

Fisher and Jensen–Shannon divergences: Quantitative comparisons among distributions. Application to position and momentum atomic densities

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The Fisher divergence (FD) and Jensen–Shannon divergence (JSD) are used in this work with the aim of providing quantitative measures of the discrepancies between two arbitrary D -dimensional distribution functions, the FD being of local character and the JSD of global one. In doing so, the concepts of Fisher information and Shannon entropy associated to a distribution are the essential quantities for building up these comparative functionals. This kind of relative measures are here applied to the study of the one-particle densities in both conjugated spaces (position and momentum) of neutral atoms, discussing the results as compared to those provided by other previous functional measures. It is clearly shown how these divergences provide relevant information on the atomic shell structure, up to a level which depends on the considered space and measure. © 2009 American Institute of Physics. [DOI: [10.1063/1.3078050](https://doi.org/10.1063/1.3078050)]

I. INTRODUCTION

In probability, statistics, or information theory, different approaches have dealt with the aim of establishing quantitative comparisons among two or more distribution functions, giving rise to a variety of definitions and measures of divergence. Each one has its own properties and characteristics, which make them more or less useful attending to the kind of problem, system, or process as well as the interpretation we are dealing with.^{1–12} In particular, the usefulness of some of them has been widely proved in the study, for instance, of different physical and chemical systems and processes in terms of meaningful and relevant distributions in their description.

Most of those theories and their associated tools are usually of general validity, i.e., they are applicable to arbitrary pairs of distributions $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$, defined over a common D -dimensional domain $\Delta \in \mathbb{R}^D$. This is the case of the most popular and simple measure, i.e., the “quadratic distance” (QD), given by the norm (defined by the Lebesgue integral on Δ) of the difference between both distributions, namely

$$\text{QD}(\rho_1, \rho_2) \equiv \left(\int_{\Delta} [\rho_1(\vec{r}) - \rho_2(\vec{r})]^2 d\vec{r} \right)^{1/2}, \quad (1)$$

with the normalization $\int_{\Delta} \rho_1(\vec{r}) d\vec{r} = \int_{\Delta} \rho_2(\vec{r}) d\vec{r} = 1$.

For our present purposes, i.e., the analysis and comparison of neutral atoms throughout the Periodic Table in terms of their one-particle densities in both conjugated position and momentum spaces [$\rho(\vec{r})$ and $\gamma(\vec{p})$, respectively], the definition domain is the whole three-dimensional ($D=3$) space \mathbb{R}^3 .

In this sense, it should be pointed out that (i) all expressions given in the present work for a specific space (position or momentum) will be also valid in the conjugated one, by only replacing properly 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 $[0, \infty)$.

Closely related to the idea of divergence appears the concept of similarity, which is fundamentally important in several scientific fields. For instance, graph theory is widely used for assessing similarities in taxonomy or for detecting protein sequence homology,¹³ and fuzzy set theory has also built up its own measures of similarity, which find application in areas such as management, medicine, and meteorology.¹⁴ Quantum similarity theory was originally developed in order to establish quantitative comparisons between molecular systems by means of their fundamental structure magnitudes, namely electron density functions. Applications of this relevant theory have been one of the cornerstones of chemical research in molecules.¹⁵ Similarities of atoms as individual components of molecules have been extensively studied by the pioneering group of Carbó-Dorca and also by other researchers,¹⁶ and more recently for neutral atoms^{17,18} and singly charged ions.¹⁹

The obvious motivation has been that the studies of similarities among electronic charge densities of diverse species could be also related to similarities among their main physical or chemical properties, according to density functional theory and Hohenberg–Kohn theorem.

Chemical similarity is often described as an inverse measure of distance in the usual space. In this work we adopt such point of view by applying two fundamental measures of

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information: Shannon entropy and Fisher information, as well as their associated divergences (all of them defined below).

Among those similarity and divergence measures susceptible of being employed in the study of atomic systems, specially relevant are the “Jensen–Shannon divergence” (JSD), the “Kullback–Leibler (symmetrized) relative entropy” (KLS), and the “quantum similarity index” (QSI).

