



Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Jensen–Tsallis divergence and atomic dissimilarity for ionized systems in conjugated spaces

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ARTICLE INFO

Article history:

Received 13 August 2010

Received in revised form 13 October 2010

Available online 23 November 2010

Keywords:

Atomic one-particle densities

Singly charged ions

Jensen–Tsallis divergence

Shell-filling patterns

ABSTRACT

A generalization of the original Jensen–Shannon divergence (JSD) is presented in this work, which gives rise to a non-extensive one-parameter divergence providing a powerful dissimilarity measure between electronic distributions. The analysis performed in this study employs the JTD measure to compare one-particle densities of neutral and ionized atomic systems, that generalizes and improves some previous results based on other measures of divergence. Such an improvement mainly arises from the capability of JTD to modify, by means of its order parameter, the relative contribution of specific relevant regions of the atomic densities under comparison, in both position and momentum spaces. Relevant information of the ionization processes attending to structural pattern and periodicity is found, as well as the strong correlation between extremal values of the neutral–cation JTD and those of the atomic ionization potential. Similar conclusions are obtained from processes involving an anion. The analysis includes a study of the dependence of JTD on its order for fixed atomic couples.

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1. Introduction

In probability theory and statistics, the Jensen–Shannon divergence (JSD) is a fundamental tool for measuring the dissimilarity between two or more probability distributions [1–3]. This JSD divergence is a symmetrized and smoothed version of the most important divergence measure in information theory, the *Kullback–Leibler divergence* [4], with the notable difference that it is always finite valued. Furthermore, it has been shown that the square root of JSD defines a true metric in the space of probability distributions [5]. This means that $JSD^{1/2}$ verifies all the mathematical axioms required to constitute a metric, namely (i) non-negativity, (ii) minimal zero value only for identical distributions, (iii) symmetry, and (iv) triangular inequality, i.e. it is bounded from below and from above in terms of the norms of the distributions. The functional JSD is not a metric despite that it obeys the first three axioms, except for the last one which is certainly satisfied by its square root.

Some generalizations of this important measure of discrimination have been studied in the last years. For instance, Taneja [6,7] introduced a two-scalar parametric generalization of JSD and, more recently, Lamberti and Majtey have investigated the properties of JSD in the framework of non-extensive Tsallis statistics [8–10]. Briët and Harremoës have also studied and generalized several properties of classical and quantum JSD [11].

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Attending to these reasons among others, the JSD has recently gained interest among physicists and statisticians and it has been widely applied to the analysis of signal or symbolic sequences; in particular, successful applications to the study of segmentation of DNA sequences [12–14] and to the detection and registration of digital images [15] have been carried out.

On the other hand, the concepts of 'divergence' and 'similarity' are closely related, the latter appears to be of fundamental importance in several scientific fields. For instance, the recognition and analysis of molecular similarities serve as the basis for understanding the link between the structural features of molecules and their physical and chemical properties [16,17], graph theory has been widely used for assessing similarities in taxonomy or for detecting protein sequence homology [18]. Further, particular measures of similarity have been employed in fuzzy set theory, which have found application in areas such as management, medicine and meteorology [19]. Recently, divergence measures have been used in the framework of quantum information theory [9,10]. In particular, the JSD was applied as a measure of entanglement [20], and also together with other similarity measures [21–27] in the study of multielectronic systems [28,29]. The focus of the present work resides in studying the differences in the electron charge densities of neutral atoms and singly charged ions in their ionization processes so as to link them with their physical and chemical properties in accordance with the Hohenberg and Kohn theorem [30]. In addition, the electron density in the conjugated space, namely the momentum density, also constitutes a very rich source of information on multielectronic systems, as it has been recently shown in the context of information theory [29,31].

First, we will introduce a one-parameter generalized divergence, the Jensen–Tsallis divergence (JTD), which is constructed by simply replacing the Shannon entropy [32] by the q -order Tsallis entropy $T^{(q)}$ [8] in the JSD definition, as will be described in the next section. The Shannon entropy, a particular case of the Tsallis one as $q \rightarrow 1$, shares with the JSD the well-known additivity property from which the joint entropy of a pair of independent random variables is just the sum of the individual entropies. In the present work, we omit this property as a constraint and, instead, the non-extensive Tsallis entropy is considered in order to construct the JTD.

This generalized divergence is later applied to explore its advantages over the JSD measure to contrast the results obtained on simple but extremely organized quantum-mechanical systems such as atoms and ions. In particular, we are interested in quantifying the informational discrepancies between the one-particle electron densities of neutral atoms and singly charged ions in order to ascertain if these entropic measures of divergence may detect successfully the pattern of the ionization processes and to predict some correlation with important experimental magnitudes like the atomic ionization potential, perhaps the most relevant one for the description of ionization processes.

Computations will be performed in both conjugated spaces, namely position (r) and momentum (p), by means of the accurate near-Hartree–Fock wavefunctions of Koga et al. [33]. The reason underlying this interest is due to the Fourier transform connection between the conjugated r and p spaces, the momentum density containing relevant information on the valence region at small momentum p values, reaching its global maximum. In this manner we will explore in this case the valence region in contrast with the position space, in which the comparative study is mainly based on the behavior of the densities within the core region.

The paper is organized as follows. In Section 2 we define the Jensen–Tsallis divergence, along with the relevant electron densities under study. In Section 3.1 the dependence of the divergence on the nuclear charge Z is analyzed, and correlations with the atomic ionization potential are clearly revealed. In Section 3.2 we show the ability and power of the JTD dependence on its q parameter in order to explore different physical regions in r and p spaces. Conclusions are collected in Section 4.

2. Jensen–Tsallis divergence JTD for one-particle electronic densities

The one-particle densities of an N -electron system in position and momentum spaces, $\rho(\vec{r})$ and $\gamma(\vec{p})$, respectively, are the basic ingredients for the study of many physical properties from a density functional theory perspective [30]. The relevant role played by $\rho(\vec{r})$ in the description of many-electron systems invites us to think about the extent to which the *similarity/dissimilarity* features between the densities corresponding to two different systems could be interpreted as indicators of analogy/discrepancy also between their physical and chemical properties, as well as the best way to quantify it. The same argument applies to divergence studies of the one-particle density $\gamma(\vec{p})$ in the conjugated space, namely the momentum one because it is also a well-known source of information on the aforementioned properties [34]. In fact, the simultaneous analysis of both, the position and the momentum space densities, has been shown to provide, within different contexts, a much more complete description of the system [28,35].

It is important to mention the pioneering work of Carbó in the quantification of similarity between two molecular structures, based on quantum chemistry and on the comparison of their charge densities [17,21,26]. Afterwards, the same research group studied the theoretical framework of quantum similarity (QS). Since then, the design of novel procedures, the implementation of new algorithms and measures as well as their practical applications have been also extensively developed. In particular, the field of quantitative structure activity/property relationships (QSAR) has demonstrated that the biological activity and the physical properties of a set of compounds can be mathematically related to some simple molecular structure parameters [36].

Information entropy is a magnitude of paramount importance in the study of many-electron systems, which can be calculated in both position and momentum spaces giving a measure of the global delocalization, spread or randomness of the electronic distribution [32,37]. This fundamental functional has been extensively used as a measure of distance between two electron distributions or processes and proposed as one of the basic ingredients of the so-called complexity measures [38,39].

