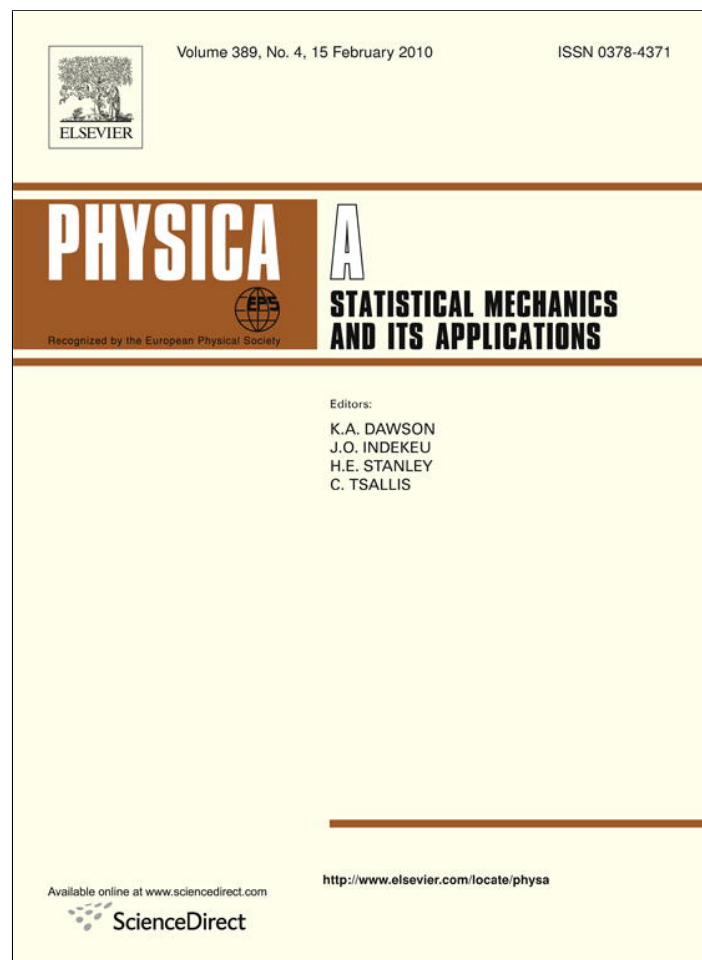


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Jensen–Shannon divergence in conjugate spaces: The entropy excess of atomic systems and sets with respect to their constituents

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ABSTRACT

The disorder of a composite system or of a set of different systems is always higher than the mere sum of the internal disorder of its constituents. One of the most widely used functionals employed for measuring the randomness of a single distribution is the Shannon entropy, from which the increase of disorder within the composite system with respect to those of the constituents is quantified by means of the Jensen–Shannon Divergence (JSD). In this work two different applications of the JSD in the study of the information content of atomic electron densities are carried out: (i) finding the contribution for a given atom of its composing subshells to the total atomic information; (ii) and similarly for selected sets of atoms, such as periods and groups throughout the Periodic Table as well as isoelectronic series. In both cases, the analysis is performed in the two conjugate position and momentum spaces, and the results are interpreted according to physically relevant quantities such as the ionization potential.

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1. Introduction

The concepts of uncertainty, randomness, disorder and delocalization are basic ingredients in the study, within an information-theoretic framework, of relevant structural properties for many different probability distributions appearing as descriptors of several chemical and physical systems and/or processes. The relevancy of these concepts has motivated new studies that pursue quantification, giving rise to a variety of density functionals, such as the Shannon entropy [1], the Fisher information [2], the disequilibrium [3], the complexity [4], and many others. These information measures have been widely employed for describing the information content and behavior in a great variety of fields [5,6] and, in particular, for the study of many-electron systems [7–11], which are also the objects analyzed in the present work.

Following the usual procedures carried out within information theory for quantifying the uncertainty or disorder of individual distributions, some extensions have been made in order to introduce the concepts of ‘distance’ or ‘divergence’ between two distributions, as comparative measures of their dissimilarity. Again different definitions of distance between two arbitrary distributions $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ appear, supposed both defined over the same domain. For the purposes of the present work, namely the study of these concepts for atomic systems, such a domain will be the whole three-dimensional space, to which the vector \vec{r} belongs. The interest in finding appropriate tools for ‘comparing’ two different systems or

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processes in terms of distribution functions is justified by the strong connection between some of the above mentioned information measures and many relevant physical and chemical properties of those systems.

