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# Non-Extensive Entropies on Atoms, Molecules and Chemical Processes

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Additional information is available at the end of the chapter

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## 1. Introduction

During the last decade, information theory [1] as applied to the basic sciences has taken two routes in the study of physical and chemical systems, considering both extensivity and non-extensivity - these concepts are fundamental to the development of new physical theories that try to describe the behaviour of natural systems. In this sense, non-extensivity is an important concept that it is necessary to incorporate into the description of atoms, molecules and chemical processes.

At present, one of the ways to incorporate the concept of non-extensivity is by using deformed entropies, or Tsallis entropy [2]. This entropy is a generalization of Shannon entropy and has a dependency of a parameter, usually denoted by " $q$ " and generally called a 'non-extensivity parameter', that permits us to perform a modulation between extensive and non-extensive behaviour. These new kinds of entropies are built using a new area of mathematics called " $q$ -algebra", or "deformed algebra" [3–5]. One important aspect to the use and application of deformed entropy is that the original definition of the entropy used for building deformed entropy needs to be strictly positive over all space and dimensionless. As such, in this work we propose a definition that fulfils this. This entropy uses the electron density obtained by the methods of quantum mechanics - this is an important point because the electron density is an observable, and so this permits us to establish a gate between the non-extensivity of classic entropies and the non-extensivity of quantum entropies. Consequently, this entropy permits us to incorporate the important concept of non-extensivity in quantum theory. In the same way, it is known that the chemistry interpretation of the same behaviour of these systems can be enriched by quantum information theory.

As we will show in this work, it is trivial to obtain some important functionals using deformed entropies. In this sense, we show how, with simple mathematical manipulations, it is possible to obtain two of the most important functionals of physics - the kinetic energy

functional of the Thomas-Fermi [6, 7] model, and the exchange energy functional of Dirac from deformed entropy. In our opinion, this opens the door to exploring the possibility of the generation of density functionals based in entropic criteria. Moreover, we will present a simple chemical process where we show the effect of the non-extensive parameter, and in the same way we present the general trends of the “ $q$ ” parameter for the first 54 atoms of the periodic table. Finally, we might raise a general question that motivates this work, that is, when does a natural system become extensive or non-extensive? As we mentioned above, this parameter “ $q$ ” has a strong relation with deformed algebra - in this algebra, all the operations have a dependence upon a parameter, “ $q$ ”, and in general when “ $q$ ” is different to that of the unit, this implies that their basic properties are not completely separable and do not necessary commute. This causes us to raise a general question, namely, can nature be represented by deformed algebra? In this context, it is necessary to incorporate the concept of non-extensivity to rewrite many expressions in terms of deformed algebra and investigate their new properties.

## 2. Theoretical background

Since the 1980s, when the first applications of Shannon entropy to chemical systems were made, we might observe two basic definitions of it, namely

$$S = - \int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r}, \quad (1)$$

and

$$S = - \int \frac{\rho(\mathbf{r})}{N} \ln \frac{\rho(\mathbf{r})}{N} d\mathbf{r}, \quad (2)$$

where  $\rho(\mathbf{r})$  is the electron density subject to  $\int \rho(\mathbf{r}) d\mathbf{r} = N$ , and  $N$  it is the electron number of the system. However, if we perform a dimensional analysis, we immediately note that neither definition of Shannon entropy is dimensionless; in addition, and in our opinion, the more serious deficiency is that neither definition is strictly positive over all space<sup>1</sup>. Given this situation, it is evident that we cannot apply these two initial definitions to chemical systems. Accordingly, we propose a redefinition of Shannon entropy [8], such that

$$S = - \int \frac{\rho(\mathbf{r})}{N} \ln \frac{\rho(\mathbf{r})}{\rho_{\max}} d\mathbf{r}, \quad (3)$$

where  $\rho_{\max}$  is the electron density in the nuclei position. In the case of a molecular system  $\rho_{\max}$ , it is necessary to take the higher value of the electron density of all the atoms that constitute the molecule. This definition fulfils the following: it is dimensionless and strictly positive over all space. In this sense, we suggest the use of the definition (3) for entropy calculations of chemical systems.

<sup>1</sup> A more detailed study of this aspect will be presented elsewhere.

On the other hand, in general the entropy of a composed system is very often equal to the sum of all its parts. This is fulfilled only when the energy is the sum of the parts and if the work performed by all the parts is the sum of the work performed by the system. That is,

$$S(A, B) = S(A) + S(B), \quad (4)$$

or in general,

$$S(A, B, C, \dots) = S(A) + S(B) + S(C) + \dots, \quad (5)$$

However, this is not quite obvious, and in some cases this may not be fulfilled. For example, consider a system composed of two different homogeneous substances - in this case, it is only possible to express the energy as the sum of the individual energies if, and only if, we neglect the interaction energy of the substances or subsystems. However, this energy plays an important role in the description of natural systems; unfortunately, the mathematical development of it is, frequently, complicated. One interesting aspect of entropies involves entropic balances [9], in which it is possible to write the joint entropy in terms of the subsystems' entropy and conditional entropy,

$$S_q(A + B) = S_q(A) + S_q(B|A) + (1 - q)S_q(A)S_q(B|A) \quad (6)$$

where

$$S_q(A) = - \iint \frac{\rho(\mathbf{a}, \mathbf{b})}{N_{AB}(q-1)} \left[ 1 - \left\{ \int \frac{\rho(\mathbf{a}, \mathbf{b})}{\rho_{\max}^A N_B} d\mathbf{b} \right\}^{q-1} \right] d\mathbf{a} d\mathbf{b}, \quad (7)$$

$$S_q(B|A) = - \iint \frac{\rho(\mathbf{a}, \mathbf{b})}{N_{AB}(q-1)} \left[ 1 - \left\{ \iint \frac{\frac{\rho(\mathbf{a}, \mathbf{b})}{N_A + N_B}}{\int \frac{\rho(\mathbf{a}, \mathbf{b})}{\rho_{\max}^A N_B} d\mathbf{b}} d\mathbf{a} d\mathbf{b} \right\}^{q-1} \right] d\mathbf{a} d\mathbf{b}, \quad (8)$$

where  $\rho_{\max}^A$  and  $\rho_{\max}^B$  are the maximum density values of the fragments<sup>2</sup>  $A$  and  $B$ , respectively.  $N_{AB}$  is the total electron number and  $N_A$  and  $N_B$  are the electron numbers of the fragments  $A$  and  $B$  respectively. The marginal densities of the probabilities are defined as

$$\int \rho(\mathbf{a}, \mathbf{b}) d\mathbf{a} = \rho(\mathbf{b}), \quad (9)$$

$$\int \rho(\mathbf{a}, \mathbf{b}) d\mathbf{b} = \rho(\mathbf{a}), \quad (10)$$

and these densities fulfil

<sup>2</sup> This implies that it is necessary to select an electron density partition scheme subject to the rules of information theory. In chemistry, the scheme that fulfils this is the Stock-Holder partition scheme [10, 11].

$$\iint \rho(\mathbf{a}, \mathbf{b}) d\mathbf{a} d\mathbf{b} = 1, \quad (11)$$

$$\int \rho(\mathbf{a}) d\mathbf{a} = 1, \quad (12)$$

$$\int \rho(\mathbf{b}) d\mathbf{b} = 1, \quad (13)$$

In all cases,  $S_q$  satisfies the following properties,

- i)  $S_q \geq 0$ ;
- ii)  $S_q$  is a continuous function of  $\rho(\mathbf{a}, \mathbf{b})$ ,  $\rho(\mathbf{a})$  or  $\rho(\mathbf{b})$ ;
- iii)  $S_q$  increases monotonically with the particle number;
- iv)  $S_q(A, B) = S_q(A) + S_q(B) + (1 - q)S_q(A)S_q(B)$ ;

From the last paragraph, it is possible to think in terms of the use of linear description; in this sense, Tsallis proposes a generalization of Boltzmann-Gibbs entropy, using the so-called 'deformed functions', and substituting the original definitions by the deformed definitions. In general, two definitions are used, namely the deformed logarithm (or  $q$ -logarithm)

$$\ln_q x := \frac{1 - x^{q-1}}{q - 1}, \quad (14)$$

and the deformed exponential (or  $q$ -exponential)

$$\exp_q^x := [1 + (1 - q)x]^{\frac{1}{1-q}}, \quad (15)$$

These definitions can be obtained by solving the differential equation  $\frac{dy}{dx} = y^q$ ,  $y(0) = 1$ ;  $q \in \mathbb{R}$ , see [12].