Some entropic measures have been proposed as indicators of *information distance* or *dissimilarity* between distributions, assumed to be normalized to unity in what follows. Probably, the most relevant measure of divergence introduced within the context of information theory is the Kullback–Leibler divergence [4]. It is defined as

$$KLD(f, g) \equiv \int f(\vec{r}) \ln \frac{f(\vec{r})}{g(\vec{r})} d\vec{r}, \tag{1}$$

for any pair of non-negative functions $f(\vec{r})$ and $g(\vec{r})$ defined over a common domain (the whole three-dimensional space in the present work) and with identical normalization, whenever the integral defining KLD converges. This functional embodies the Shannon entropy [32]

$$S(f) \equiv - \int f(\vec{r}) \ln f(\vec{r}) d\vec{r}. \tag{2}$$

The Kullback–Leibler divergence can be also interpreted as a *relative entropy* or an *entropy gain*, which are fundamental concepts of information theory and Bayesian inference.

The JSD constitutes a symmetrized version of the Kullback–Leibler measure of divergence and quantifies the entropy excess between the Shannon entropy of a mixture of two (or more) distributions and the mixture of the entropies of the distributions. It is given by [1–3,5]

$$JSD(f, g) \equiv S\left(\frac{f+g}{2}\right) - \frac{1}{2}[S(f) + S(g)]. \tag{3}$$

Some important properties and generalizations of this measure of dissimilarity are quoted in Ref. [11]. In particular, the following features are to be noted: (i) it possesses the same mathematical properties and interpretability as that of KLD, provides straightforward interpretations in the framework of statistical physics and information theory, (iii) it is the square of a true metric, and (iv) it can be generalized to more than two distributions, allowing to take into account the different sizes of the objects under comparison. Distances between quantum states play a central role in quantum information theory and extensions in this direction have also been done [9,10,20].

The central role of Shannon entropy in information theory has stimulated the proposal of several generalizations and extensions during the last decades. One of the best known of these generalizations is the family of Rényi entropies, which includes the Shannon entropy as a limiting case, and it has been used in several applications [40]. The Shannon and Rényi entropies share the well-known additivity property, which sets the joint entropy of a pair of independent random variables as the sum of the individual entropies. In other generalizations the additivity property does not constitute a requirement, yielding the non-extensive entropies. These generalized entropies retain much of the formal structure of the standard thermodynamics theory and have been applied to many anomalous physical systems [41–43].

The Tsallis entropy [8] defined below is a generalization of the standard Shannon entropy.

$$T^{(q)}(f) \equiv \frac{1 - \omega_q(f)}{q - 1}, \tag{4}$$

where q is a positive real parameter and $\omega_q(f) \equiv \int f^q(\vec{r}) d\vec{r}$ is the so-called *frequency moment* of order q of the distribution. The convergence of the involved integral depends on the short- and long-range behaviors of the distribution we are dealing with, and the limiting case $q \rightarrow 1$ provides the Shannon entropy, i.e. $T^{(1)}(f) = S(f)$. As we have pointed out, $T^{(q)}$ with $q \neq 1$ is not extensive, in the sense that given two independent variables A and B for which the joint probability satisfies $p(A, B) = p(A)p(B)$, then

$$T^{(q)}(A, B) = T^{(q)}(A) + T^{(q)}(B) + (1 - q)T^{(q)}(A)T^{(q)}(B). \tag{5}$$

From this result, it is evident that the parameter q measures the departure from extensivity. In some complex processes or systems the additivity property is often violated and some of these phenomena seem to be susceptible of being described by using approaches drawn from non-extensive entropies, such as the Tsallis one [8].

Numerous applications of this entropy in non-extensive thermodynamics or statistical mechanics, among many other scientific fields have been carried out. This entropy has also been used for modeling certain complex physical phenomena (such as those exhibiting, for instance, long-range interactions, microscopic memory, power-law behavior or multifractal behavior) reflecting a hierarchical pattern or fractal structure [44].

Then, replacing the Shannon entropy by the Tsallis one in the JSD definition provides us with a new functional of two densities, the Jensen–Tsallis divergence of order q ,

$$JTD^{(q)}(f, g) \equiv T^{(q)}\left(\frac{f+g}{2}\right) - \frac{1}{2}[T^{(q)}(f) + T^{(q)}(g)]. \tag{6}$$

For a given couple of densities (f, g) , the Jensen–Tsallis divergence constitutes a measure of the degree of extensiveness, within the local density approximation (LDA), of the Tsallis entropy density functional defined in Eq. (4). This new divergence generalizes the previously introduced JSD as $JTD^{(1)} = JSD$ preserving its main properties. Non-negativity of $JTD^{(q)}$ is

guaranteed for arbitrary $q > 0$ due to the convex (concave) character of the frequency moments for q above (below) unity. For lower q values the integrands become smooth, hence enhancing the relative contribution of the outermost region of the atomic or molecular domain. This capability of enhancing/diminishing the relative contribution of different regions within the domain of the distributions under comparison is the main feature of this divergence measure. Some other non-extensive or non-logarithmic divergences [45], closely related to the JSD one, have been also defined and applied in the fields of symbolic sequence segmentation [9], image registration [46–49], machine learning [50] and atomic shell structure [51].

It is also worthy to remark another relevant particular case, namely the second order divergence $JTD^{(2)}(f, g) = \frac{1}{4}QD^2(f, g)$, where QD stands for the usual 'quadratic distance' given by $QD(f, g) \equiv (\int [f(\vec{r}) - g(\vec{r})]^2 d\vec{r})^{1/2}$. The functional QD corresponds to a true metric, as also the square root of JSD does.

Other types of divergence measures exhibit a deep local character, which is the case of the Fisher divergence, built up from the so-called 'Fisher information' [52]. The local sensitivity arises from its definition as a functional enclosing the gradient of the distribution. This divergence has been recently proposed with the aim of analyzing the similarity and discrepancy among neutral atoms throughout the whole periodic table. In spite of its local character as compared to the global one of JSD or JTD, the Fisher divergence is almost insensitive, as also happens with the QD measure, to the atomic shell structure when dealing with position space distributions. In that case, the Fisher divergence constitutes only, in fact, a measure of how close the compared systems are located at the periodic table, independently of the groups they belong to. The analysis in momentum space is required in order to get information on the shell-filling patterns [29].

To the best of our knowledge, the only relative measures, which have been employed for atoms and ions, aside of the JTD ones analyzed in the present study, were defined in terms of the Rényi entropy [40]. They are defined as functionals of a pair of distributions which contain, in some sense, relevant information of the corresponding physical or chemical systems. The aforementioned applications on atomic systems are the following.

- (i) The 'relative Rényi entropy' $RRE^{(q)}$ is employed in Ref. [53] by comparing the electron density of a neutral atom to those of hydrogen-like systems which are considered, in fact, as extremely simplified 'reference models'. The relative Rényi entropy of order q embodies the KLD divergence as a particular case. The finiteness of the relative Rényi measure requires the fulfilment of constraints on its characteristic parameter, arising from the long-range behavior of the densities considered. For the aforementioned reference densities in position space, the constraint is as strong as $0 < q < 1$.
- (ii) The 'Jensen–Rényi Divergence' $JRD^{(q)}$, which has been applied recently [54] in its generalized version to the study of shell-filling patterns in neutral atoms, their decomposition as a set of subshells as well as the computed densities within different models. This divergence also requires the aforementioned constraint on its order to perform an appropriate description of the systems and/or processes considered, in order to guarantee non-negative divergence values.