The last one (QSI) is the overlap integral between both distributions (known as “quantum similarity measure”) normalized as

$$\text{QSI}(\rho_1, \rho_2) \equiv \frac{\int \rho_1(\vec{r})\rho_2(\vec{r})d\vec{r}}{\sqrt{\int [\rho_1(\vec{r})]^2 d\vec{r} \int [\rho_2(\vec{r})]^2 d\vec{r}}} \quad (2)$$

(i.e., with a normalization factor given by the corresponding “autosimilarities”), which ranges within the interval $[0,1]$, reaching the maximum value of 1 if and only if both distributions are identical. It is also interesting to notice that both the QD and the QSI are defined in terms of exactly the same three integrals (the overlap one and both autosimilarities), but in a different way.^{15,18–21}

The other measures mentioned above (JSD and KLS) are strongly related to the so-called Shannon entropy $S(\rho) \equiv -\int \rho(\vec{r})\ln \rho(\vec{r})d\vec{r}$ of the density, which is well known to play a relevant role within an information-theoretic framework because it constitutes a measure of *spreading* of the density over its domain.²²

The Shannon entropy S is an information quantity usually referred as a measure of *global* character because its value quantifies the content of information of the considered distribution as a whole over its domain, being very little sensitive to more or less strong changes within small-sized regions. Such a global behavior is also shared by other well-known information measures (e.g., variance, Rényi² and Tsallis^{23,24} entropies, disequilibrium²⁵) as well as the just defined quantum similarity measure and index.²⁶

It appears natural to wonder on the existence of a measure, in a similar fashion as the Shannon entropy, in order to quantify how distant the density $\rho(\vec{r})$ is from a given *a priori* one $\rho_0(\vec{r})$.^{3,4,9,10} An answer to this question was given in Ref. 3 by defining the KL or relative entropy $\text{KL}(\rho_1, \rho_2) \equiv \int \rho_1(\vec{r})\ln[\rho_1(\vec{r})/\rho_2(\vec{r})]d\vec{r}$, which symmetrized version (KLS) reads as

$$\text{KLS}(\rho_1, \rho_2) \equiv \int \rho_1(\vec{r})\ln \frac{\rho_1(\vec{r})}{\rho_2(\vec{r})}d\vec{r} + \int \rho_2(\vec{r})\ln \frac{\rho_2(\vec{r})}{\rho_1(\vec{r})}d\vec{r}. \quad (3)$$

This functional possesses the appropriate properties to be interpreted in the sense described above. It is symmetric, and non-negative as far as both densities be equally normalized, the minimum value zero being reached if and only if both densities are identical.

This divergence measure, also called “information gain,” is related to other important quantities studied in information theory and has been extensively used in Bayesian updating through the minimum-cross-entropy principle.²⁷ Another recent and important application falls in the field of quantum information theory, where relative entropy can be used as a

measure of distinguishability between quantum systems and therefore as a quantum entanglement measure.²⁸

Relative entropy, using a hydrogenlike model density, has been studied in atomic systems, and other differences and similarities of atomic and molecular electron densities have also been obtained.^{29–31} Very recently a new application of the KL measure to the study of molecular chirality has been carried out.³²

Let us also point out that the concept of Shannon entropy provides additional ways of defining functionals, displaying adequate properties (namely non-negativity and saturation for identical distributions, as occurs with QD, KLS, and QSI), with the aim of comparing distribution functions, as, e.g., the so-called JSD, among others. It is defined as^{9,11,12}

$$\text{JSD}(\rho_1, \rho_2) \equiv S\left(\frac{\rho_1 + \rho_2}{2}\right) - \frac{1}{2}[S(\rho_1) + S(\rho_2)], \quad (4)$$

which represents the difference between the Shannon entropy of the mean density and the mean value of the individual entropies. Its non-negativity arises from the convex character of the Shannon entropy functional. Attending to the definition of the KL measure, it is not difficult to express the JSD divergence in terms of KL relative entropies as

$$\text{JSD}(\rho_1, \rho_2) = \frac{1}{2} \left[\text{KL}\left(\rho_1, \frac{\rho_1 + \rho_2}{2}\right) + \text{KL}\left(\rho_2, \frac{\rho_1 + \rho_2}{2}\right) \right], \quad (5)$$

which provides an additional interpretation of the JSD divergence as the mean value of the “distances” (understood as the KL measures) of each density to the mean one. This divergence has been recently used in segmentation, classification, clustering, pattern recognition, and has been also generalized and applied in the context of quantum information theory.^{33–35}