The term ‘distance’ should be understood as a measure of how dissimilar the two functions are, not necessarily verifying all mathematical properties required for a true distance, as the usual quadratic distance does. Nevertheless, that is not the only definition within an information-theoretic framework for the aforementioned purpose. In fact, additional definitions arise from primary density functionals such as the information quantifiers previously mentioned. However, all of them keep as main distance properties the non-negativity, the symmetry (invariance under exchange of functions) and saturation (minimal zero value only for identical distributions).

Such is the case for the so-called ‘Kullback–Leibler relative entropy’ [12]

$$KL(\rho_1, \rho_2) \equiv \int \rho_1(\vec{r}) \ln \frac{\rho_1(\vec{r})}{\rho_2(\vec{r})} d\vec{r} \quad (1)$$

whose absence of symmetry motivated producing its symmetrized version, the ‘Kullback–Leibler symmetrized entropy’. It is immediately observed that the above expression is strongly related to the Shannon entropy $S(\rho) \equiv - \int \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}$ by just replacing a density by unity.

Other measures of information, distance and similarity have also been employed in the study of atomic systems and their interpretation in terms of structural and physical properties, such as complexities [13], the Fisher information [14] and its associated relative Fisher information and Fisher divergence [15], as well as the quantum similarity index [16]. It is remarkable that, for most information measures previously studied, the structural and periodicity patterns are only displayed in one of the two conjugate spaces.

At this point, it is worth introducing another distance based on the Shannon entropy and strongly related to the KL relative entropy, known as the ‘Jensen–Shannon Divergence’ (JSD). There exist different ways of defining the JSD divergence, but the pioneering one arises from the interest of comparing the Shannon entropies of two distributions in a method of building up a ‘distance’ or measure of how far they are from each other:

$$JSD(\rho_1, \rho_2) \equiv S\left(\frac{\rho_1 + \rho_2}{2}\right) - \frac{1}{2}[S(\rho_1) + S(\rho_2)], \quad (2)$$

that is, the difference between the Shannon entropy of the mean density and the mean value of their respective entropies. This information functional fulfils the main properties previously noted for other distances, the non-negativity arising from the convexity of the Shannon functional $S(\rho)$, and the others being trivially checked just by considering the JSD definition given by Eq. (2).

Those properties can be readily interpreted as follows: higher deviations of the densities from each other make their JSD increase, as should be expected from a usual ‘distance measure’. Such a deviation among themselves makes, of course, both of them deviate from the mean one, as can also be interpreted by attending to the expression for the JSD divergence in terms of the relative Kullback–Leibler entropy (KL):

$$JSD(\rho_1, \rho_2) = \frac{1}{2} \left[KL\left(\rho_1, \frac{\rho_1 + \rho_2}{2}\right) + KL\left(\rho_2, \frac{\rho_1 + \rho_2}{2}\right) \right], \quad (3)$$

as obtained from the JSD and KL definitions, given by Eqs. (1) and (2), after trivial manipulations.

These divergences have been recently applied [15] in the study of relevant properties (structure and shell-filling) for atomic systems, and earlier the JSD one in other different fields [17,18].

It is worth remarking that the Jensen–Shannon divergence is a measure that, in spite of being defined in terms of the Shannon entropy, possesses a remarkably different meaning. While the Shannon entropy provides information on how delocalized a given distribution is (a well-known characteristic as widely analyzed in many different frameworks), the JSD between two densities quantifies how near or far their associated entropies are, independently of both being, or not being, highly delocalized. Dealing with a couple of densities with similar high values of their entropies does not imply their mutual JSD also reaching large values. So, the JSD functional represents an informational concept different from that of the Shannon entropy, as is also trivially understood by paying attention to their multiple- and single-density dependences.

The main aim of this work is to employ generalized expressions for the JSD starting from the initial definition given by Eq. (2). Those extensions are built up in two complementary ways: (i) by increasing the number of distributions under comparison, with JSD being interpreted as a ‘mean distance’ among the constituents of a set with a number of functions higher than 2; and (ii) by appropriately weighting the distributions to be compared according to their specific characteristics or those of the systems that they represent, such as their size.

In doing so, let us remember the interpretation given to the expression for JSD in Eq. (2), as the difference between the entropy of the mean density and the mean value of the entropies. This interpretation also remains valid if one considers an arbitrary number M of distributions $\{\rho_1, \dots, \rho_M\}$ as well as density and entropy means calculated by considering non-uniform weights, defining their Jensen–Shannon Divergence (JSD) as follows:

$$JSD(\{\omega_j, \rho_j\}_{j=1}^M) \equiv S\left(\sum_{j=1}^M \omega_j \rho_j\right) - \sum_{j=1}^M \omega_j S(\rho_j) \quad (4)$$

where the weights ω_j ($j = 1, \dots, M$) verify $\sum_{j=1}^M \omega_j = 1$. It is immediately observed that the present definition reduces to the initial one on just considering the particular case $M = 2$ and $\omega_1 = \omega_2 = 1/2$.