Note that the Jensen–Rényi divergence $JRD^{(q)}$ constitutes a non-negative similarity measure under a very strict constraint on its order. This is not the case for the Jensen–Tsallis divergence $JTD^{(q)}$, whose non-negativity for arbitrary q arises from the convex (concave) character of the frequency moments ω_q for values of q above (below) unity. So the only constraints on the value of q arise from the convergence of the involved integrals according to the long- and short-range behaviors of the distributions under comparison, as also happens with the Rényi-like measures $RRE^{(q)}$ and $JRD^{(q)}$, even for values of q lesser than one. For the JTD of atomic systems, any $q > 0$ is allowed for position space densities, while $q > 3/8$ is required in the momentum one, as will be discussed in the next section. It is worthy to remark that there are no restrictions from above on the values of q neither in position nor in momentum spaces.

For our present purposes, i.e. the analysis and comparison of neutral atoms and ionized species throughout the periodic table in terms of their one-particle densities in both conjugated position and momentum spaces, the domain of definition is the whole three-dimensional space. In this sense, it should be pointed out that (i) all analytical expressions given in the present work for a specific space (position or momentum) will also be valid in the conjugated one by replacing the corresponding variables and distributions, and (ii) for atomic systems in the absence of external fields, it is sufficient to deal with the spherically averaged densities $\rho(r)$ and $\gamma(p)$ defined over the non-negative real line $[0, \infty)$.

3. Applications of JTD to atomic ionization processes

As discussed in the previous section, the main feature of the Jensen–Tsallis divergence $JTD^{(q)}$ as compared to other ones and, particularly, to the Jensen–Shannon divergence JSD, is its capability of enhancing/diminishing the relative contribution of different regions within the domain of the distributions under comparison. This usefulness is clearly emphasized in the present study for the divergence analysis of neutral and ionized atomic systems by means of their one-particle densities. Different values and ranges of q are shown to allow the interpretation of their divergence $JTD^{(q)}$, from a physical point of view, by crossing a critical q value which enables to get a relevant valence subshell contribution within the domain of the densities. Such a region provides, in fact, the main information regarding the characteristic shell-filling patterns of the atomic systems.

In what follows, we will focus on the analysis of atomic ionization processes by means of the Jensen–Tsallis divergence $JTD^{(q)}(XY)$ between the one-particle density of the system X , and that of the system Y which results from the ionization of X . That is, we compare the corresponding densities of the initial and final systems involved in the ionization, either by removing or by adding one or two electrons, keeping the nuclear charge fixed. Some comments are in order: (i) the systems considered in the present study are neutral atoms (N) as well as singly charged cations (C) and anions (A), all of them at

their ground state, (ii) their nuclear charge belongs to the range $Z = 1\text{--}55$, dealing with a global of 150 systems (54 neutral atoms, 43 anions and 53 cations), (iii) the ionization processes will be labeled according to the initial and final systems, such as 'NC' when removing an electron from a neutral atom giving rise to a singly charged cation, and similarly when the initial system is an anion with notation 'AC' and 'AN'; these three ionization processes (NC, AC, AN) are associated to the electron(s) ejection, but with identical interpretation in terms of electron addition according to the JTD values. And (iv) the whole study will be done in both position and momentum spaces.

The next subsections involve two different types of analyses in terms of JTD. First, the JTD for a fixed value of the parameter q is considered for the ionization processes through the range of nuclear charges $Z = 1\text{--}55$. This will be done for different selected values of q , each one corresponding to a curve displayed in order to analyze the dependence of JTD, for fixed q , on the nuclear charge Z , as well as its correlation with physically relevant quantities such as the first atomic ionization potential. And second, the magnitude $JTD^{(q)}(XY)$ is analyzed as a function of q , say $f(q)$, for fixed systems X and Y . This will be done for several couples (X, Y) in order to study the main structural properties of the corresponding function $f(q)$, such as monotonicity, convexity, asymptotic behavior, ordering or fittings, among others.

3.1. Dependence of JTD on the nuclear charge Z

The ionization of a given atom with nuclear charge Z , independently of its global charge, constitutes a process with consequences apart from the mere addition or subtraction of electrons. According to the goal of this work, we wonder about the charge density of the electronic cloud and the extent to which the ionization modifies its spatial distribution as well as the momentum distribution of electrons. In this sense it appears very relevant to find a connection, if exists, between the changes experienced by the one-particle densities and the relevant physical properties within the analysis of ionization processes. Among them, it is worthy to mention the value of the nuclear charge, the ionization potential and the shell-filling pattern.

3.1.1. JTD order: physical usefulness and constraints

In order to carry out a quantitative study in the sense described above, it is first necessary to quantify properly the notion of similarity or divergence between the atomic densities of the system before and after the ionization took place. In doing so, the Jensen–Tsallis divergence $JTD^{(q)}$ will be considered as a measure of dissimilarity between both distributions. The availability of the order parameter q allows to establish the comparative quantification according to the relative contribution of different specific regions within the domain where the distributions are defined, namely the whole three-dimensional position or momentum space. In this sense, it is worthy to remember that the Tsallis entropy $T^{(q)}(\rho)$ is defined in terms of the frequency moment $\omega_q(\rho)$ given by the integral of the function $\rho^q(r)$, and similarly in momentum space by considering the function $\gamma^q(p)$. The normalization constraint reads as $\omega_1 = 1$ in both cases. Additionally, it is worthy to remark that the convergence conditions for the finiteness of the frequency moments are verified in position space for arbitrary $q > 0$, due to the exponentially decreasing long-range behavior of the charge density. However, the asymptotic behavior $\gamma(p) \sim p^{-8}$ for large p in momentum space [55] restricts the order as $q > 3/8$ for both ω_q and $JTD^{(q)}$ of atomic momentum densities. In what follows, the subscripts 'r' and 'p' will be used according to the space where JTD is considered.

The values and structure of $\rho^q(r)$ and similarly for $\gamma^q(p)$ are determined, of course, from those of the density itself. Structural characteristics such as the presence of local extrema or the global spreading are modified, in what concerns their relevance, when powering the density as done for evaluating ω_q . In this sense, opposite modifications occur according to the cases of the order q being above or below 1. So, a value $q > 1$ makes the local extrema (maxima and minima) of the density $\rho(r)$ to be enhanced in $\rho^q(r)$, while their attenuation is the consequence for order $q < 1$ giving rise to a more sparse function. The same argument applies in what concerns the momentum space density. Consequently, the relative contribution of specific regions to the whole frequency moment varies according to the diverse values of the order.

3.1.2. Structure of neutral–cation JTD curves: physical interpretation

Let us gain insight into the physical conclusions obtained from the Jensen–Tsallis divergence values for the single ionization of a neutral atom giving rise to a singly charged cation. This quantity, to be denoted by $JTD^{(q)}(NC)$ according to the notation described above, is displayed in Fig. 1 for both conjugated spaces, namely position (Fig. 1a) and momentum (Fig. 1b), for not very large values of the parameter q , bounded as $q \leq 1.4$. The particular case $q = 1$ is included, corresponding to the Jensen–Shannon divergence in accordance with the equality $JTD^{(1)} = JSD$.