It is worthy to point out that the aforementioned global character of the Shannon entropy translates also into both KLS and JSD information measures, as also occurs with QD and QSI due to the involved integrals in their definition.

Taneja *et al.*^{11,12} extensively studied and generalized some of the above information and divergence measures. In particular, a two-parameter generalization recovering Pearson,¹ Rényi,² Kullback–Leibler,³ Jeffreys,⁴ Bhattacharya,⁵ Hellinger,⁶ Sibson,⁷ and Burbea–Rao³⁶ divergences has been shown. Properties and inequalities among these global information measures have also been obtained, and more recently a new generalization including weighted measures has been provided.^{11,12,37,38}

However, it would be also of great interest to dispose of information measures displaying a deeper *local* character, namely their values being more sensitive to the aforementioned strong local changes. The main quantity studied and

employed in the literature with such a characteristic (in what concerns measures on a single distribution) is the so-called Fisher information I ,^{39–43} defined as

$$I(\rho) \equiv \int \rho(\vec{r}) |\vec{\nabla} \ln \rho(\vec{r})|^2 d\vec{r}, \quad (6)$$

which can be interpreted as the expectation value of the quadratic (D -dimensional) logarithmic derivative of the density. The presence of the squared density derivative makes this information quantity to be much more sensitive to changes in its gradient content even at a local level, notably increasing in the presence of numerous and/or strongly peaked local extrema. In what follows we will refer to the “local character” for emphasizing such sensitivity, as opposite to the “global character” as introduced when defining Shannon entropy and other related measures.

The Fisher information has been also applied to emphasize the aforementioned local character of other relevant information measures, such as the so-called complexity of a given system, by considering it as one of the factors which usually determine the complexity, giving rise recently to the concepts of Fisher–Shannon and Cramer–Rao complexities^{44–46} successfully applied to the study of structural properties of atomic systems.

Attending to the characteristics of Shannon (global character) and Fisher (local character) functionals, and having in mind the definition given by Eq. (3) of the Shannon-based global comparison KLS between two distributions, a measure of local character based on the Fisher information concept can be also built up in a similar way, namely,

$$\begin{aligned} \text{FD}(\rho_1, \rho_2) \equiv & \int \rho_1(\vec{r}) \left| \vec{\nabla} \ln \frac{\rho_1(\vec{r})}{\rho_2(\vec{r})} \right|^2 d\vec{r} \\ & + \int \rho_2(\vec{r}) \left| \vec{\nabla} \ln \frac{\rho_2(\vec{r})}{\rho_1(\vec{r})} \right|^2 d\vec{r}, \end{aligned} \quad (7)$$

which will be referred as “Fisher divergence” (FD) in what follows, according to the concept of divergence among distributions, previously introduced by other authors in the information-theoretical context.^{11,12} From the FD definition, it is immediately observed that it preserves the aforementioned properties desirable for establishing the quantitative comparison, namely symmetry, non-negativity, and saturation for identical distributions.

It is worthy to point out that each individual term of the FD definition is known as “relative Fisher information,” which scarce applications have been carried out with similar aims to those of the Kullback–Leibler relative entropy, that is, to perform a comparison of a distribution respect to an *a priori* one,^{47,48} being not the objective of the present job.

Instead, both the FD and JSD measures are employed in this work in order to analyze the divergence among different position- and momentum-space one-particle densities in atomic systems, interpreting the obtained results according to the main physical characteristics of the atoms considered,

such as nuclear charge, valence subshells and their occupation numbers, or groups of the Periodic Table they belong to, among others. To the best of our knowledge, the application of both the FD and the JSD divergences to the study of multielectronic systems is carried, for the first time, in the present work.