Using the deformed logarithm, we can obtain the deformed entropy, which has the following explicit form

$$\begin{aligned} S_q &= - \int \frac{\rho(\mathbf{r})}{N} \ln_q \frac{\rho(\mathbf{r})}{\rho_{\max}} d\mathbf{r}, \\ &= - \int \frac{\rho(\mathbf{r})}{N} \left[ \frac{1 - \left( \frac{\rho(\mathbf{r})}{\rho_{\max}} \right)^{q-1}}{1 - q} \right] d\mathbf{r}, \\ &= \frac{1}{1 - q} + \frac{1}{N(q - 1)\rho_{\max}^{q-1}} \int \rho(\mathbf{r})^q d\mathbf{r}, \end{aligned} \quad (16)$$

where  $q \in \mathfrak{R}$ , and for a composed system, this entropy is

$$S_q(A + B) = S_q(A) + S_q(B) + (1 - q)S_q(A)S_q(B), \quad (17)$$

This implies that the subsystems are correlated, and immediately we can note that for  $q \neq 1$  the entropy of a composed system is non-extensive, though if we select  $q \rightarrow 1$ , then the definition (16) becomes the definition (3), that is,

$$\lim_{q \rightarrow 1} \left\{ \frac{1}{1 - q} + \frac{1}{N(q - 1)\rho_{\max}^{q-1}} \int \rho(\mathbf{r})^q d\mathbf{r} \right\} = - \int \frac{\rho(\mathbf{r})}{N} \ln \frac{\rho(\mathbf{r})}{\rho_{\max}} d\mathbf{r}, \quad (18)$$

and recover the extensive behaviour.

Now, using Eq. (16), if we select that  $q = \frac{4}{3}$ , we obtain

$$S_{q=4/3} = -3 + \frac{3}{N\rho_{\max}^{1/3}} \int \rho(\mathbf{r})^{4/3} d\mathbf{r}, \quad (19)$$

In this expression, we can note immediately that the integral has the same form as that of the exchange functional of Dirac, and if we select that  $q = \frac{5}{3}$ ,

$$S_{q=5/3} = -\frac{3}{2} + \frac{3}{2N\rho_{\max}^{2/3}} \int \rho(\mathbf{r})^{5/3} d\mathbf{r}, \quad (20)$$

this integral corresponds to the Thomas-Fermi kinetic energy functional. Consequently, it is trivial to obtain any density functional that involves some of the powers of electron density. Naturally, it is a simple matter to rewrite both functionals in terms of the deformed entropy - this allows us to hypothesize that the electronic energy of a system can be rewritten as a linear combination of deformed entropies. This, of course, implies that the local density functionals are a particular case of the deformed entropy. This allows us to raise the following question: for any electron density, to what does the value of  $q$  correspond?

The definition (16) can be simplified if we perform a series expansion of the term  $\left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right)^{q-1}$ ,

$$\begin{aligned} \left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right)^{q-1} &= \frac{\rho_{\max}}{\rho(\mathbf{r})} + \frac{\rho_{\max}}{\rho(\mathbf{r})} \log \left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right) + \\ &\quad \frac{\rho_{\max}}{2\rho(\mathbf{r})} \log \left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right)^2 + \frac{\rho_{\max}}{6\rho(\mathbf{r})} \log \left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right)^3 + \dots + \\ &\quad \frac{\rho_{\max}}{n!\rho(\mathbf{r})} \log \left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right)^n, \end{aligned} \quad (21)$$

and if we suppose that only the first term contributes to the general behaviour and that it is the most important term,

$$\left(\frac{\rho(\mathbf{r})}{\rho_{\max}}\right)^{q-1} \sim \left(\frac{\rho_{\max}}{\rho(\mathbf{r})}\right), \quad (22)$$

Replacing this in Eq. (16), namely

$$\begin{aligned} S_q^{\text{approx}} &= - \int \frac{\rho(\mathbf{r})}{N} \left[ \frac{1 - \left(\frac{\rho_{\max}}{\rho(\mathbf{r})}\right)}{1 - q} \right] d\mathbf{r}, \\ &= \left[ \frac{1}{q - 1} + \frac{\rho_{\max}}{N(1 - q)} \right] \int d\mathbf{r}, \end{aligned} \quad (23)$$

this is a good result, because it is possible to perform a simple computational implementation of  $S_q^{\text{approx}}$  and explore the behaviour of those very large systems for which the *ab initio* calculations of the electron density are very expensive (for example, for systems constituted by more than  $10^4$  atoms). This definition satisfies the condition of the dimensionless of the entropy.

### 3. Characterization of atoms in the basal state

One of the principal questions that emerges in this study is concerned with the parameter “ $q$ ”, namely, for an atomic system in a basal state, what is its  $q$  value? For this, we calculated the electron density in the position space using the following functionals, B3LYP, BHandH, M062x, MP2, MP3 and TPSS, and with the following *ab initio* methods, CCS, CCSD, CISD, using a standard quantum chemistry program, Gaussian 09 [13], with the basis set DGDZVP [14, 15], to obtain the energy value and the corresponding wave function. The electron density in the position space was calculated with the DGrid program [16] using the wave function obtained through several methodologies, and for the entropy calculations we used the integration algorithm designed by Pérez-Jordá *et al.* [17] with a precision of  $1 \times 10^{-5}$ .

In the Figures 1(a) - 1(f)), we show the results of  $S_q$  using  $q = 0.9, 1.1, 1.3, 1.5, 1.7, 1.9$ , in which we note that the entropy has no dependence upon the methods, and it is possible to recognize the periodicity of the elements in the periodic table. Naturally, when the  $q$  parameter changes, the difference is magnified between the different periods of the periodic table; however, with the atoms that involve *d*-orbitals, we note a small disruption in this tendency. In general, we can observe that the Shannon entropy increases with respect to the atomic number in a natural way, if we appeal to the interpretation of this information measure, we can specify that the content of the information tends to increase. This assumption is based on the follow interpretation: if we consider an ideal gas, this system has a uniform particle distribution; therefore, the entropy is maximum. As such, we expect that the entropy increases in proportion to the electron number -in principle- and, considering the physics of the system, when the number of particles increases the Shannon entropy tends to the Thomas-Fermi limit as a consequence of a decrease in the Wigner-Seitz radii [18]. Thus, the definition proposed in this work permits us to recover the original idea of the content of

the information of a system in relation to the physical interactions between the electrons of systems, such that when the number of particles,  $N$ , tends to infinity,  $q$  will tend to the unit.

On the other hand, if we consider a system in a basal state and in equilibrium, what is the value of the parameter  $q$ ? To address this question, we propose a computational form to find this value,

$$q_{i+1} = q_i + \frac{S_{q_i}}{S_{q_{i+1}}}, \quad (24)$$

This approximation requires that  $S_{q_i} \approx S_{q_{i+1}}$  - when this condition occurs, it also satisfies that  $\left(\frac{\partial S_{q_i}}{\partial q_i}\right) \approx \left(\frac{\partial S_{q_{i+1}}}{\partial q_{i+1}}\right)$ . With this assumption, the slope of  $S_q$  tends to zero, and this corresponds to the zone where  $q$  does not change. This will be the  $q$  value for the system; moreover, we can fix the precision with  $1 \times 10^3$  and the error was calculated as

$$\%Error = \left| \frac{S_{q_{i+1}} - S_{q_i}}{S_{q_{i+1}}} \right|, \quad (25)$$