The analysis of Fig. 1a ($JTD_r^{(q)}$ between position space densities of the neutral system and its cation) reveals some remarkable characteristics. First, it is observed that the curves displayed for $JTD_r^{(q)}(NC)$ are perfectly ordered, from above to below, as q increases. Their shapes appear similar, at least roughly, for low q values. However, their structure strongly depends on the specific value of q in what concerns number, location and enhancement of local extrema. A similar comment can be also done regarding the order of magnitude of $JTD_r^{(q)}$ (note the log-scale in the figure). As one should expect, lowering q makes the relative contribution of the outermost region in both systems for the computation of their $JTD_r^{(q)}$ to increase. Such a region of the electron density is the most sensitive to the effects of the ionization, as clearly revealed by the highly structured $JTD_r^{(q)}$ curves for low q . Consequently, this quantity appears to depend strongly on the surrounding of the nuclei

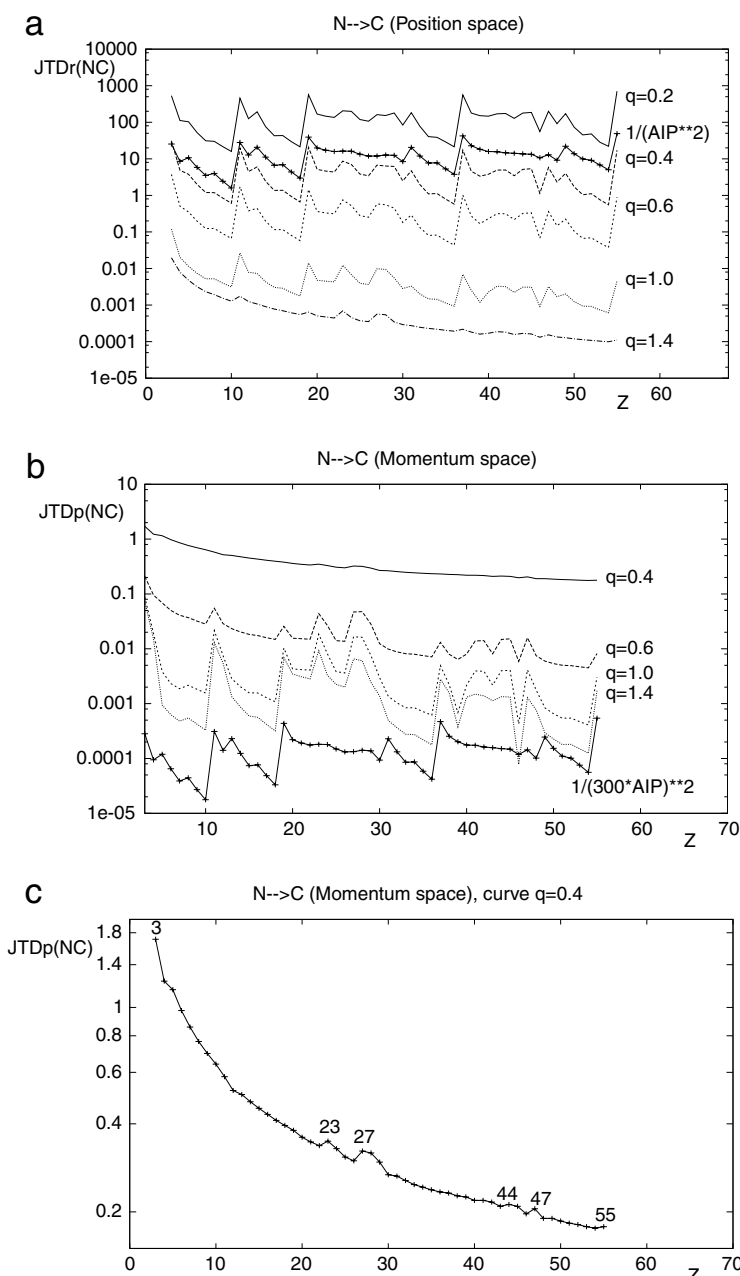


Fig. 1. Jensen–Tsallis divergence $JTD^{(q)}$ (interval $q = 0.2-1.4$) among neutral atoms (N) and singly charged cations (C), and atomic ionization potential AIP for systems with nuclear charge $Z = 3-55$, in (a) position and (b) momentum spaces, and (c) curve of momentum space $JTD^{(q)}$ with $q = 0.4$ including labels for its local maxima. Atomic units are used.

as q increases. That region is governed mostly by the electron–nucleus attractive potential. Consequently, the curves of divergence for the neutral–cation pair becomes softer as q increases, due to the lower dependence of JTD on the valence region as compared to that on the nuclear charge.

According to the above discussion in what concerns the valence region, it appears interesting to analyze the extent to which the $JTD_r^{(q)}$ between the initial and the final system is related to the energy needed to perform the ionization, quantified by means of the atomic ionization potential (AIP) of the neutral atom. Such a correlation is clearly observed in Fig. 1a which includes the AIP, where the inverse of its square is displayed. In a global sense, it is shown a good structural agreement among this curve and those of $JTD_r^{(q)}$ for low q , being not so accurate for transition metals.

The Fig. 1b allows an identical study of the neutral–cation divergence $JTD_p^{(q)}(NC)$ in momentum space, as previously done in the position one. The results displayed are interpreted again according to the structural characteristics of the atomic momentum density. Now, the enhancement of the valence region contribution to the value of JTD is achieved for large q , while that of the nuclear surrounding occurs for low q . In order to justify this opposite trend concerning the dependence on q , as compared to that in position space, it is worthy to note that the valence subshell is populated by low-momentum electrons, corresponding to the momentum distribution around its origin at $p = 0$. The momentum density reaches its

maximum value at the origin (for most atoms) or very close to it (for the rest of them). The enhancement of this absolute maximum by means of a large q provokes an increase of the contribution from the valence subshell to $JTD_p^{(q)}$, as clearly displayed attending to the structure of the different curves. On the contrary, the curves successively soften as q decreases, due to the increase of the contribution of inner subshells to the JTD. Additionally, there exists again a strong correlation between JTD and the ionization potential AIP, with the same functional dependence as in the position space (a shifting constant has been included in order to avoid overlaps among AIP and JTD curves).

3.1.3. Sensitivity of JTD to the valence subshell features

Let us now discuss in detail the location of extrema for the neutral–cation Jensen–Tsallis divergence $JTD^{(q)}(NC)$ in both position and momentum spaces, attending to the physical characteristics of the systems involved in the ionization process, namely a neutral atom and its singly charged cation. Additionally, the correlation between the aforementioned extrema and those of the atomic ionization potential AIP is also analyzed.

Disregard of the space (r or p) or the value of q we note that all local maxima of $JTD^{(q)}(NC)$ belong to one of the following three categories of ionization processes.

1. An 's' subshell becomes empty ($Z = 3, 11, 19, 23\text{--}24, 27\text{--}29, 37, 41\text{--}42, 44\text{--}45, 47, 55$).
2. A 'p' subshell becomes empty ($Z = 5, 13, 31, 49$).
3. A 'p' subshell becomes half-filled ($Z = 8, 16, 34, 52$).

Several observations are in place: (i) whenever the ionization involves alkali metals ($Z = 3, 11, 19, 37, 55$) an 's' subshell becomes empty (first set of systems above) whereas for other atoms the valence subshell 3d or 4d is involved, (ii) most systems with half-filled 's' subshells promote electrons to other types of subshells with the exceptions $Z = 23, 27, 28$ for which a completely filled 's' type subshell disappears, and (iii) whenever a 'p' type subshell is involved in the ionization it corresponds to the valence region.