The paper is structured as follows. Section II is devoted to the numerical analysis of FDs in position and momentum spaces for neutral atoms throughout the Periodic Table, including a study of the results as compared to those provided by other information measures such as the QD. In Sec. III, a similar study is carried out for the JSD values, being also discussed taking into account those analyzed in the previous section for the FD and providing the appropriate interpretation from a physical point of view. Finally, the most relevant conclusion will be given in Sec. IV.

II. FD IN ATOMIC SYSTEMS

The main aim in this section is the numerical study of the FD between pairs of atomic electron densities in position and momentum spaces, $\rho(\vec{r})$ and $\gamma(\vec{p})$, respectively, as well as to provide an appropriate physical interpretation of the FD values. First of all, let us remember that the one-particle densities $\rho(\vec{r})$ and $\gamma(\vec{p})$ are obtained from the total wave function $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ of the N -electron atom and its Fourier transform $\tilde{\Psi}(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$ by integrating $|\Psi|^2$ and $|\tilde{\Psi}|^2$ on all variables except the first one. Additionally, the spherical averages $\rho(r)$ and $\gamma(p)$ of the aforementioned one-particle densities are quite enough for the density-based study of isolated atomic systems.

In order to clarify the notation, all quantities considered in what follows will be denoted by adding a subscript to determine the space they belong to (unless not needed for results or expressions of general validity in both conjugated spaces), while systems will be referred by means of their nuclear charge Z . For illustration, $\text{FD}_r(3, 5)$ will denote the FD in position or r -space of the atoms with nuclear charges $Z=3$ and $Z=5$.

The numerical analysis has been carried out by using near-Hartree–Fock wave functions⁴⁹ for neutral atoms with nuclear charge $Z=1–103$. First, let us show the FD in position space $\text{FD}_r(Z, Z')$ between each atom Z' belonging to a given group as compared to each one of the whole Periodic Table, $Z=1–103$. For illustration, the associated curves (as functions of Z) are shown in Fig. 1(a) for noble gases (i.e., $Z'=2, 10, 18, 36, 54, 86$). It is observed that all curves (corresponding to the systems of the chosen group) behave in a similar fashion, first monotonically decreasing until reaching the minimal zero value for $Z=Z'$, and then monotonically increasing as Z increases. Such a behavior is displayed not only for all systems of the present group but also for all other groups of the Periodic Table. This fact can be interpreted, attending to the meaning of divergence associated to the FD definition, in the sense that it only measures how different the atomic nuclear charges Z and Z' are. However, no information on other physically relevant characteristics (e.g., shell filling, periodicity, etc.) is obtained by means of $\text{FD}_r(Z, Z')$.