Given this consideration, we obtain the trends shown in Figure (2), where the general trend for  $q$  was calculated using the functionals B3LYP, TPSS and M062x, and with the wave function methods CCS, CCSD, MP2, MP3 and CISD with the basis set DGDZVP. In this figure, we note that only for the block  $d$  of the periodic table the tendency of  $q$  parameter, has a breaking of the tendency, this would be attributed to the basis set, but in respect to the methodologies the general trend of  $q$  permanence without considerable changes, this permit us establish that the  $q$  values has not a dependency of the methodologies. It is important to note that, according to the physics of the system, we expect that when the system sees a considerable increase in the number of electrons, the general behaviour will be like that of a Fermi gas, and consequently the system becomes an extensive system. This implies that the entropy becomes extensive, that is  $q \rightarrow 1$ , and that Eq. (16) becomes as in Eq. (3). From these results, we also obtain that

$$\lim_{q \rightarrow q^{op}} S_q = 1. \quad (26)$$

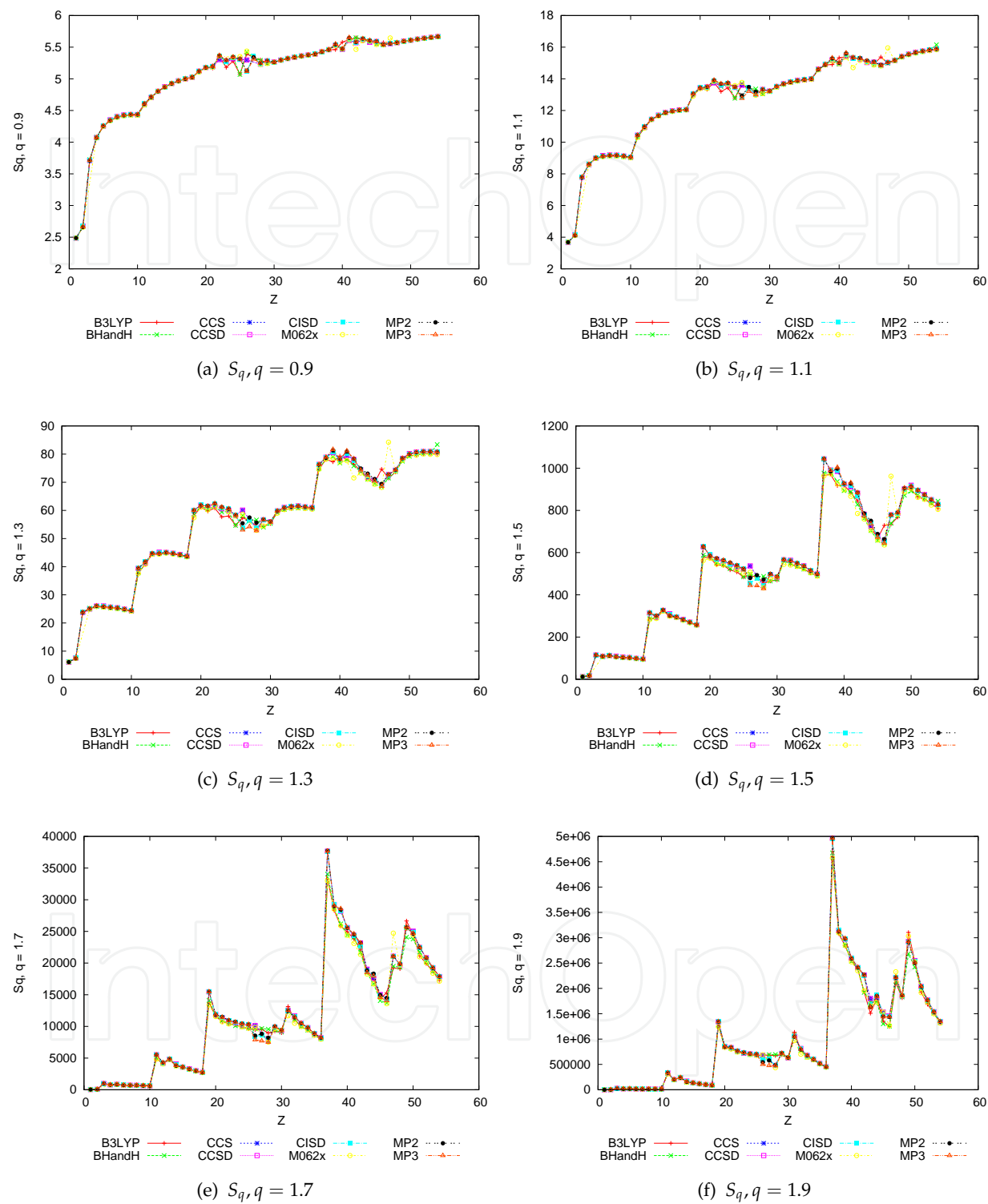
In the Figure (3) we present the general trend of  $q$  with CCSD/DGDZVP with dotted-crosses, and the following polynomial,

$$f(q) = C_1 + C_2 \exp\{-C_3 Z + C_4\} + C_5 \exp\{-C_6 Z^2 + C_7\}, \quad (27)$$

with a continuous line, where the coefficients have the values listed in Table (1).

$Z$  denotes the atomic number, and in Table (2) we show the  $q_{opt}$  values for the first 54 atoms of the periodic table. Analysing the values of this table, we note that in all cases the characteristic value of each atom in the basal state is close to the unit when the electron number increases.





**Figure 1.** Effect of the variation of the parameter  $q$  for the trends of entropy, using several methodologies of quantum chemistry with the DGDZVP basis set.

$$\begin{aligned}
 C_1 &= 1.0055300 \\
 C_2 &= 0.0526141 \\
 C_3 &= 0.9959850 \\
 C_4 &= 0.2739020 \\
 C_5 &= 0.0738875 \\
 C_6 &= 0.1080680 \\
 C_7 &= 0.3578360
 \end{aligned}$$

**Table 1.** Values of the constants of Eq. (27).

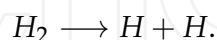
Z	$q_{opt}$	Z	$q_{opt}$	Z	$q_{opt}$	Z	$q_{opt}$
1	1.1597116	15	1.0219020	30	1.0123013	44	0.9981021
2	1.1383104	16	1.0207019	31	1.0120013	45	1.0004019
3	1.0920058	17	1.0198019	32	1.0117012	46	1.0087011
4	1.0698041	18	1.0190017	33	1.0113013	47	1.0085011
5	1.0556034	19	1.0178018	34	1.0110012	48	1.0086010
6	1.0470029	20	1.0178016	35	1.0109012	49	1.0083010
7	1.0409027	21	1.0198014	36	1.0107012	50	1.0081010
8	1.0364026	22	1.0037026	37	1.0107012	51	1.0080010
9	1.0332024	23	1.0106020	38	1.0104011	52	1.0079010
10	1.0306023	24	1.0035025	39	1.0036017	53	1.0077009
11	1.0277023	25	1.0016026	40	1.0144007	54	1.0076009
12	1.0268022	26	1.0095018	41	0.9954024		
13	1.0246022	28	1.0132014	42	1.0024017		
14	1.0228021	29	1.0105015	43	0.9947024		

**Table 2.** Values of  $q_{opt}$  using CCSD(full)/DGDZVP.

#### 4. Characterization of a Simple Chemical process

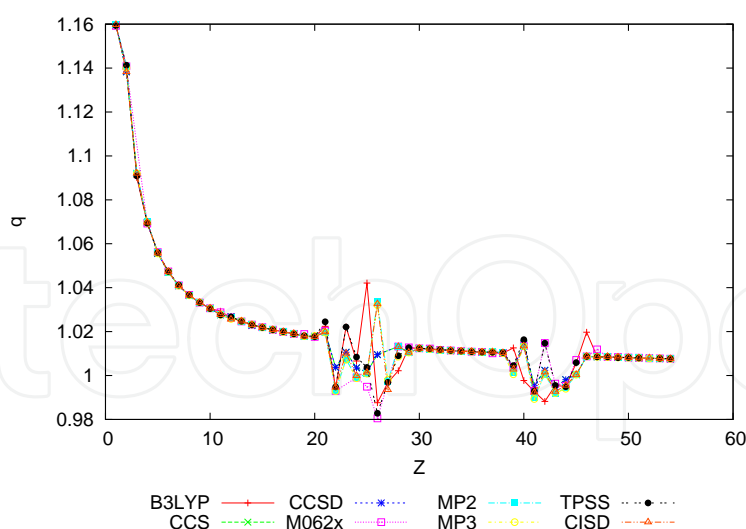
One of the interests of this work is in the study of the effect of the parameter “ $q$ ” in a dissociation process. The idea is to study the effect of small interactions when a homonuclear system is dissociated.

In this case, we select the dissociation of the  $H_2$  molecule,

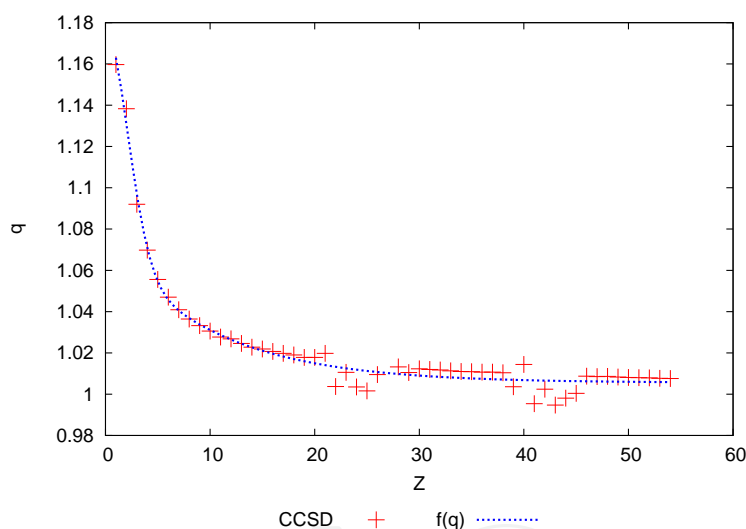


The calculations were performed with Gaussian 03 [19] with CCSD(full) and the basis set cc-pVTZ [20]. For the entropy calculations, we used the wave function generated by Gaussian 03 to generate the electron density, while  $\rho_{\max}$  was calculated in the position of the nuclei of each atom of the molecular system, in this case by the symmetry  $\rho_{\max}(A) = \rho_{\max}(B) = \rho_{\max}$ . The electron density was calculated with DGrid and the algorithm of integration that we used was designed by Pérez-Jodá *et al.* with a precision of  $1 \times 10^{-5}$ .