Some comments are in order: (i) the aforementioned properties for the $M = 2$ uniformly weighted JSD divergence also remain for the above generalization; and (ii) the same is also true for the expression for JSD as the mean of the associated KL relative entropies:

$$\text{JSD}(\{\omega_j, \rho_j\}_{j=1}^M) = \sum_{j=1}^M \omega_j \cdot \text{KL} \left(\rho_j, \sum_{k=1}^M \omega_k \rho_k \right). \quad (5)$$

This generalization also provides a measure of global distance among the elements of a given set of distributions or, equivalently, of the sum of distances from each element to their mean value.

In recent years researchers have been interested in rigorous properties and parametric generalizations of this divergence measure of information. In particular, and just for discrete probability distributions, Lin and Wong derived some simple properties for JSD [19,20] and later they also proposed some identities and inequalities [21]. Taneja introduced [22,23] two scalar parametric generalizations of JSD. More recently, Lamberti and Majtey have investigated and generalized the properties of JSD in the framework of non-extensive Tsallis statistics [24–26].

These measures have found deep applications in statistics and many other fields. JSD has been widely applied in the analysis and characterization of symbolic sequences or series, and in particular in the study of segmentation of DNA sequences [27]. However, its use in the framework of quantum information theory [28,29] and in the study of multielectronic systems [15] is completely new.

The JSD constitutes a powerful tool for carrying out comparative analysis among distribution functions. This applies in particular when employing it in the study of multielectronic systems. A wide variety of applications arise, such as in the correlation between relevant physical and chemical properties (e.g. atomic ionization potential, shell-filling patterns) when comparing systems whose characteristic distributions are considered within a given framework or model. Such is the main aim of the present work, by considering a Hartree–Fock based approach, but many others will be addressed in the near future, for example the comparison of results obtained by employing more sophisticated wavefunctions including correlation and relativistic effects. A first step in this sense of dealing with different models has been made recently, by analyzing the ‘model distance’ for a fixed system, obtaining relevant conclusions on the effects of the interelectronic repulsion by means of the JSD between the Hartree–Fock and the bare Coulomb field wavefunctions [30].

The main interest of considering the generalized JSD arises when dealing with distributions where normalization and size appear as relevant characteristics to take into account when comparing them. Such is the case, for instance, for the application which will be carried out in Section 2, where the JSD divergence of atomic one-particle densities is built up as the sum of those of each subshell, contributing to the global charge according to their occupation numbers. For carrying out a detailed numerical study, near-Hartree–Fock atomic densities are employed for neutral atoms throughout the whole Periodic Table as well as some isoelectronic series. In Section 3, the global distributions for selected sets of atomic systems (e.g. groups, periods as well as the aforementioned cationic series) are studied by means of the associated JSD divergences. Finally, some concluding remarks will also be given.

2. Jensen–Shannon divergence and atomic shell-filling

The spinless wavefunction of an N -electron atom $\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)$ and its Fourier transform $\tilde{\Psi}(\vec{p}, \vec{p}_2, \dots, \vec{p}_N)$ allow one to determine the one-particle densities in position and momentum spaces, $\rho(\vec{r}) = \int |\Psi|^2 d\vec{r}_2 \dots d\vec{r}_N$ and $\gamma(\vec{p}) = \int |\tilde{\Psi}|^2 d\vec{p}_2 \dots d\vec{p}_N$ respectively, both being essential quantities in the description and quantification of the main atomic properties. For most purposes it is sufficient to deal with their spherical averages $\rho(r)$ and $\gamma(p)$. In what follows, all expressions and numerical analyses are considered in both spaces.

The total density $\rho(r)$ is a linear combination of the (n, l) -subshell densities $\rho_{nl}(r)$. Considering the total and the subshell densities normalized to unity, the linear combination is

$$N\rho(r) = \sum_{nl} N_{nl}\rho_{nl}(r) \quad (6)$$

for the N -electron atom, with N_{nl} being the number of electrons belonging to the (n, l) subshell. Consequently

$$N = \sum_{nl} N_{nl} \quad (7)$$

or equivalently

$$\sum_{nl} \omega_{nl} \equiv \sum_{nl} \frac{N_{nl}}{N} = 1 \quad (8)$$

where $\omega_{nl} \equiv \frac{N_{nl}}{N}$ will be referred to as the ‘ (n, l) -subshell relative weight’ and represents the contribution of the subshell to the total charge.

