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Research paper

# Informational energy as a measure of electron correlation

N. Flores-Gallegos

Benemérita Universidad de Guadalajara, Centro Universitario de los Valles, Carretera Guadalajara – Ameca Km. 45.5, C.P. 46600 Ameca, Jalisco, Mexico

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## ABSTRACT

In this letter we introduce a redefinition of the Onicescu's discrete informational energy, and show that our definition may be used as a correlation measure in atomic and molecular systems, we analyzed the correlation effects atoms and in a set of 1864 molecules.

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## 1. Introduction

The phenomena of electron correlation probably are one of the most important concepts in the chemistry, physics, and biology, in fact, without this concept, most of the modern theories cannot reproduce appropriate results. In this context, there are considerable works about the correlation, and several measures have been proposed. With the recent fusion between chemistry and information theory [1] many concepts of the chemistry can be explicated using concepts of Shannon's model, actually in 1992 Collins [2] linked the correlation energy to Shannon's entropy (also called Jaynes' entropy [3,4]) and proposed a conjecture that pointed that the correlation energy and the entropy could be related in the following way,  $E_{corr} = \kappa \sum_i n_i \ln n_i$ , where  $\kappa$  is a positive constant to be determined, and  $n_i$  are the occupation numbers obtained from a diagonal first-order density matrix, basically Collins proposed that  $E_{corr} = -\kappa S$ ; several studies have been done in this address [5–15], and showed that the information theory could be used to describe, probably, one of the most complex phenomena of the natural sciences, the correlation among many bodies.

In this context, the study of the correlation phenomena is interesting not only, from the mathematical or computational point of view as was pointed by Dirac, who wrote [16], 'The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It, therefore, becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.'

Actually, since the 1950s with the develop of the methodologies of the quantum chemistry, we generally, use a concept called correlation energy defined by Löwdin [17] as follows: 'The correlation energy for a certain state with respect to specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration.' In fact, during more than fifty years the concept of correlation energy has been being part of the traditional analysis in the field of the electronic structure, however, such as Mulliken wrote [18], 'The more accurate the calculations become, the more the concepts tend to vanish into thin air.' Thus, in this letter we propose a measure of correlation applicable to atomic or molecular systems, considering the simplicity.

It is not strange, that some works ensure that the correlation energy it is an *ad hoc* concept, however in this letter we use a correlation energy theorem that is as follows,

**Theorem 1.** *If the approximate correlated wave function  $\Psi'$  is selected with a variational criteria from a Hilbert space  $\mathcal{H}$  of functions such that the function base  $\Psi_0$ , and the functions are normalized so that,*

$$\langle \Psi_0 | \Psi_0 \rangle = \langle \Psi_0 | \Psi' \rangle = 1, \quad (1)$$

*then, the expression for the correlation energy will be,*

$$E_{corr} = \langle \Psi_0 | \hat{H} | \Phi \rangle, \quad (2)$$

*where  $\Phi = (\Psi' - \Psi_0)$ , and considering  $\langle \Psi_0 | \Phi \rangle = 0$ , we obtain,*

$$E_{corr} = E' - E_0 = \frac{\langle \Psi' | \hat{H} | \Psi' \rangle}{\langle \Psi' | \Psi' \rangle} - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle. \quad (3)$$

See Ref. [19] for the demonstration of this theorem. If we choose  $E_0 = E_{HF}$  and  $E' = E_{CISD}$  in Eq. (3), then the expression for the correlation energy will be comparable to the Löwdin's expression,

E-mail address: [nelson.flores@profesores.valles.udg.mx](mailto:nelson.flores@profesores.valles.udg.mx)

$$E_{corr} = E_{CISD} - E_{HF} \leq 0. \quad (4)$$

With the knowledge of the first-order density matrix we can determinate all mono-electronic properties of the systems [20], this density matrix is defined as,

$$\gamma(1|1') = \sum_i \lambda_i \psi_i(1) \psi_i^*(1'), \quad (5)$$

where the  $\lambda_i$  are the occupation numbers, and for a pure state, this density matrix fulfills the idempotency criteria:  $\text{Tr} \Gamma_\psi^2 = \text{Tr} \Gamma_\psi = 1$ , meanwhile for a mixed state  $\text{Tr} \Gamma_\psi^2 \neq \text{Tr} \Gamma_\psi$ , therefore using the idempotency property and Eq. (4), we defined an expression for the correlation as,

$$I_{corr} = \text{Tr} \Gamma_{CISD}^2 - \text{Tr} \Gamma_{HF}^2 = \sum_i n_i^2 - 1, \quad (6)$$

where we used the fact that  $\text{Tr} \Gamma_{HF}^2 = 1$ , and as in the case of Eq. (4),  $I_{corr} \leq 0$ . On the other hand, Eq. (6) has a similar form to the informational energy introduced by Onicescu in 1966 [21], this expression for the energy is,