In Figure (4), we present the general trend of this simple chemical process, where we can note that the internuclear equilibrium distance is 0.754 Å, which corresponds to the minimum electronic energy; the dissociation process was carried out more than two times the van der



**Figure 2.** Trends of the parameter  $q$  for the atoms  $1 < Z < 54$  using several methodologies with the basis set DGZVP; all calculations were performed in Gaussian 09.



**Figure 3.** Trends of the parameter  $q$  for the atoms  $1 < Z < 54$ , with CCSD(full)/DGDZVP in Gaussian 09.

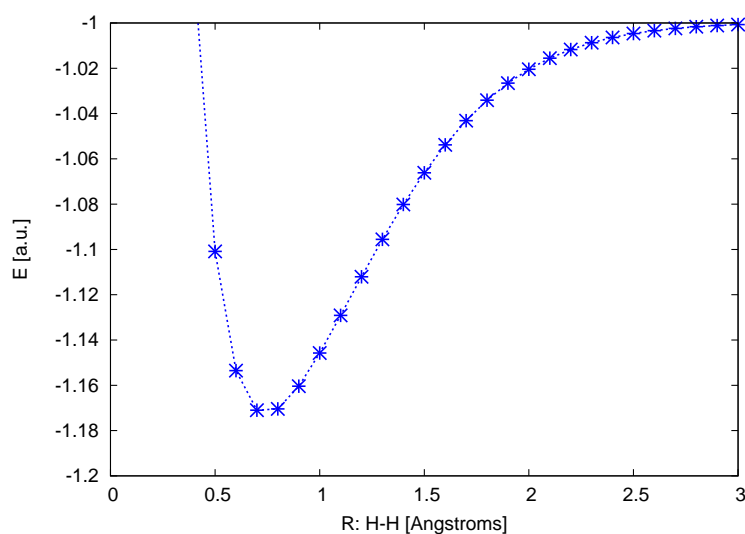
Waals radii of the hydrogen atom in the basal state ( $1.2 \text{ \AA}$ ) to ensure that no weak chemical interactions were present. With this in mind, in this case it is natural to think that, for an internuclear distance of  $3.0 \text{ \AA}$ , the electronic energy will be twice that of the electronic energy of the hydrogen atom in the basal state; however, this does not occur, and the value obtained with CCSD(full)/cc-pVTZ is  $-1.0007258069 \text{ a.u.}$  Consequently, there exists a difference of  $0.0007258069 \text{ a.u.}$  ( $1.9056 \text{ kJ/mol}$ ) - this energy value is closer to that of hydrogen bonding. In principle, the explanation of this anomaly can be addressed in the following way: by definition, the wave function is extended over all space, and by construction the wave function used in a quantum mechanics calculation is a finite superposition of the basis set functions,  $\psi = \sum_i^n \chi_i \phi_i$ . However, notwithstanding that, in a limit this function will be exact, the correct description obtained with this wave function will be correct only in the equilibrium. This condition is not obvious, and how we see is not fulfil, this probable

permit us talk about of a necessity of a different statistical ensemble for the more adequate description of the systems, and with this new ensembles possible we can describe of a more appropriate some phenomena present in the quantum world. The real justification for proposing (and postulating) the existence of this new set of definitions will reside in their implications, namely the incompleteness of the descriptions obtained by the actual tools and theories.

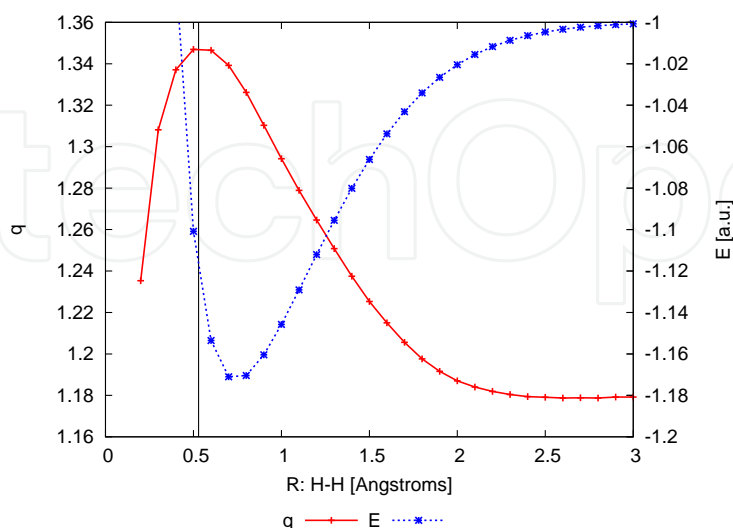
In Table (3), we present the values of the electron energy for the hydrogen molecule at an internuclear distance of 3.0 Å using several methodologies of quantum chemistry, and with the basis sets cc-pvDZ, cc-pvTZ, cc-pvQZ and cc-pv5Z. The basis sets are designed to converge systematically on the complete basis set, such that this basis set permits us to analyse the improvement of the electron energy, and we note that the best result that we can obtain corresponds to CCSD(full)/cc-pvTZ. However, even using this sophisticated methodology and basis set, there exists an excess energy of 0.0012563951 a.u. (3.2986 kJ/mol). Here, it is convenient to observe that it is not necessary to make use of a bigger basis set corresponding to a better description (again, this is in reference to Tables (3) and (4), in which the best energy value corresponds to CISD/cc-pvTZ and not to cc-pv5Z, which is the more complete basis set of all those used in this work). In all cases, all the methodologies and basis sets overestimate the energy over large distances, but in the case of MP2, PBE and B3LYP, the overestimation is of the order of the energy of a simple covalent bond, such as an oxygen molecule (145 kJ/mol), or a simple bond of a nitrogen molecule (170 kJ/mol).

On the other side, and continuing our discussion, in Figure (4) we observe that the system can be additive but not necessarily extensive. To explain this in the Figures (6(a)-6(f)), we present a comparison of the electron energy and the deformed entropy using several  $q$  values, where we note that for different  $q$  values the minimum of the entropy change of the position, for  $q = -4.1, -2.8, 0.3, 1.5, 1.8$  and a distance greater than of 2.0 Å, the slope of tendency it is zero, that is, the entropy is constant and consequently it is additive, but not extensive, because for a this values,  $S_q$  is constant, now if we consider that this system its constituted by identical subsystems we have,  $S_q(A, B) = S_q(A) + S_q(B) + (1 - q)S_q(A)S_q(B)$  and by the system characteristics  $S_q(A) = S_q(B)$  so we have  $S_q(A, B) = 2S_q(A) + (1 - q)[S_q(A)]^2$ . This opens the door to an interesting question: in physical systems, it is the same additive that extensive? In our opinion, they are different concepts and it is probable that the use of these concepts as synonyms is a result of the historical background. It is interesting to note that, for  $q = -2.8 = -14/5$ , the minimum of the entropy corresponds to the minimum of the energy (see Figure (6(b))); consequently, if we find the appropriate  $q$  value for the system, it is possible to reproduce the electron energy behaviour. The interesting aspect of this is that the deformed entropy, that it is a local functional (because has not dependency of external potential), that we can found the same tendencies of the energy in which are present the effects of an external potential. Another notable characteristic of this tendency is presented in Figure (6(c)), where in the final state of the system the slope again tends to zero but the total entropy is greater than the initial content. This implies that the term  $(1 - q)S_q(A)^2$  is greater than  $2S_q(A)$ , and if we retake the interpretation of the term  $(1 - q)S_q(A)^2$  then, like the degree of non-separability, we can conclude that the representation of the system with  $q = 0.3$  is non-extensive over all processes, even if the internuclear distance implies that the system has no physical interactions. This is consistent with the interpretation that the wave function is extended over all space - if we accept this, probably we can establish a link between non-extensivity and quantum entanglement [21]. Consequently, it is possible to build a bridge between quantum information theory and non-extensive statistical mechanics

and reclaim the idea that we can improve our understanding of nature by not only analysing behaviour exclusively in terms of matter and energy (even at the level of elementary particles), but also that study using the techniques and methods of modern physics and chemistry integrate concepts and tools that allow us to comprehensively investigate the behaviour of natural systems in order to deepen our understanding of them to incorporate information measures that take into account concepts such as entanglement, known since the early days of Quantum Mechanics, for which, however, there are no measures in many modern theories, at a more fundamental level, it has become clear that an Information Theory based on the principles of Quantum Mechanics, expands and complements the Classical Information Theory [22]. In addition to the quantum generalizations of classical notions such as sources, channels and codes, this new theory includes two complementary types of quantifiable data: classical information and quantum entanglement.