The lists of systems given above enclose all those corresponding to the aforementioned three types of ionization processes, with very few of them not being associated to a local extremum neither in the AIP nor in the position or momentum JTD curves, at least for the range of q here considered. In this sense, it should be emphasized the role played by the 's' electrons as compared to the 'p' ones, according to the systems conforming the first set: all of them appear as maxima of the position space $JTD_r^{(q)}$ for the whole range $q = 0.2\text{--}1.4$, with the only exception of $Z = 29$ which corresponds to the period filling up the valence subshell 3d. For that specific case, a value as low as $q = 0.2$ in $JTD_r^{(q)}$ is required in order to distinguish a maximum so close to the $Z = 27$ one.

Concerning the 'p' ionization processes, most of them (with the only exception $Z = 5$) are also revealed as maxima in some $JTD_r^{(q)}$ curves, that is, for specific q ranges depending on the value of Z considered. So, a given maximum at Z disappears for q 's out from its aforementioned range. For systems losing a 'p' subshell, a maximum in $JTD_r^{(q)}$ is displayed for all q up to 1.2 ($Z = 49$), 1.0 ($Z = 31$) and 0.8 ($Z = 13$), while for the half-filled ones (i.e. $p^4 \rightarrow p^3$) the ranges are $0.5 \leq q \leq 0.8$ ($Z = 8$), $q \leq 0.8$ ($Z = 52$), $0.4 \leq q \leq 0.6$ ($Z = 34$) and $q \leq 0.5$ ($Z = 16$). The only system losing a 'd' subshell as a consequence of the ionization, namely $Z = 39$, does not display an extremal JTD value neither in position nor in momentum space, independently of the order q considered. From this data we conclude that, in spite of the ability of $JTD_r^{(q)}$ to detect almost all relevant ionization effects, there exists a much higher sensitivity for processes involving 's' electrons as compared to the 'p' or 'd' ones. Nevertheless, let us emphasize that the previous studies based on the Jensen–Shannon divergence JSD [31] did not reveal most of the 'p' processes here discussed, such as those corresponding to systems $Z = 8, 13, 16, 34, 52$ which appear as extrema of the position space Jensen–Tsallis divergence for low enough q below unity. The same comment applies to the particular case $Z = 29$, among those suffering ionization in an 's' subshell, as explained above.

3.1.4. Relationship between JTD and the ionization potential

Apart from the physical interpretation of these results in terms of shell structure features, it is also interesting to perform a study on the correlation between the neutral–cation JTD and the first atomic ionization potential AIP. Attending again to the extrema of both quantities, it is worthy to remark not only that all minima of the AIP belong to one of the three 'ionization sets' enumerated above (independently of being characterized by 's' or 'p' type ionization processes), but also the resemblance with the $JTD_r^{(q)}(NC)$ maxima previously discussed, as shown in Fig. 1a. Additionally, it is found that the correspondence among AIP and JTD extrema occurs for the whole range $q \leq 1.4$ when the ionization involves 's' electrons, while for narrower ranges for the 'p' ones.

A similar comparative analysis performed by means of the momentum space divergence $JTD_p^{(q)}(NC)$ provides again a notable correlation between its maxima and the AIP minima, but only for the 's' ionization processes (see Fig. 1b). In this sense, it should be pointed out that (i) for these processes, the systematic (i.e. for all q) appearance of JTD maxima in position space is also observed in the momentum one (the observation of maxima, in spite of their existence, becomes increasingly difficult as q decreases below 0.6; see Fig. 1c for a magnified display of the curve $q = 0.4$), with very few exceptions for which a minimum value $q \geq 0.6$ is required, and (ii) there is no detection of 'p' ionization by means of the momentum JTD, apart from the only system $Z = 8$ for the range $1.0 \leq q \leq 1.4$, as shown in Fig. 1b. A deeper analysis shows that the lower limit of the detection range for this system extends up to $q = 0.8$.

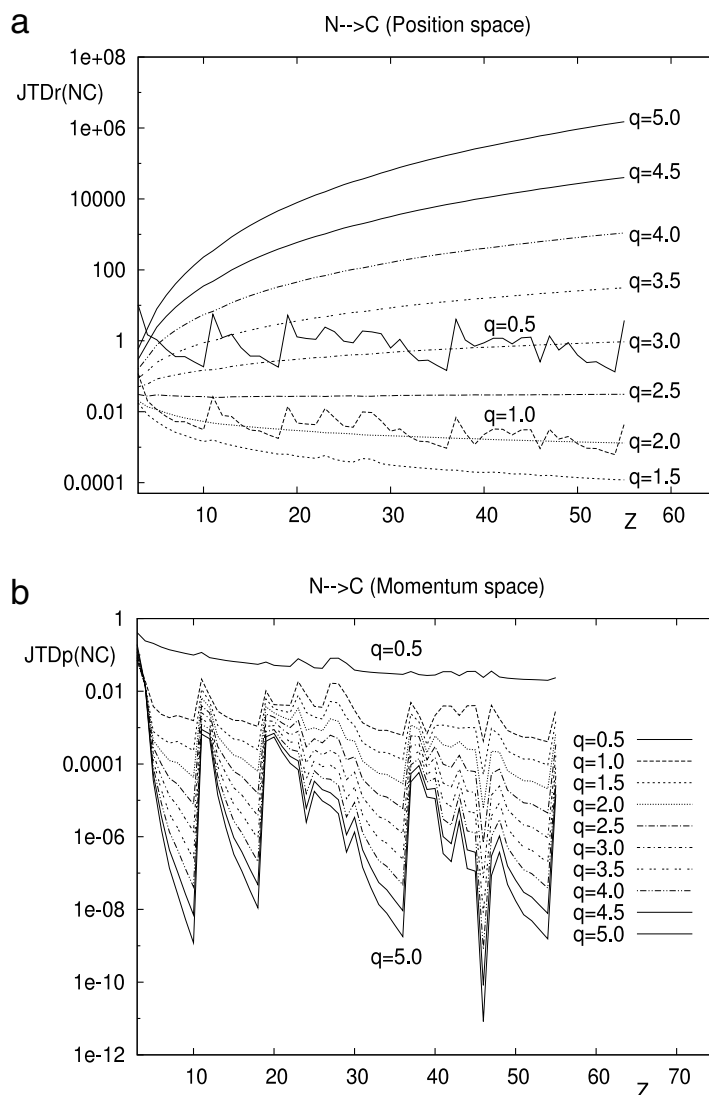


Fig. 2. Jensen–Tsallis divergence $JTD^{(q)}$ (interval $q = 0.5$ – 5.0) among neutral atoms (N) and singly charged cations (C) with nuclear charge $Z = 3$ – 55 , in (a) position and (b) momentum spaces. Atomic units are used.

3.1.5. Trends of JTD for large order

Once established the connection among the position and momentum neutral–cation JTD, the value of the atomic ionization potential and the shell-filling process, we wonder about the preservation of the above discussed patterns when considering higher values of the parameter q , going beyond the previous upper limit $q = 1.4$. In order to study the JTD trends for large q , let us analyze the curves in Fig. 2, corresponding again to $JTD^{(q)}(NC)$ in position (Fig. 2a) and momentum (Fig. 2b) spaces, but with a much wider range of values for the parameter, namely $0.5 \leq q \leq 5.0$. As previously observed, increasing even more the value of q makes the JTD curves in position space to soften progressively, reaching a monotonic behavior after crossing a critical q value in between 1.5 and 2.0, and also inverting there (roughly) their ordering as increasing q . Such a behavior of JTD as a function of the parameter q will be analyzed in the next subsection. Concerning the momentum space JTD curves, both the enhancement of their structure as well as their ordering are preserved for higher values of q . It is consequently concluded that the previous interpretation of the results in Fig. 1 for position and momentum spaces are corroborated from the analysis of Fig. 2, where the structural features of JTD for large q follow similar trends as those displayed in Fig. 1 when approaching the value $q = 1.4$ from below.