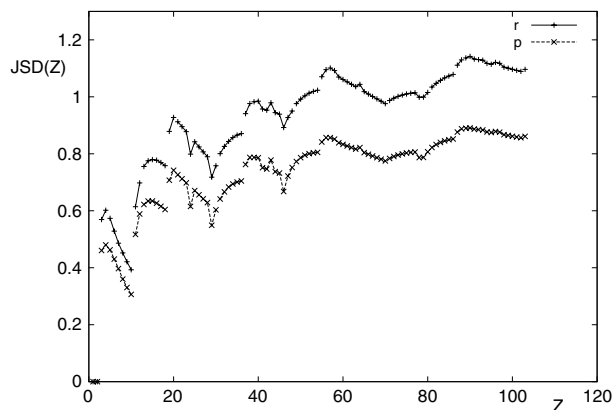


Fig. 1. The Jensen–Shannon Divergence, $JSD(Z)$, for the subshells of neutral atoms with nuclear charge $Z = 1$ –103 in position (r) and momentum (p) spaces. Atomic units are used.

Consequently, from the previous discussion, the density $\rho(r)$ of the whole atomic system can be considered as an appropriately weighted linear combination of its ‘constituent pieces’, i.e. the (n, l) subshell densities, the weights being determined by the subshell occupation numbers N_{nl} and the total number of electrons N of the complete system.

As for any arbitrary distribution, the internal disorder of each subshell density as well as that of the total density can be quantified by means of their corresponding Shannon entropies $S(\rho_{nl})$ and $S(\rho)$. An interesting question arising from the connection between the subshell and total densities is: to what extent is the disorder of the global system conditioned by the disorders of its constituents? The solution to this problem can be better understood by analyzing Eq. (4), corresponding to the weighted JSD for a set of distributions.

The JSD definition should be considered as the difference between two quantities: the Shannon entropy of the total density and the mean entropy of the subshells. Taking into account the non-negativity of JSD, the aforementioned mean entropy constitutes a lower bound to the total entropy of the composite system. Consequently, JSD should be interpreted as the deviation (from above) of the total entropy from its allowed minimal value or, in other words, the ‘entropy excess’ of the whole system with respect to the subsystem entropies.

Attending to the saturation property of JSD (i.e. it reaches the minimal value for identical distributions), it is clear that lower JSD values will correspond to similar subshell distributions and, consequently, to similar subshell entropies, independently of their values being higher or lower. In order to make JSD reach higher values it is necessary to deal with strongly different levels of disorder or entropy of the subshells. So, the JSD considered for an atomic system provides additional information on how similar or different the internal disorders of the subshells composing the system are.

In Fig. 1, the JSD divergences of the subshell densities for neutral atoms with nuclear charge $Z = 1$ –103 in both position and momentum spaces are shown, denoted respectively as $JSD_r(Z)$ and $JSD_p(Z)$ for the sake of simplicity. In computing them, the accurate near-Hartree–Fock wavefunctions of Koga et al. [31,32] have been employed.

Some comments are in order. Firstly it is observed that the JSD values in the two conjugate spaces have similar orders of magnitude and, in fact, belong to a not very wide interval excepting the trivial single-orbital cases, i.e. $Z = 1, 2$. Furthermore, the shapes of the two curves are almost identical, differing only (roughly) by a shifting constant. Also a strong relationship between the location of extrema and the shell-filling process can be clearly appreciated. In fact, local extrema (maxima and minima) appear in both curves at exactly the same Z values. Most of them are associated with the so-called ‘anomalous shell-filling’, as opposed to the usual shell-filling pattern characterized by the successive addition of electrons to the outermost (valence) subshell, the inner ones (core) remaining completely occupied. Locations of extrema appear determined by systems suffering the aforementioned anomalous process, for which adding an electron to the valence subshell additionally makes an inner one (at least) lose one or more electrons. Such is the case for the systems $Z = 24, 42, 57, 64, 78, 90, 96$, as well as for some closed-shell atoms ($Z = 4, 10, 18, 20, 70, 102$). It is remarkable that, in both cases, the type of extremum (maximum or minimum) displayed is determined by the value of the ‘ l ’ quantum number of the ‘anomalous’ or the valence subshell, respectively. In the first case, maxima appear for systems having the outermost ‘s’ subshell completely filled ($Z = 57, 64, 90, 96$) while minima occur for half-filled ones ($Z = 24, 42, 78$). As regards systems with closed shells, maxima are associated with outermost ‘s’ subshells ($Z = 4, 20$) and minima with ‘p’ ($Z = 10, 18$) and ‘f’ ($Z = 70, 102$) ones. The only exception to these rules is for the maximum at $Z = 15$, corresponding to the half-filled 3p subshell.