**Figure 4.** Trends of the electron energy of the dissociation process of  $H_2$ , with CCSD(full)/cc-pvTZ.



**Figure 5.** Comparison between the electron energy and the  $q_{opt}$  parameter for the dissociation process of  $H_2$  with CCSD(full)/cc-pvTZ.

Basis set	CCSD	CISD	MP3
cc-pVDZ	-0.99955061881	-0.99955059355	-0.98767847037
cc-pVTZ	-1.0007258067	-1.0007257401	-0.98174230596
cc-pVQZ	-1.0010904704	-1.0010905136	-0.97990255011
cc-pV5Z	-1.0012563951	-1.0012563405	-0.97874184183

Basis set	MP2	PBE	B3LYP
cc-pVDZ	-0.92566086120519	-0.937015225619	-0.933130505886
cc-pVTZ	-0.92835582370175	-0.939927619001	-0.936467455835
cc-pVQZ	-0.92932919850342	-0.940569300858	-0.937152190049
cc-pV5Z	-0.92968788957241	-0.940901783377	-0.937514589740

**Table 3.** Values of the electron energy for  $H_2$  at an internuclear distance of  $3\text{\AA}$  (in a.u.). The energy calculations were performed in Gaussian 09.

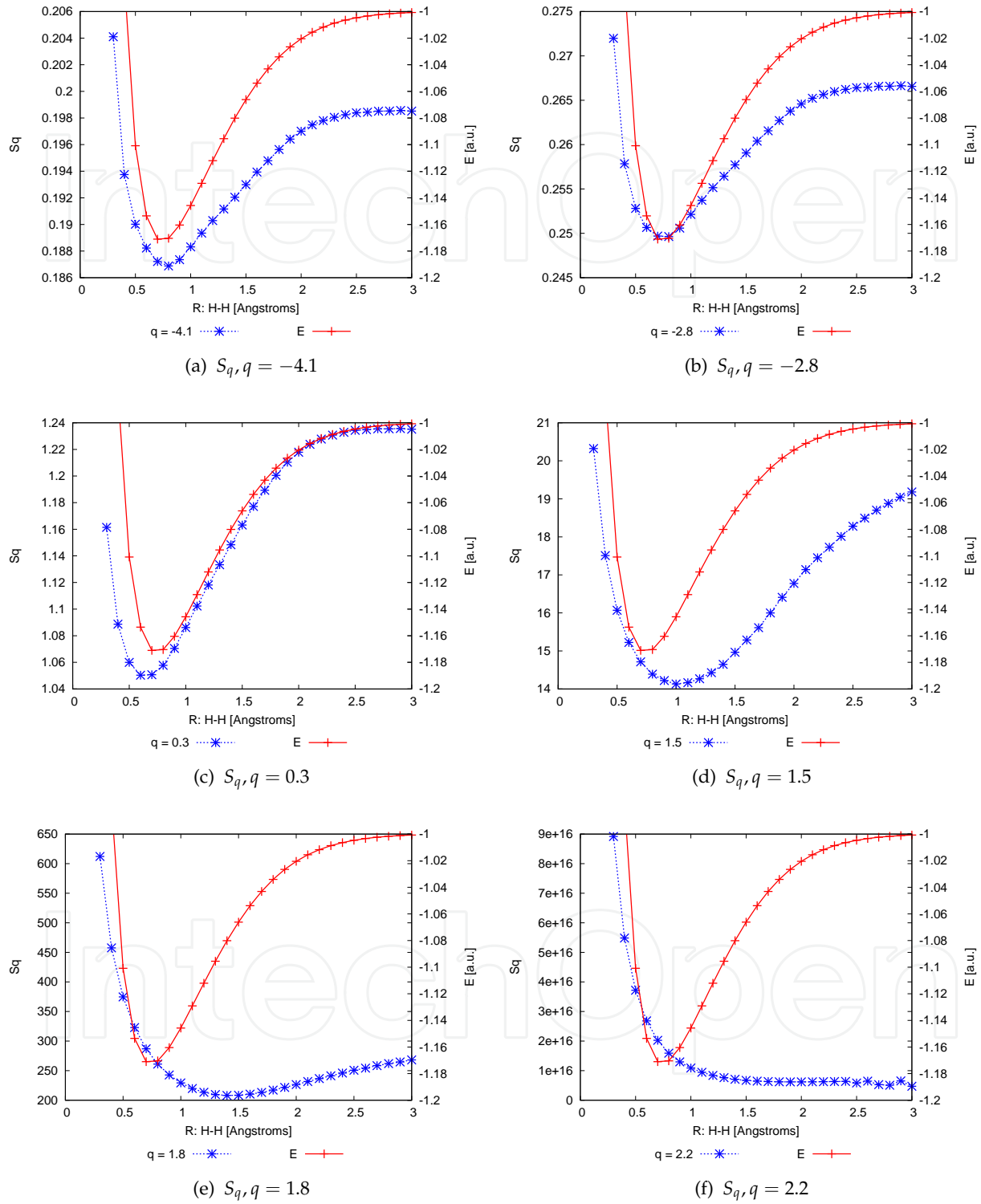
Basis set	CCSD	CISD	MP3
cc-pVDZ	1.179850	1.179916	32.350176
cc-pVTZ	1.833750	1.905430	47.935576
cc-pVQZ	2.863030	2.863143	52.765854
cc-pV5Z	3.298665	3.298521	55.813294

Basis set	MP2	PBE	B3LYP
cc-pVDZ	195.17740	165.36652	175.56585
cc-pVTZ	188.10178	157.72003	166.80469
cc-pVQZ	185.54618	156.03530	165.00692
cc-pV5Z	184.60444	155.16236	164.05544

**Table 4.** Absolute difference of values between the electron energy of  $H_2$  at  $3.0\text{\AA}$ , and  $2H$  with several methodologies and with the cc-pvTZ basis set. All values are kJ/mol.

In the Figure (5), we show the general trend of  $q_{opt}$  compared with the electron energy, in which the tendency of  $q_{opt}$  has a maximum in approximately  $0.529\text{\AA}$ , plotted as a vertical continuous black line, this value correspond at the first Bohr radii for the Hydrogen atom, this is an interesting point because it is possible talk about a non-extensive radii of the systems, where the non-extensivity it is maximum and the point of this is that the we can associate the  $q$  parameter at a physical property like the distances between the subsystems, so we suspect that the non-extensive behaviour is closely related at two characteristics; the distance and the particle number.



**Figure 6.** Comparison between the trends of the  $S_q$  entropy using several  $q$  values and the electron energy for the dissociation process of a  $H_2$  molecule.



