument. Collins' conjecture links the correlation energy with the entropy, its validity has been under scrutiny for years[12–14, 27]. The current study shows that proportionality exists not only between the correlation energy and the entropy near equilibrium nuclear distance, but also between the kinetic energy difference and the entropy, and between the potential energy difference and the entropy. This may be expected due to the virial theorem[63, 64].

The present work also find that the proportionality between the potential energy difference and the entropy extends to even larger nuclear distances. If we take the nucleus-nucleus Coulomb potential into account (its value is same in both CI and HF), the whole potential energy is that of a neutral system. There is cancellation effect within electron-electron, nucleus-electron, and nucleus-nucleus Coulomb interactions at first. Taking the difference between CI and HF calculations will leave a part well behaved as the entropy. A modification to Collins' conjecture is by replacing the correlation energy with the potential energy difference, as Eq.(19).

The modification implies the following scheme to estimate the energy

$$E = -\frac{1}{2}\sum_i n_i\langle\chi_i|\nabla^2|\chi_i\rangle + V_0 + \kappa\sum_i n_i \log n_i \tag{20}$$

The entropy here is used to improve the Hartree-Fock potential energy V_0. κ is the proportional constant or the slope for the curve $V_0/2 - V/2$ in Fig. 5 and Fig.7, which is approximately 0.18 for H_2 and 0.26 for N_2. Similar results for O_2 and F_2 have also been found, with κ around 0.24 and 0.27, respectively. The data may slightly change due to the choice of different basis set and the active space in calculation. In an isoelectronic series, κ is likey a constant.

It is interesting to compare the above equation with Eq.(16) of RDMFT. In both cases, the kinetic energy is expressed in its exact form with the natural orbitals and their occupation numbers. The difference is in the treatment of the potential energy. The entropy approach relieves one from the heavy electron-electron potential energy calculation. Energy lowering from the Hartree-Fock approximation is immediate by construction because $\log n_i$ is negative with $0<n_i<1$. The statistic nature of information entropy may trade off some accuracy of the exact Hamiltonian, but it helps to accelerate the computation of energy.

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