Summarizing the results of this section, the ‘intrinsic’ divergence of atomic systems in both conjugate spaces appears to be strongly correlated with the shell-filling patterns, providing information on the relevant characteristics of such a process. It is interesting to note that the JSD divergences provide information about shell structure patterns in both spaces [15], which is in contrast with the case for other distances [15,33] and also for the Shannon entropy, which show this behavior for only one space.

Additionally it can be concluded that the level of disorder of the total system having as reference the internal disorders of the isolated subshells is strongly determined by specific characteristics (i.e. the value of the ‘ l ’ quantum number) of the outermost subshells.

Table 1

The Jensen–Shannon Divergence (JSD) for the groups IA–VIII A of neutral atoms within the Periodic Table, in position (JSD_r) and momentum (JSD_p) spaces. Atomic units are used.

Group	JSD_r	JSD_p
IA ($Z = 3, 11, 19, 37, 55$)	0.08258	0.04019
IIA ($Z = 4, 12, 20, 38, 56$)	0.07544	0.03872
IIIA ($Z = 5, 13, 31, 49, 81$)	0.08347	0.03755
IVA ($Z = 6, 14, 32, 50, 82$)	0.07409	0.03626
VA ($Z = 7, 15, 33, 51, 83$)	0.06635	0.03481
VIA ($Z = 8, 16, 34, 52, 84$)	0.06047	0.03357
VIIA ($Z = 9, 17, 35, 53, 85$)	0.05626	0.03259
VIIIA ($Z = 10, 18, 36, 54, 86$)	0.05363	0.03202

3. Jensen–Shannon divergence of atomic sets within the Periodic Table

As mentioned in the Introduction, finding appropriate ways of comparing two or more systems among themselves in terms of representative distribution functions appears very interesting, especially for describing the similarity among relevant physical and chemical properties in terms of their distributions. Such is for instance the case for atomic systems, considered now in the present section as whole objects, with the aim of analyzing the correlation between their similarity in terms of distribution functions and meaningful properties such as shell structure, the total number of electrons and the atomic ionization potential (AIP).

In doing so, let us consider a collection of M atomic systems and their corresponding densities (ρ_1, \dots, ρ_M). Considering equally weighted distributions will lead to their JSD providing information on the spreading of their entropy values according to their shapes, instead of their size or normalization. All densities are here normalized to unity.

Different atomic sets are suited for analysis by means of the JSD, attending to the main properties that we are interested in. We will consider three interesting kinds of sets, each possessing its own characteristics, in order to provide information on the shell-filling process as well as the entropy dependence on the nuclear charge for fixed number of electrons.

3.1. Atomic groups of neutral systems

The Periodic Table of elements is divided into different groups, each one characterized by the valence subshell of the atoms (neutral) according to the Aufbau principle. The elements of a given group are characterized by the angular quantum number ' l ' of the corresponding valence subshell and its occupation number. Not all groups are composed of the same number of elements, according to the shell-filling rules.

For illustration, and in order to consider groups with a high enough number of elements, let us carry out the above mentioned JSD analysis for groups IA to VIII A. They are characterized by having valence subshells of type 's' (IA and IIA) or 'p' (IIIA to VIIIA). The number of elements of these groups ranges between 5 and 7, and the principal quantum number within the interval $n = 1-7$. For comparison purposes, we will deal with sets of identical numbers of elements: $M = 5$ for all of them, corresponding to the values $n = 2-6$, which are the only ones common to all of those groups.

The five-element JSD values in both spaces for these groups are shown in Table 1. Some comments are in order. First, it is observed that all values of JSD_p belong to a very narrow interval, which is wider for the position space ones. This means that the shapes of the position space densities are more sensitive to the valence subshell ' n ' principal quantum number than to the momentum ones. Additionally, there exists a general decreasing trend of JSD in both spaces on adding electrons to the valence subshell (in fact, the decreasing monotonicity is strict in momentum space). In other words, the higher the valence subshells filled, the more similar the densities. Such an effect is more apparent in position space than in momentum space.