## 5. Characterization of the Chemical Reaction $H_2 + H^-$

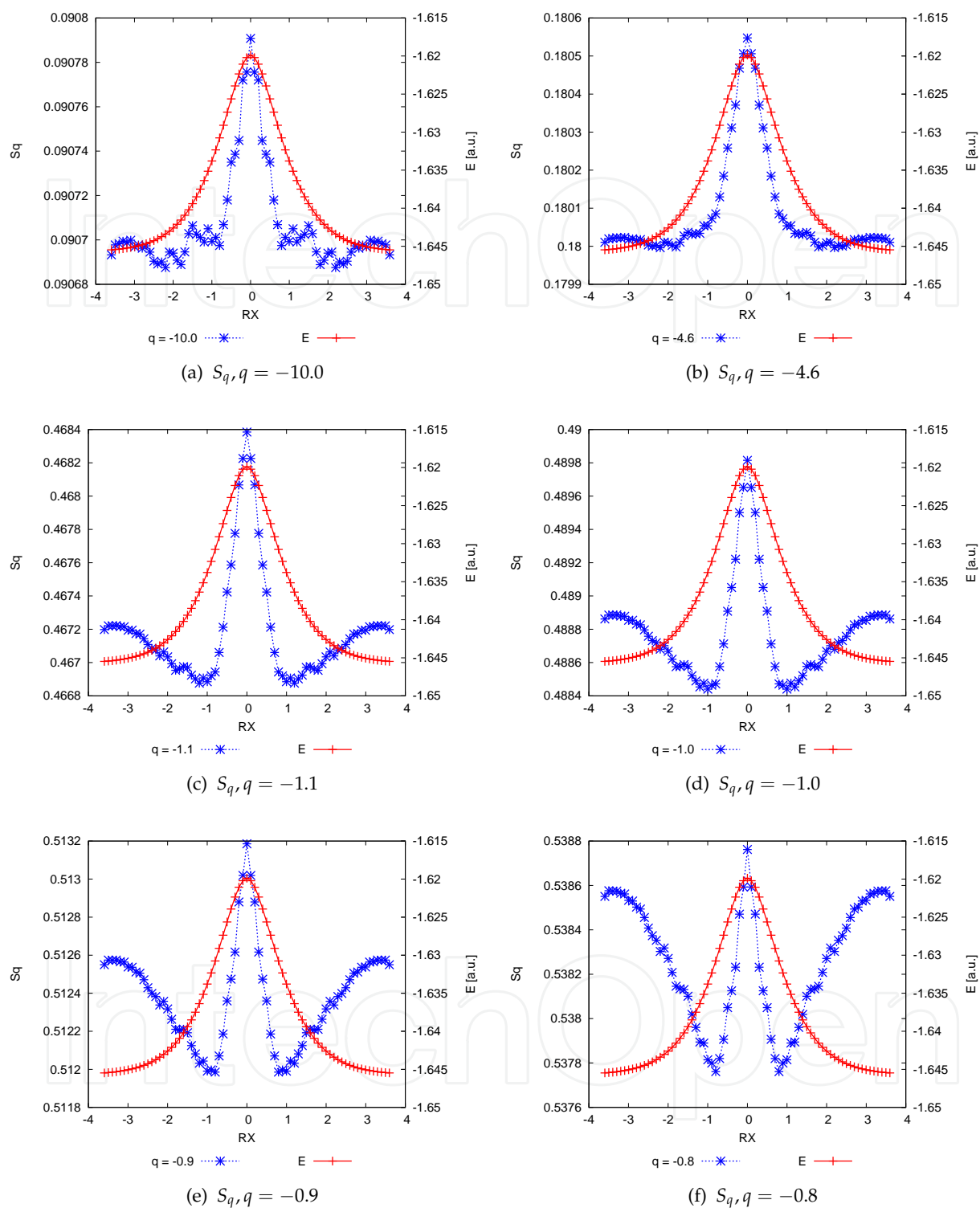
In this section, we present the results of the reaction  $H_2 + H^- \rightarrow H_2 + H^-$ . This reaction is one of the more studied reactions and it is very well-characterized [23–25]. The IRC calculation was performed with MP2(full)/6-311G, and the singles points with CISD/6-311++G\*\*, both in Gaussian 03. This reaction is symmetric, has a maximum in the transition state (which has an energy of -1.6501559031 a.u.) and an internuclear distance of 0.93236 Å between each hydrogen atom. Naturally, the electron energy in the reactants is the same as in their products (-1.6680093713 a.u.). In the Figures (7(a))–(8(f)), we present the tendency of the deformed entropy using several values of the  $q$  parameter, with  $q = -10.0$ , Figure (7(a)). The entropy has a maximum value at  $RX = 0.0$  and a possible local minimum in  $RX = -2$  and  $RX = 2$ . However, is not very clear how to determine whether this  $q$  value is associated with the changes of the entropy for some other parameters related at changes physical or chemical, when we use the  $q = -4.6$ , Figure (7(b)), the entropy tendency has a maximum value at  $RX = 0.0$  and it is similar at the tendency of the energy. The more interesting aspects of the changes in the entropy are in the interval  $-1.1 \leq q \leq 1.6$ , in Figure (7(c)); with  $q = -1.1$ , the entropy has a minimum in  $RX = -1$  and  $RX = 1$ , and these minimums are associated at a zone where the process of the breaking and forming of the chemical bonds occurs. This zone corresponds to a zone where the normal modes of vibration have negative frequencies. In Figure (9(a)), we show this comparison, and in the same way we compare this tendency with the distances of the hydrogen's involved in the process, we labeled the atoms like  $H_{in}$  for the Hydrogen that will be form the new bond and  $H_{out}$  for the Hydrogen that gonna be break the bond, in this case, the critic region where the physical changes occurs is  $-0.5 \leq RX \leq 0.5$ , see the Figure (9(b)), this only can be observed in the same zone of the entropy where has a small change in their slope, in this sense, it is possible that changing the value of  $q$  or increase the precision we can observe with more detail the changes that occurs in this zone. Figure (9(c)) presents a comparison of  $S_q, q = -0.7$  with the Dipolar Moment, how occurs in the case of the frequencies this parameter has a maximums in  $RX = -0.85$  and  $RX = 0.85$ , is it in this zone where the most important changes of the electron density occurs. In general, we can say that the changes in the deformed entropy permit us to discover some zones where the most important changes of the electron density of a system occurs; however, it is not yet known how to select the appropriate value of  $q$ , for example, when we use a value of  $q = -0.7$ , the tendency of the entropy has minimums in  $RX \sim -0.9$  and  $RX \sim 0.9$ . We can say that this tendency is related to the change of the electron density, but in the case of  $S_q, q = -0.1$  the entropy behaves like a specular image of the energy (see Figures (8(a)) and (8(c))). With this evidence, we believe that it is possible to derive some density functionals in which a combination of different entropic terms can be expressed, not only the deformed entropy with the form of Eq. (16), but also a contribution of a deformed Fisher entropy (for this, it will be necessary to write the gradient of the electron density in terms of deformed algebra). That is,

$$E[\rho] = \sum_i x_i S_q + x_i I_q, \quad (28)$$

where

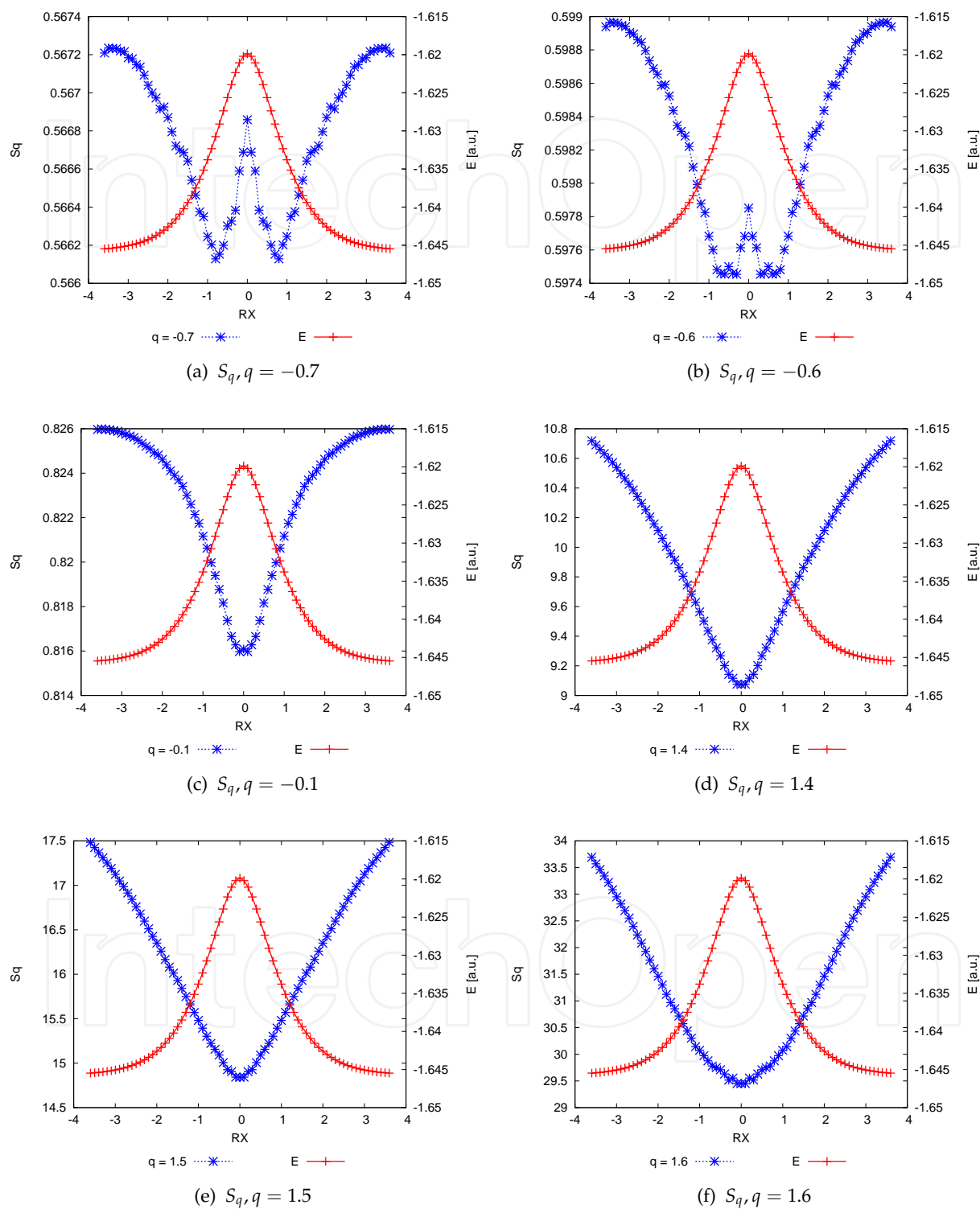
$$I_q = \int \varrho(\mathbf{r}) |\nabla \ln_q \varrho(\mathbf{r})|^2 d\mathbf{r}, \quad (29)$$