3.1.6. Ionization of singly charged anions

Now let us consider other ionization processes, involving a singly charged anion, namely anion–neutral (AN) and anion–cation (AC) processes by removing one or two electrons, respectively, from the initial anionic system. Similar conclusions to those obtained from the study of the ionization of neutral atoms (NC) are obtained, in what concerns structural patterns, ordering, fitting and correlation with the ionization potential. For illustration, these JTD values are displayed in Fig. 3 for the range $q \leq 1.4$, in position space for the AC case (Fig. 3a) and in momentum space for AN processes (Fig. 3b). The opposite trends displayed by JTD in both conjugate spaces as q varies are observed again, as also happens with the other

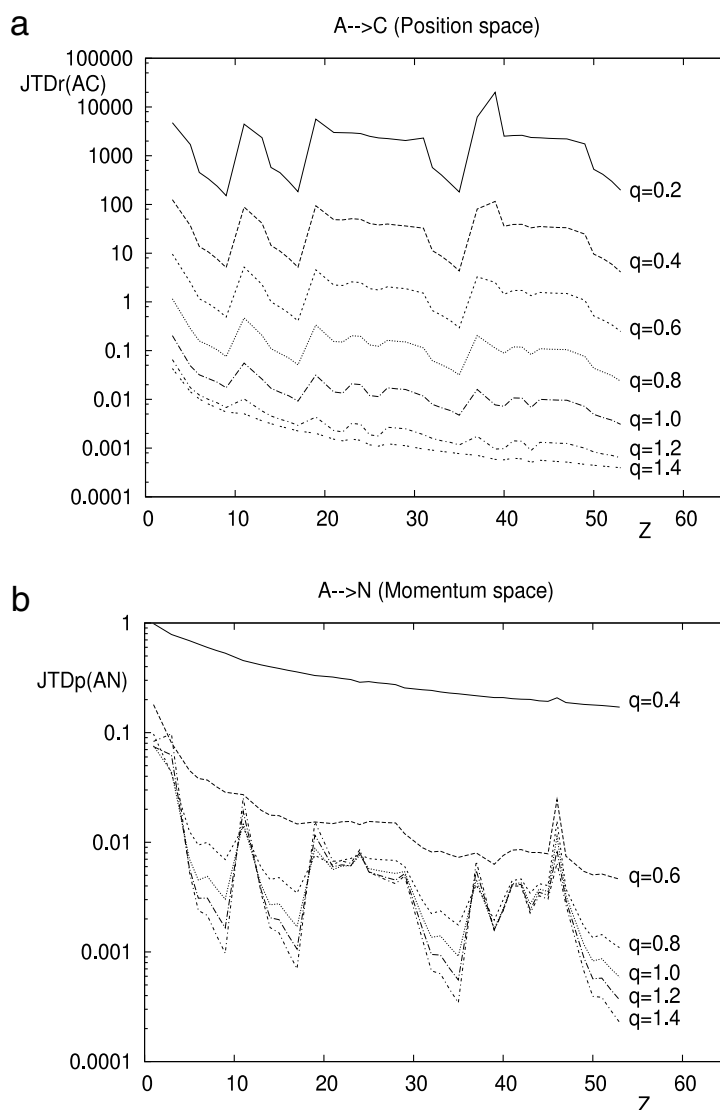


Fig. 3. Jensen–Tsallis divergence $JTD^{(q)}$ among (a) singly charged anions (A) and cations (C) in position space, and (b) singly charged anions (A) and neutral atoms (N) in momentum space, with nuclear charge $Z = 3\text{--}55$. Atomic units are used.

cases not shown here (position AN and momentum AC). The whole discussion, as well as the arguments to justify the results obtained for the NC process, also applies for the AC and AN ones in both spaces, though.

3.2. Dependence of JTD on the Tsallis-parameter q

As previously discussed in detail for the ionization of neutral atoms giving rise to a singly charged cation (NC), the shape, magnitude and structural characteristics of the different curves in both position and momentum spaces strongly depend on the value considered for the q parameter. Consequently it appears relevant to analyze, for a given pair NC, the functional dependence of the Jensen–Tsallis divergence $JTD^{(q)}(NC)$ on its order q .

Here such a study is carried out for all systems with nuclear charge $Z = 3\text{--}55$, classified in Fig. 4a and b according to their valence subshell or, equivalently, the row (period) they belong to in the periodic table. The classification is made as follows: (i) valence subshell ‘s’ or ‘p’ with principal quantum number $n = 2, 3, 4, 5$, (ii) transition metals (‘d’ valence subshell), and (iii) the alkaline Cs ($Z = 55$) with valence subshell $6s^1$. The range $0.4 \leq q \leq 3.8$ is considered for both spaces.

A first look at Fig. 4a allows one to realize that the 53 curves drawn, corresponding to the different NC couples under study, display extremely similar structural characteristics, attending to the following properties.

- (a) The JTD in position space appears systematically as a unimodal and convex function of q . In fact, it is a log-convex function, by taking into account the logarithmic scale employed in the figure. It is very apparent how the ‘degree of curvature/convexity’ of the different curves increases, within a given group of the periodic table, as the nuclear charge increases.

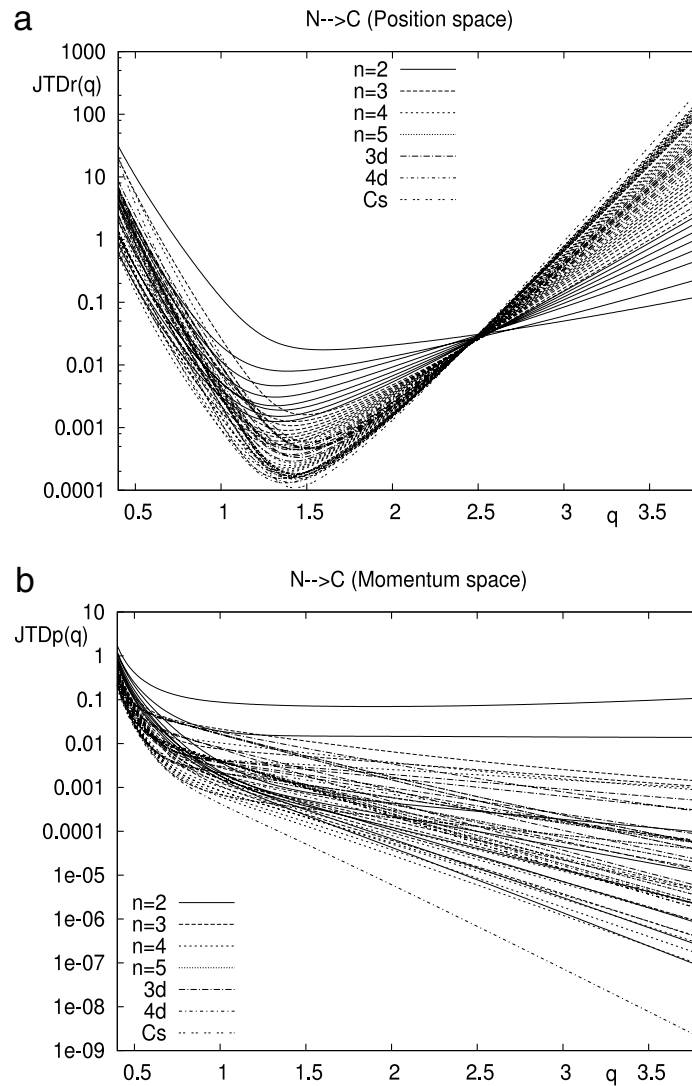


Fig. 4. Jensen–Tsallis divergence $JTD^{(q)}$, as a function of its order q , among neutral atoms (N) and singly charged cations (C) with nuclear charge $Z = 3–55$, in (a) position and (b) momentum spaces. Atomic units are used.