A physically relevant quantity, strongly associated with the shell-filling patterns, is the first atomic ionization potential (AIP), clearly dependent on the characteristics of the atomic valence subshell. We wonder about the relationship between such an experimentally accessible quantity and the Jensen–Shannon divergence studied here. In order to establish such a relationship, two different analyses are carried out in the following figures. In Fig. 2(a) the JSD in momentum space is depicted for groups IIIA up to VIIIA of the Periodic Table (all of them with 'p' as the outermost subshell). It is observed from the figure that within a given atomic group the distance calculated between the element with the smallest atomic number ($n = 2$) and the rest of them ($n = 3$ to 6) shows an increasing behavior as n grows. In order to analyze the relation between the divergences in momentum space (Fig. 2(a)) with respect to the AIP, we have depicted in Fig. 2(b) the values of the ionization potential of the elements belonging to a given group (IIIA to VIIIA) and we observe an opposite behavior, i.e. JSD_p increases as the AIP decreases within each group.

A very noticeable connection between the JSD and the AIP is clearly displayed in Fig. 3. For ionizing (once) a neutral atom, the effort needed to perform such a process is quantified by the AIP. In this figure, the position and momentum space JSD between the starting neutral system (N) and the resulting singly charged cation (C), to be denoted by $JSD(NC)$, are compared to the AIP for systems with a number of electrons up to 54. It is worth noting the high level of structure displayed by all curves; it is especially remarkable that the most relevant extrema of both JSD and AIP appear at identical positions, strongly conditioned by the usual shell-filling process as well as the anomalous shell-filling. However, those extrema have opposite character (i.e. maximum or minimum) for the JSD and the AIP. Lower AIP values are mostly associated with systems having

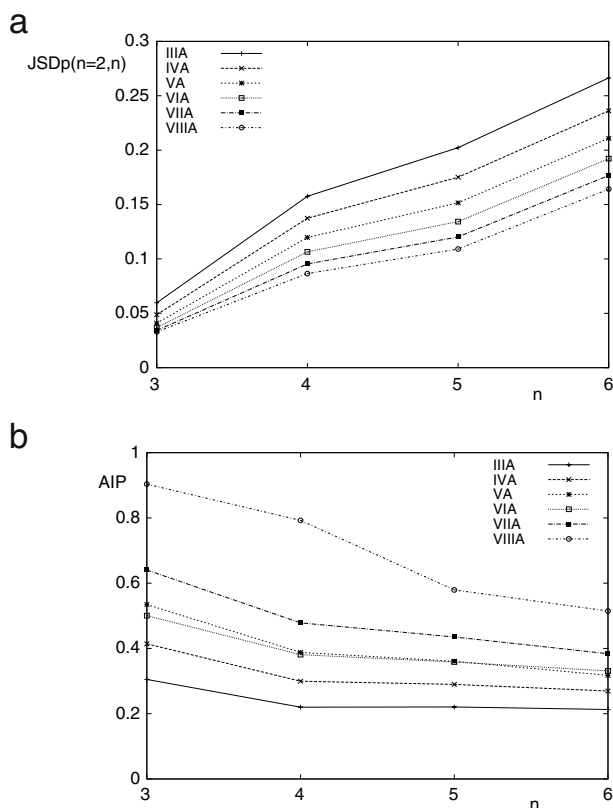


Fig. 2. (a) The momentum space Jensen–Shannon Divergence, $JSD_p(n = 2, n)$, for groups IIIA to VIIIA of the Periodic Table, between the system with valence subshell principal quantum number $n = 2$ and those with $n = 3–6$, and (b) the atomic ionization potential (AIP) for the latter. Atomic units are used.

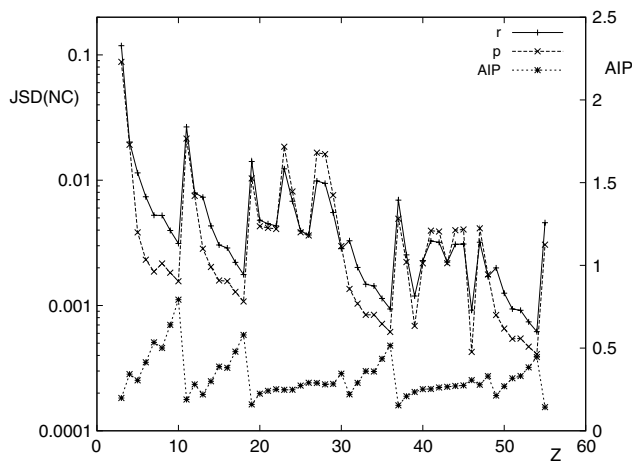


Fig. 3. The Jensen–Shannon Divergence, $JSD(NC)$, between neutral atoms (N) and singly charged cations (C) in position (r) and momentum (p) spaces, and the atomic ionization potential (AIP) of the neutral atoms, with nuclear charges $Z = 1–103$. Atomic units are used.

a single electron in the valence subshell, the ionization making such a subshell completely disappear, and consequently the JSD between the initial and final systems notably increases as compared with those between couples of systems with identically occupied subshells.