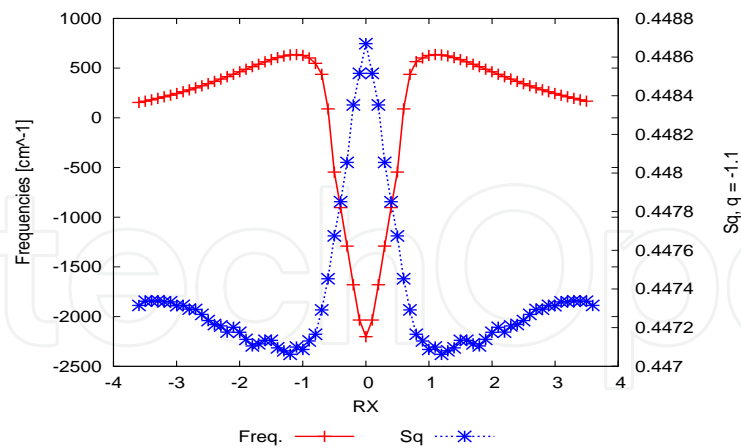


**Figure 7.** Comparison between the trends of the  $S_q$  entropy using several  $q$  values and the electron energy for the reaction  $H_2 + H^-$ .

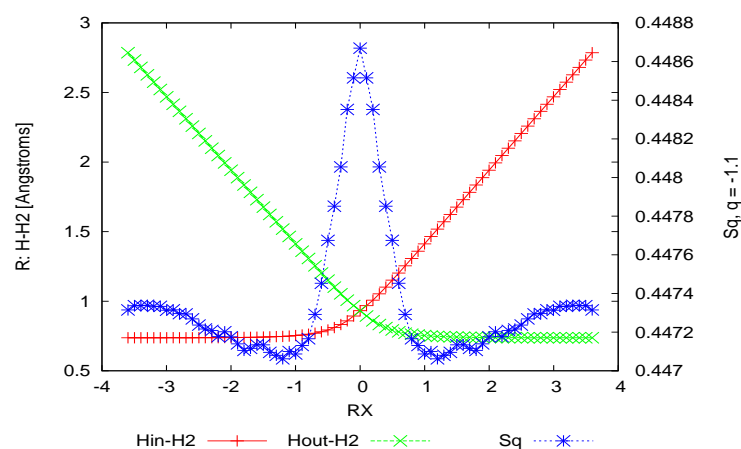
and  $\varrho(\mathbf{r})$  is the shape factor, defined as  $\varrho(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N}$ .



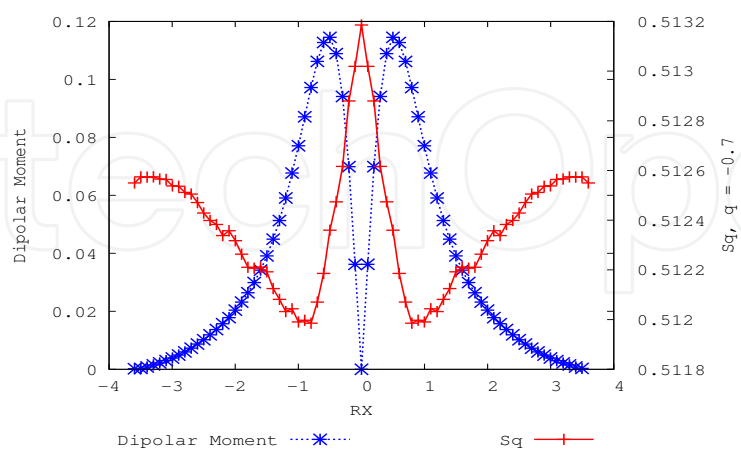
**Figure 8.** Comparison between the trends of the  $S_q$  entropy using several  $q$  values and the electron energy for the reaction  $H_2 + H^-$ .