- (b) All curves possess a unique minimum for a value $q = q_{\min}$, as provided in Table 1. It is observed that (i) all q_{\min} belong to the narrow range 1.32–1.51 with the only exception $q_{\min} = 1.60$ for lithium ($Z = 3$), (ii) highest values of q_{\min} are associated to ionization of ‘s’ subshells (e.g. all alkalines and the alkaline-earth $Z = 38$, as well as the transition metals $Z = 23, 27, 28$ for which the ionization involves two ‘s’ electrons, one ejected and the other one moving to the 3d subshell), and (iii) with the exception of lithium, light atoms (filling up the subshells 2s and 2p with principal quantum number $n = 2$) display lower q_{\min} values as compared to those for medium or heavy atoms, i.e. with $n \geq 3$ valence subshells. At times, the range of q_{\min} values is extremely narrow within a given group or period, as also shown in Table 1. Let us also note that the ‘double-s ionization’ cases are associated to $q_{\min} = 1.51$, the highest value observed in the table apart from that of lithium.
- (c) The existence of a ‘crossing interval’, which could be roughly associated to a ‘critical q ’ where all position space JTD curves display an almost identical value is clearly observed. A detailed analysis of the JTD intervals for a given q allows to assert that the JTD of order $q = 2.50$ belongs to the interval

$$JTD_r^{(2.50)}(NC) = 0.029 \pm 0.005 \quad (7)$$

for all atomic pairs $Z = 3–55$. In order to have an idea of the narrowness of such an interval, let us note that the ratio between the maximum and minimum JTD values at that q is as low as 1.2, while the corresponding ratio for the whole JTD-axis is 10^6 . The reason (if exists) for this behavior at that particular value still remains to be understood.

Let us analyze the results provided in Fig. 4b, corresponding to the momentum space functional $JTD_p^{(q)}(NC)$. It is first observed that most curves display a convex and monotonically decreasing trend, with few exceptions corresponding to (i) very light atoms (solid lines on the top) for which a unique minimum appears again, consequently with the unimodal shape, and (ii) some heavy atoms for which convexity is lost within a small-sized region. It is also remarkable that the almost

Table 1

Value q_{\min} of the Jensen–Tsallis order q for which the neutral–cation divergence in position space $JTD_p^{(q)}(NC)$ reaches its minimum value, along groups IA–VIII A (principal quantum number from $n = 2$ to $n = 5, 6$) and valence subshells 3d–4d. Atomic units are used.

Group	$n = 2$		$n = 3$		$n = 4$		$n = 5$		$n = 6$	
IA	1.60		1.49		1.45		1.51		1.43	
IIA	1.39		1.42		1.40		1.51			
IIIA	1.32		1.41		1.42		1.35			
IVA	1.32		1.39		1.40		1.40			
VA	1.32		1.37		1.38		1.43			
VIA	1.35		1.37		1.38		1.43			
VIIA	1.34		1.35		1.37		1.41			
VIIIA	1.33		1.34		1.36		1.43			
Subshell	$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$
3d	1.41	1.41	1.51	1.45	1.42	1.42	1.51	1.51	1.45	1.42
Subshell	$5s^2 4d^1$	$5s^2 4d^2$	$5s^1 4d^4$	$5s^1 4d^5$	$5s^2 4d^5$	$5s^1 4d^7$	$5s^1 4d^8$	$5s^0 4d^{10}$	$5s^1 4d^{10}$	$5s^2 4d^{10}$
4d	1.35	1.40	1.44	1.43	1.41	1.43	1.43	1.37	1.43	1.41

linear behavior of all curves for large q , translates into a long-range functional dependence as

$$JTD_p^{(q)}(NC) \sim \exp(-\alpha q) \quad (8)$$

by taking into account the logarithmic scale employed. The constant α in the exponential is determined according to the slope of the curve in the large q limit, with different values for each NC couple as clearly observed in the figure, displaying an increasing tendency as the systems considered become heavier.

Such a decay is obtained from the analysis of the numerical results, not necessarily arising (to the best of our knowledge) as a consequence of any physical property, and consequently the expression provided in Eq. (8) does not constitute a theoretical rigorous result. Additional research regarding a physical reason for such a behavior still remains to be carried out.

4. Conclusions

We have proposed the non-extensive Jensen–Tsallis divergence measure JTD, based on informational theoretic methods, to study the discrepancies among atomic species involved in ionization processes. Such a non-extensivity is measured by an order parameter q , whose usefulness mainly arises from its capability to modify the relative contributions of relevant specific regions of the electronic densities under comparison.

An exhaustive analysis of different ionization processes, by taking into account the atomic subshell structure and the dependence of JTD on the nuclear charge, has been carried out. It is shown that JTD captures relevant differences in any of the conjugated spaces, which is not the case of other divergences employed in the previous studies with multielectronic systems.

In particular, the extrema of the Jensen–Tsallis divergence have been deeply correlated to those of the most important experimental quantity related to this type of processes, the atomic ionization potential. Additionally, the dependence of JTD on its characteristic parameter q has been analyzed in detail.

We have shown the extent to which some information-theoretic tools, such as the Jensen–Tsallis divergence, have an important versatility and predictive power when being compared to experimentally accessible quantities. This work on atomic ionization processes constitutes a benchmark, in order to deal with more complex and strongly organized systems.

The employment of the JTD functional as a measure of divergence can be applied not only to compare a couple of probability distributions, but also an arbitrary number of them, even assigning different weights to each distribution, apart from the weighting effect of the JTD characteristic parameter. Further, applications of this generalized divergence are actually being carried out, including comparisons among distributions computed within different models for a given system, or among parts or components of the global system.

On the other hand, the universality and generality of the techniques here employed allow the extension of this study to many relevant physical and chemical systems or processes such as, for instance, molecules of special interest in nanotechnology or pharmacology, as well as the initial and final products in chemical reactions. For all those systems, it appears interesting to consider also additional distribution functions as well as physically relevant quantities defined in terms of the one-particle densities. Such is the case, for instance, of their gradients and Laplacians, as well as the Fourier transforms of the position and momentum space densities, namely the form factor and the reciprocal form factor, respectively, which in fact constitute two of the main sources of experimental information on the atomic one-particle densities. A similar study can be done with the Compton profile, an experimentally accessible quantity whose derivative is determined by the momentum density occurs with the Compton profile. The results of those studies are being currently investigated in our laboratories and they will be provided elsewhere.

Acknowledgements

This work was supported in part by the Spanish MICINN project FIS-2008-02380, the grants FQM-4643 and FQM-2445 (S.L.R. and J.C.A.) of Junta de Andalucía, and the Mexican grants from CONACyT and PROMEP-SEP. All authors belong to the

Andalusian research group FQM-0207. R.O.E. wishes to acknowledge financial support from the Ministerio de Educación of Spain through grant SAB2009-0120 and also thanks J.C. Angulo and J.S. Dehesa for their kind hospitality during his sabbatical stay at the Departamento de Física Atómica, Molecular y Nuclear (University of Granada, Spain).