3.2. Atomic periods of neutral systems

After studying the dependence of JSD on the valence subshell principal quantum number ' n ' keeping its occupation number fixed, let us now analyze the JSD values associated with all systems with the same valence subshell. In this case, the number of systems composing a given set depends on the value of the ' l ' quantum number of the valence subshell, which is 2, 6, 10 and 14 for types 's', 'p', 'd' and 'f', respectively.

In Table 2, the JSD values in conjugate spaces are given for each subshell involved in the filling process for all neutral atoms with nuclear charge $Z = 1–103$. In this table it is especially remarkable that almost identical values are obtained

Table 2

The Jensen–Shannon Divergence (JSD) for subshell-filling in neutral atoms within the Periodic Table, in position (JSD_r) and momentum (JSD_p) spaces. Atomic units are used.

Subshell	JSD_r	JSD_p
1s	0.07574	0.06936
2s	0.04112	0.04033
3s	0.00896	0.00893
4s	0.00432	0.00431
5s	0.00178	0.00178
6s	0.00110	0.00110
7s	0.00064	0.00064
2p	0.06337	0.05808
3p	0.02887	0.02829
4p	0.00765	0.00761
5p	0.00401	0.00400
6p	0.00179	0.00179
3d	0.01488	0.01452
4d	0.00938	0.00931
5d	0.00289	0.00289
4f	0.00473	0.00468
5f	0.00323	0.00322

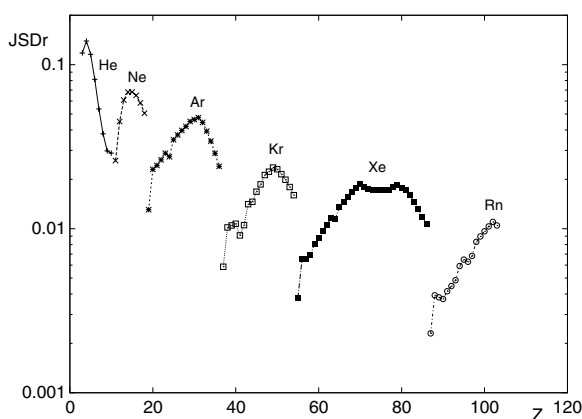


Fig. 4. The position space Jensen–Shannon Divergence, JSD_r , between a closed-shell system (He, Ne, Ar, Kr, Xe and Rn) and an open-shell one of the next period, with nuclear charge up to $Z = 103$. Atomic units are used.

independently of the space considered, with very few exceptions. The general trend again is a decreasing behavior for increasing ‘ n ’ principal quantum number while keeping the ‘ l ’ angular one fixed. It is concluded that shapes of systems belonging to the same period become more similar for heavy than for light atoms.

The process of successively adding electrons to a closed-shell system, which can be interpreted as ‘moving along a period’, is also analyzed, attending to the results displayed in Fig. 4. The position space JSD_r between a noble gas and the following elements along the whole period just below such a system are observed to (roughly) display a unimodal shape. Starting to add electrons to the new subshell of the reference system makes the JSD progressively increase as a consequence to a more noticeable dissimilarity, until reaching a maximum value (appreciably different for each period) where the JSD starts to decrease, while adding electrons makes the atom get closer to another noble gas. Consequently, the divergence with respect to the preceding closed-shell system depends not only on the number of additional electrons, but also on the distance to the next closed-shell atom. The very few and slight exceptions as regards the aforementioned unimodality are mostly associated with systems suffering from anomalous shell-filling, and the location of the ‘maximal JSD system’ tends to appear later as long as lower periods are considered.

3.3. Isoelectronic series

An isoelectronic series is a collection of atomic systems with an identical number N of electrons but with different nuclear (Z) or total ($Q \equiv Z - N$) charges. Let us consider the nine isoelectronic series with $N = 2-10$, each one composed of the corresponding neutral atom and its first twenty cations, the total charges ranging consequently in $Q = 0-20$. The Jensen–Shannon Divergence (JSD) of a given series provides information on the level to which the densities change when modifying the nuclear charge Z while keeping the number of electrons fixed. Previous studies on the physical characteristics of atomic systems belonging to a given isoelectronic series have been carried out [34], but usually by analyzing the isolated densities separately instead of by employing multi-density functionals as in the present work.