$$E(p_i) = \sum_{i=1}^n p_i^2, \quad (7)$$

where  $\{p_i\}_{i=1}^n$  is a discrete probability distribution subject to  $\sum_{i=1}^n p_i = 1$  and  $0 \leq p_i \leq 1$ , actually this definition does not have energy units, and the term 'energy' it is because, as in the case of the thermodynamic energy, Eq. (7) is a convex function, and it will be minimum if  $\sum_{i=1}^n p_i = N$  and maximum if  $\sum_{i=1}^n p_i = 1$ . A generalization of the Onicescu's energy was done by Theodorescu [22],

$$E^\alpha(p) = \sum_{i=1}^n \left( \frac{1}{\alpha - 1} \right) p_i^\alpha, \quad \alpha \neq 1, \quad \alpha \in \mathfrak{R} > 0, \quad (8)$$

where  $p_i$  is a discrete probability set, that also fulfills  $\sum_{i=1}^n p_i = 1$  and  $0 \leq p_i \leq 1$ ; for  $\alpha = 2$  Eq. (8) becomes into Eq. (7); a classification of order- $\alpha$  information energy, was done by Bathia [23] who has proved that Eq. (8) had the follow properties (i) it is recursive, (ii) it is symmetric and (iii) it is differentiable. Recently, the informational energy has been used to define other informational concepts such as the informational temperature [24], and in the context of the density functional theory, a Euler equation of orbital-free density functional theory has been defined [25], and also, has showed that this informational measure is related to the chemical reactivity [26,27]; in 1995 a similar expression for the Onicescu's energy was

proposed as a disequilibrium measure [28], this last one measure has been used profusely in the field of the statistical complexity [29-42].

On the other hand, to apply Eq. (7) is necessary select a scheme of occupation numbers that fulfills the informational criteria [43] and also fulfills with the invariant rotational criterion [44-46], such property permit us to obtain a population analysis without a strong dependency of the basis sets or methods.

In the follow section we present the results of  $I_{corr}$  applied to atomic and molecular systems.

## 2. Results of informational energy in atoms and molecules

In this letter, we present two study cases: (i) atoms in their basal state, where we analyzed the effect of the methodology and basis set on the correlation measure proposed in this work and (ii) a large set of molecules and compare  $I_{corr}$  with  $E_{corr} = E_{CISD} - E_{HF}$ . All the calculations of energy were done with Gaussian 09 [47] and the occupation numbers were performed with NBO 5.0 [48].

### 2.1. Atoms

In this section, we present the results of Eq. (6) with the first fifty-four neutral atoms of the periodic table using the basis set DGDZVP and with the first thirty-six atoms with the basis sets 6-311G, 6-311+G, 6-311++G, 6-311G\*, 6-311G\*\*, 6-311+G\*, 6-311+G\*\*, 6-311++G\* and 6-311++G\*\*, in both cases we used CCSD(full) and CISD(full).

In Fig. 1 we present the general trends of  $I_{corr}$  and the correlation energy for the first fifty-four elements in their basal state. The calculations of  $I_{corr}$  and  $E_{corr}$  were performed with CISD(full), CCSD(full) and the basis set DGDZVP. The trends obtained of  $I_{corr}$  have a periodic variation according to the periodic table, each step in Fig. 1 correspond to the periods of the periodic table, but this measure, in contrast with the correlation energy, also can separate the atoms respect to their block, that is, the values of the second step of  $I_{corr}$  in Fig. 1 correspond to Li and Be; meanwhile the third step correspond to block *p* elements: B, C, N, O, F, and Ne. The same observation is for the rest of the elements. In this Figure, we noted a numerical inconsistency only for the yttrium, this anomaly could be attributed to a bad description of the population analysis with this basis set used.

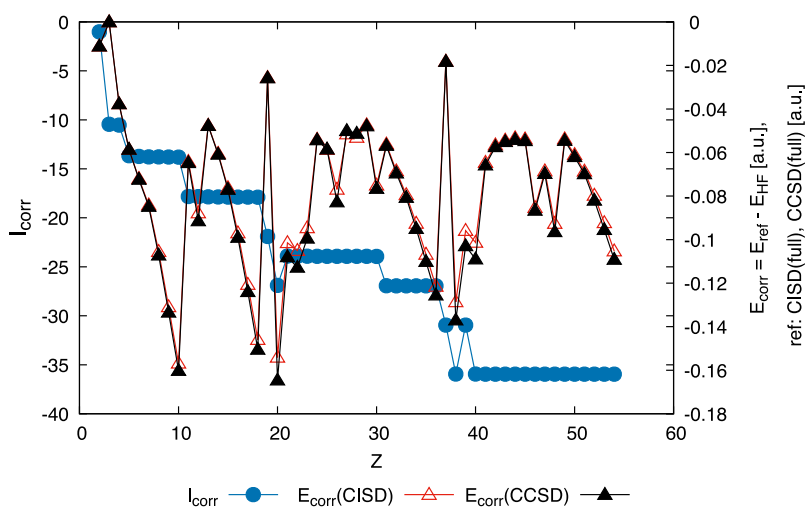


Fig. 1. General trends of  $I_{corr}$ , and the correlation energy,  $E_{corr} = E_{ref} - E_{HF}$ , where  $E_{ref} = E_{CISD(full)}, E_{CCSD(full)}$  with the basis set DGDZVP.

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