References

- [1] A.K.C. Wong, M. You, *IEEE Trans. Pattern Anal. Mach. Intell.* 7 (1985) 599.
- [2] C.R. Rao, T. Nayak, *IEEE Trans. Inf. Theory* 31 (1985) 589.
- [3] J. Lin, *IEEE Trans. Inf. Theory* 37 (1991) 145.
- [4] S. Kullback, R. Leibler, *Ann. Math. Statist.* 22 (1951) 79.
- [5] A.P. Majtey, P.W. Lamberti, D.P. Prato, *Phys. Rev. A* 72 (2005) 052310.
- [6] I.J. Taneja, On generalized information measures and their applications, in: P.W. Hawkes (Ed.), *Advances in Electronics and Electron Physics*, Academic Press, New York, 1989, pp. 327–413.
- [7] I.J. Taneja, P. Kumar, *Inf. Sci.* 166 (2004) 105.
- [8] C. Tsallis, *J. Statist. Phys.* 52 (1988) 479.
- [9] P.W. Lamberti, A.P. Majtey, *Physica A* 329 (2003) 81.
- [10] P.W. Lamberti, A.P. Majtey, A. Borrás, M. Casas, A. Plastino, *Phys. Rev. A* 77 (2008) 052311.
- [11] J. Briët, P. Harremoës, *Phys. Rev. A* 79 (2009) 052311.
- [12] R. Román-Roldán, P. Bernaola, J.L. Oliver, *Phys. Rev. Lett.* 80 (1998) 1344.
- [13] W. Li, *Phys. Rev. Lett.* 86 (2001) 5815.
- [14] P. Bernaola-Galván, I. Grosse, P. Carpena, J.L. Oliver, R. Román-Roldán, H.E. Stanley, *Phys. Rev. Lett.* 85 (2000) 1342.
- [15] J.F. Gómez, J. Martínez, A.M. Robles, R. Román-Roldán, *J. Math. Imaging Vision* 13 (2000) 35.
- [16] R.F. Nalewajski, R.G. Parr, *Proc. Natl. Acad. Sci. USA* 97 (2000) 8879.
- [17] R. Carbó-Dorca, X. Girones, P.G. Mezey (Eds.), *Fundamentals of Molecular Similarity*, Kluwer Academic/Plenum Press, New York, 2001.
- [18] D. Bielinska-Waż, P. Waż, T. Clark, *Chem. Phys. Lett.* 445 (2007) 68.
- [19] V. Cross, T.A. Sudkamp, *Similarity and Compatibility in Fuzzy Set Theory: Assessment and Applications*, Springer-Verlag, Heidelberg, 2002.
- [20] A.P. Majtey, A. Borrás, M. Casas, P.W. Lamberti, A. Plastino, *Int. J. Quantum Inf.* 6 (2008) 715.
- [21] R. Carbó-Dorca, J. Arnau, L. Leyda, *Int. J. Quantum Chem.* 17 (1980) 1185.
- [22] A. Borgoo, M. Godefroid, K.D. Sen, F. de Proft, P. Geerlings, *Chem. Phys. Lett.* 399 (2004) 363.
- [23] M. Solá, J. Mestres, J.M. Oliva, M. Durán, R. Carbó-Dorca, *Int. J. Quantum Chem.* 58 (1996) 361.
- [24] M. Ho, V.H. Smith Jr., D.F. Weaver, C. Gatti, R.P. Sagar, R.O. Esquivel, *J. Chem. Phys.* 108 (1998) 5469.
- [25] S. Janssens, A. Borgoo, C. van Alsenoy, P. Geerlings, *J. Phys. Chem. A* 112 (2008) 10560.
- [26] D. Robert, R. Carbó-Dorca, *Int. J. Quantum Chem.* 77 (2000) 685.
- [27] F. de Proft, P.W. Ayers, K.D. Sen, P. Geerlings, *J. Chem. Phys.* 120 (2004) 9969.
- [28] J.C. Angulo, J. Antolín, *J. Chem. Phys.* 126 (2007) 044106.
- [29] J. Antolín, J.C. Angulo, S. López-Rosa, *J. Chem. Phys.* 130 (2009) 074110.
- [30] R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
- [31] S. López-Rosa, J.C. Angulo, J. Antolín, R.O. Esquivel, *Phys. Rev. A* 80 (2009) 012505.
- [32] C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication*, University of Illinois Press, Urbana, 1949.
- [33] T. Koga, K. Kanayama, S. Watanabe, A.J. Thakkar, *Int. J. Quantum Chem.* 71 (1999) 491.
- [34] G.A. Henderson, *Phys. Rev. A* 23 (1981) 19.
- [35] N.L. Allan, D.L. Cooper, *J. Math. Chem.* 23 (1998) 51.
- [36] R. Carbó-Dorca, L. Amat, E. Besalu, X. Girones, D. Robert, *J. Mol. Struct. (Theochem)* 504 (2000) 181.
- [37] T.M. Cover, J.A. Thomas, *Elements of Information Theory*, Wiley-Interscience, New York, 1991.
- [38] R. López-Ruiz, H.L. Mancini, X. Calbet, *Phys. Lett. A* 209 (1995) 321.
- [39] J.C. Angulo, J. Antolín, *J. Chem. Phys.* 128 (2008) 164109.
- [40] A. Rényi, On measures of entropy and information, in: *Proc. 4th Berkely Symp, Math. Stat. Probability* vol. 1, 1961.
- [41] G.F.J. Añáños, F. Baldovin, C. Tsallis, *Eur. Phys. J. B* 46 (2005) 409.
- [42] A.M. Scarfone, T. Wada, *Prog. Theor. Phys.* 162 (2006) 45.
- [43] A. Hamadou-Ibrahim, A.R. Plastino, A. Plastino, *Braz. J. Phys.* 39 (2009) 408.
- [44] C. Tsallis, *J. Comput. Appl. Math.* 227 (2009) 51.
- [45] C. Tsallis, *Phys. Rev. E* 58 (1998) 1442.
- [46] A. Ben Hamza, *J. Electron. Imaging* 15 (2006) 013011.
- [47] S. Sun, L. Zhang, C. Guo, *Int. J. Biol. Life Sci.* 2 (2006) 2.
- [48] J. Mohanalin, P.K. Kalra, Nirmal Kumar, *Int. J. Comput. Theory Eng.* 1 (2009) 1793.
- [49] Waleed Mohamed, A. Ben Hamza, Khaled Gharaibeh, *Lecture Notes in Computer Science*, vol. 6026, 2010, 199.
- [50] A.F.T. Martins, N.A. Smith, E.P. Xing, P.M.Q. Aguiar, M.A.T. Figueiredo, *J. Mach. Learn. Res.* 10 (2009) 935.
- [51] J. Antolín, S. López-Rosa, J.C. Angulo, R.O. Esquivel, *J. Chem. Phys.* 132 (2010) 044105; *Virtual J. Quantum Inf.* 10 (2) (2010).
- [52] R.A. Fisher, *Proc. Cambridge Philos. Soc.* 22 (1925) 700.
- [53] E. Romera, A. Nagy, *Phys. Lett. A* 372 (2008) 4918.
- [54] J.C. Angulo, S. López-Rosa, J. Antolín, R.O. Esquivel, *Int. J. Quantum Chem.* 111 (2011) 297.
- [55] R. Benesch, V.H. Smith Jr., *Wave Mechanics: The First Fifty Years*, Butterworths, London, 1973.