(a)  $S_q, q = -1.1$  and Frequencies



(b)  $S_q, q = -1.1$  and Distances

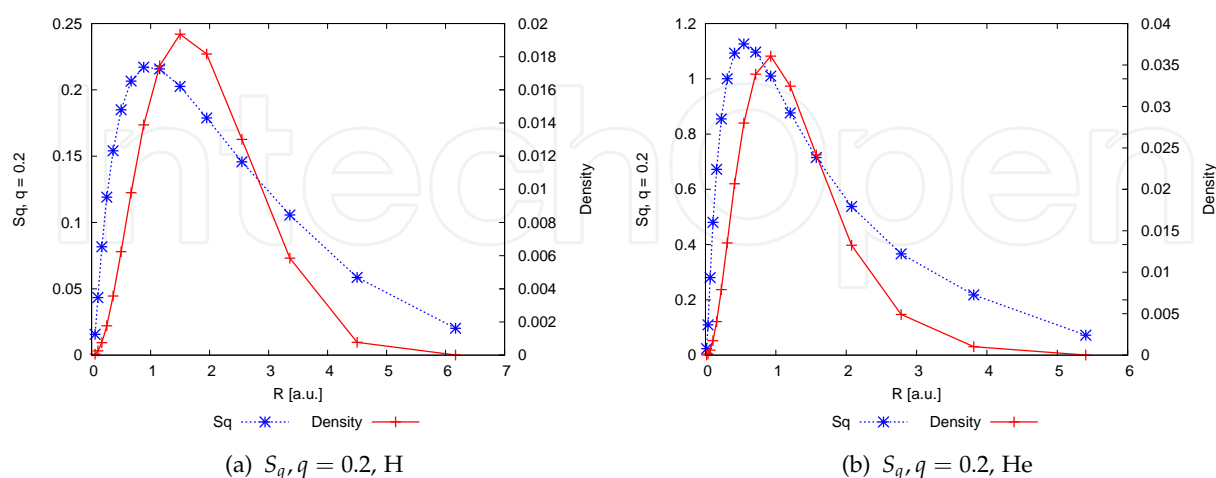


(c)  $S_q, q = -0.7$  and Dipolar Moment

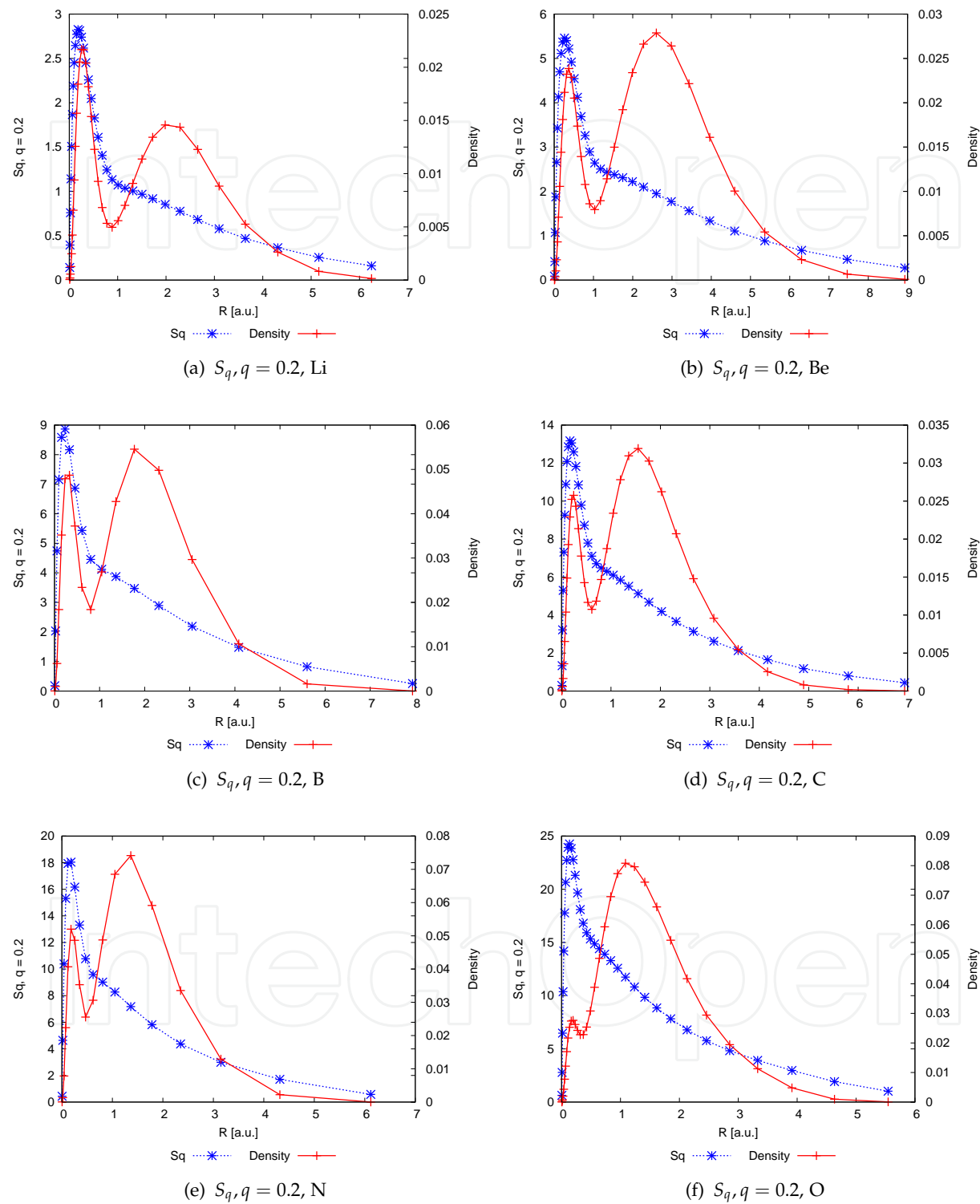
**Figure 9.** Comparison between the trends of the  $S_q$  entropy using several  $q$  values, frequencies, distances and Dipolar moment for the reaction  $H_2 + H^-$ .

## 6. Entropic profiles of atoms

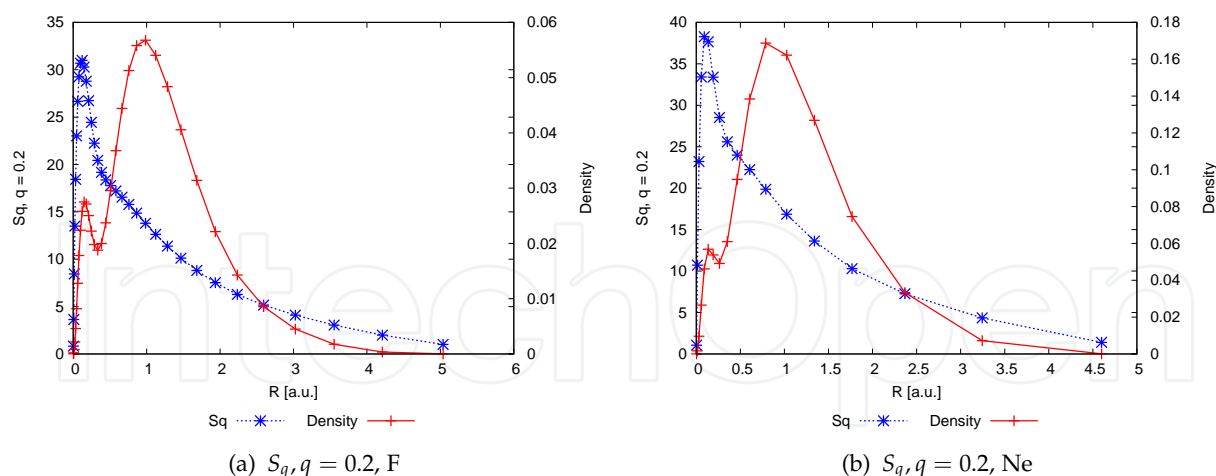
In this section, we present the results of the entropic profiles from hydrogen to neon. The density was calculated with a precision of  $1 \times 10^{-5}$  with CCSD(full)/DGDZVP obtained in Gaussian 09. It is our particular interest to characterize the hydrogen atom, because the simplicity of this system permits us to determine and - as far as possible - try to find some periodic properties. In this sense, in the Figure (10(a)), we present the entropic profile for this system, in which we note that the maximum present is in  $R \approx 1a.u.$ , that is, the first Bohr radii. It is possible to speculate that it is at this distance when the system exhibits the maximum degree of non-extensivity. In the case of He, the maximum value of the entropy is displaced close to the nucleus,  $R = 0.545a.u.$ , Figure (10(b)). For the second period (lithium to neon, Figures (11(a)-12(b))), the maximum of the entropy coincides with the first maximum of the electron density, and the minimum of the electron density coincides with the inflection point of the entropy trend; subsequently, in the region of the maximum density the entropy there is a small change in their slope. Finally, the electron density and the entropy tends to zero. In general, we also propose verifying the changes of the entropy tendency using several values of  $q$  in the interval  $0 \leq q \leq 10$  with a step size of 0.1, though we cannot observe significant changes. In this sense, it is possible that the critical points of the deformed entropy are in relation to the chemical reactivity parameters, such as the Fukui function [26–28], hardness, softness [29], [30], chemical potential, *inter alia*, [31]. However, it will be necessary to perform studies of the relation between the  $q$  parameter and these chemical descriptors. We consider that it will be important to carry this concepts into the field of deformed algebra.



**Figure 10.** Comparison between the trends of the  $S_q$  entropy with  $q = 0.2$  and the electron density for hydrogen and helium.



**Figure 11.** Comparison between the trends of the  $S_q$  entropy with  $q = 0.2$  and the electron density for lithium to oxygen.



**Figure 12.** Comparison between the trends of the  $S_q$  entropy with  $q = 0.2$  and the electron density for fluorine and neon.

## 7. Conclusion

In this work, we applied the fundamental idea of Tsallis of entropy generalization and we propose a definition of deformed entropy that is applied to the description of the first 54 atoms in the basal state of the periodic table, showing that each chemical system has a characteristic  $q$  value. Furthermore, we show that the characteristic  $q$  value can be related to the first Bohr radii, in which we suppose that there corresponds a distance where the non-extensive behaviour of the system is dominant. In the same way, we show the numerical tendencies of the deformed entropy compared to the variation of the electron density for the first 10 atoms in the basal state and observe that the changes of the deformed entropy are in relation to the significant changes in the electron density.

This has allowed us to start a new line of investigation, and with some of these results we continue with the study of the formalisms for the construction of a functional based in a principles of physics and information theory. In addition, we intend to continue with the development of models that permit us to find a direct relation between electron energy and chemical reactivity concepts with deformed entropy.

On the other hand, the application of the concepts of information theory permit us form a description that is more accurate than that based on energetic criteria alone; we speculate that it is possible to define or find a form that derives the Density Functional Theory from some fundamental expression.

Finally, with these examples we have tried to link information from a system that is subjected to a process with physical and chemical changes. Thus, we have linked the concept of *information*, which is an epistemological concept completely with ontological concepts and the interpretation of the results allows us feedback these concepts in ontological terms, according to the authors, is probable that today do not exist a orthodoxal definition of what actually is the *information*, beyond that presented by Shannon and its guidelines, criteria, characterization of it, among other things, the interpretation and the relationship with other

concepts, such as energy, electron density, chemical reactivity parameters and many others need be discussed to try of establish a formal relation between concepts.

Is it clear that information concept and the model itself is interdisciplinary or transdisciplinary. The concept of information and -moreover- the model itself promote a systematic relation with causal analogies and parallelism with scientific knowledge, which transcends the framework of the source domain and extends in various directions, thus making the knowledge acquire an unusual resonance. Accordingly, we believe it is feasible to complement the explanations of natural processes and natural systems.

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