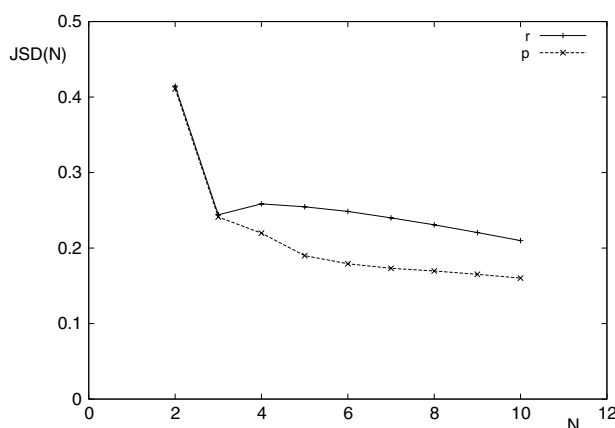


Fig. 5. The Jensen–Shannon Divergence, $JSD(N)$, for the 21-element isoelectronic series with $N = 2$ –10 electrons, in position (r) and momentum (p) spaces. Atomic units are used.

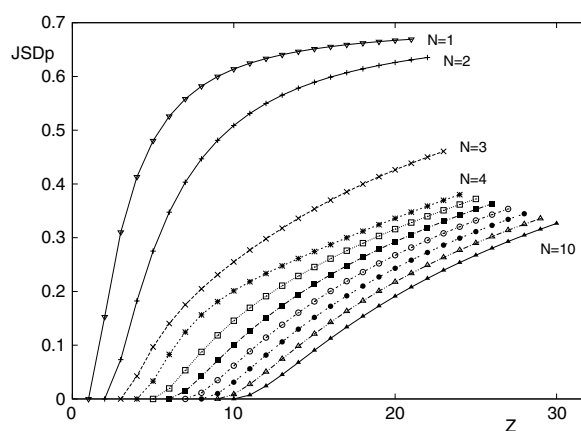


Fig. 6. The momentum space Jensen–Shannon Divergence, JSD_p , between a neutral N -electron atom and each of its successive twenty cations with nuclear charge $Z = N + 1$ to $Z = N + 20$, for the isoelectronic series $N = 2$ –10. Atomic units are used.

The divergence values $JSD(N)$ for $N = 2$ –10 for all elements (twenty one) from an N -electron series are shown in Fig. 5 for position (r) and momentum (p) spaces. In computing them, the near-Hartree–Fock wavefunctions of Ref. [35] have been employed. The main feature displayed in this figure is the decreasing trends for JSD in both conjugate spaces (with only one exception in position space) on increasing the number of electrons characterizing the series. This fact is in agreement with the discussion of results corresponding to the previously studied atomic sets, in the sense that differences among the densities appear smaller for heavy atoms than for light ones. It should be pointed out that increasing N makes all systems forming the series increase their nuclear charge and, consequently, their masses. It is interesting to note that the ranges of values for JSD_r and JSD_p are not only similar but also very small, and in fact for the first two series are almost identical.

Like in the two previous subsections (groups and periods), a JSD analysis is carried out associated with the process of increasing the nuclear charge of a starting system, the neutral atom in the present case. In doing so, the momentum space JSD_p between the uncharged system and the successive ones obtained by increasing the nuclear charge is as displayed in Fig. 6. This is for the isoelectronic series with a number of electrons $N = 1$ –10, each series consisting of twenty one elements. The results are essentially the same for the two spaces, and the most relevant conclusions are: (i) the series appear perfectly ordered, the higher JSD values corresponding to series with a lower number of electrons; (ii) increasing the nuclear charge quickly increases JSD, with the trend of reaching a limiting value after a high enough nuclear charge value; and (iii) the $N = 1, 2$ series are clearly distinguished from the others, as a consequence of possessing as principal quantum number of the valence subshell $n = 1$ and $n = 2$, respectively.

4. Conclusions

The generalized Jensen–Shannon divergence for arbitrary number of distributions and appropriate weights has been shown to provide a very useful tool for quantifying the information content of a composite system or set with respect to that of the constituents. The application in the study of many-electron systems within an information-theoretic framework reveals the strong connection between the divergence values in position and momentum spaces, and relevant physical

characteristics, such as (i) the atomic ionization potential, (ii) the shell-filling process in neutral atoms and (iii) the entropy excess dependence on the nuclear charge and the number of electrons.

Also remarkable is the very similar information (almost identical in some cases) provided by the JSD measure independently of the space that we are dealing with, contrary to the case for most comparative measures employed in the study of neutral atoms and ions.

The universality of the method employed here makes it suitable for being used for informational analysis of other relevant density functions, such as those describing molecular systems and or processes (e.g. reactions), also in the two conjugate spaces, as will be done elsewhere. Other kinds of generalizations arising by considering divergences defined in terms of Renyi and Tsallis entropies as well as the Fisher information are now being carried out.

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