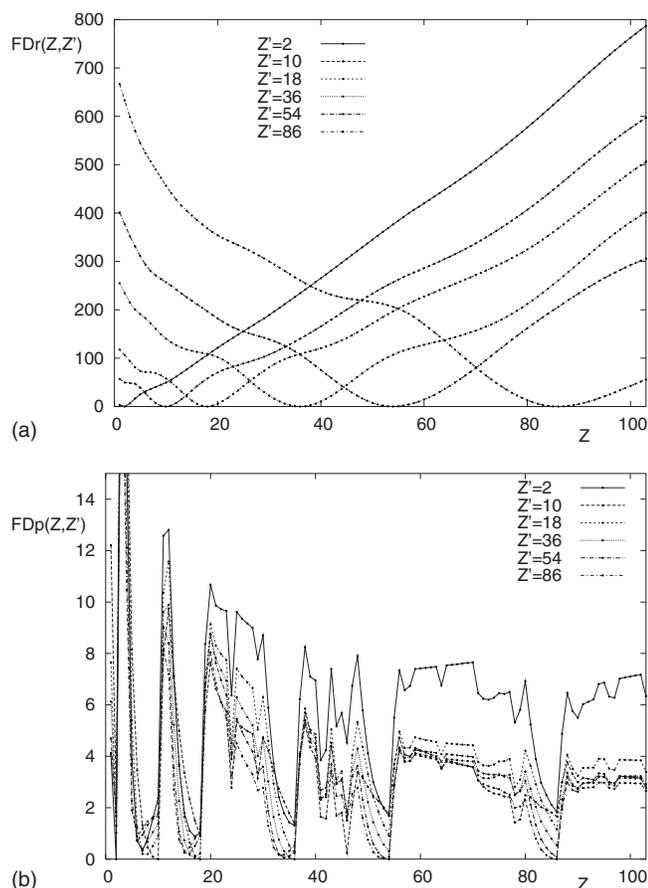


FIG. 1. $FD(Z, Z')$ of noble gases ($Z' = 2, 10, 18, 36, 54, 86$) for $Z = 1-103$ in (a) position and (b) momentum spaces. Atomic units are used.

The previous unimodal shapes in Fig. 1(a) strongly differ from those displayed when performing a similar comparison in terms of the $FD_p(Z, Z')$ in momentum space as given in Fig. 1(b) for the previously chosen group, namely noble gases; the same comments for the rest of groups of the Periodic Table also remain valid. Now, a significant number of local extrema (maxima and minima) appear in all curves, which behavior is consequently far from the previously mentioned systematically unimodal one in position space.

Focusing our attention on minima (intuitively associated with the concept of “close” or “similar” systems) it is observed, at a first glance, the existence of a small number of clearly distinguishable minima located at (roughly) the same positions for all curves, as well as a larger number of not so deep/high peaks along them. Concerning the most relevant minima, their locations are around the values of the Z' nuclear charges of the systems conforming the group under study. This situation is much more in accordance with the aforementioned interpretation of a divergence between atomic distributions as a measure of their distance or dissimilarity interpreted in terms of their main physical characteristics because the $FD_p(Z, Z')$ values are highly conditioned by the valence occupation numbers or, equivalently, by the groups the compared atoms belong to. So, and contrary to the position-space divergence FD_r , the momentum-space one FD_p is shown to be able of providing information on physical properties of neutral atoms beyond the difference between their nuclear charges.

While the higher peaks are associated with comparisons between members of the same group of the Periodic Table, there also appear a set of much smaller local extrema for specific values of the nuclear charge Z . Most of those peaks occur when one of the systems being compared is an atom suffering an anomalous shell filling. The appearance of those peaks for these “anomalous systems” is systematic, in the sense of being displaying independently of the other system which is being compared to.

The similar behavior of all elements belonging to the same group is a common feature of all groups within the Periodic Table. For all of them, moreover, increasing the nuclear charge of contiguous atoms makes their difference in momentum space (attending to the divergence values) to decrease, that is, similar trends are displayed by contiguous systems belonging to different groups. In particular, filling a p subshell and even more for the d and f ones provides lower values of the divergence among themselves. For instance, transition metals as well as lanthanides and actinides display very similar trends within their periods.

The differences between the FD behaviors in position and momentum spaces arise from the asymptotic behaviors of the involved densities. In position space, the atomic density $\rho(r)$ has an exponentially decreasing behavior, so that the values of the involved integrals are mainly determined by the regions surrounding the nuclei, where the density behavior is governed by the nuclear charge Z . However, the low-speed regions are associated with the outermost subshells (valence ones), being consequently those mainly determining the FD values.

Some conclusions of the previous comments are emphasized by analyzing the structural behaviors of curves corresponding to FDs of elements belonging to different groups. In doing so, it is enough to choose a couple of them as done in Figs. 2(a) and 2(b), corresponding to their divergences in both conjugated position and momentum spaces, respectively. Let us consider two systems with similar values of their nuclear charges but significantly different according to their valence orbitals, such as, for instance, $Z' = 18$ and $Z' = 20$ as done in those figures. Concerning their position-space divergences $FD_r(Z, Z')$ as functions within the range $Z = 1-103$, it is observed in Fig. 2(a) how both curves display almost identical shapes, differing roughly only by a small shift according to the small difference $2 = 20 - 18$ between their nuclear charges, which is also the distance between the locations of their absolute minima. This figure corroborates the above comment concerning position-space FD_r divergences, in the sense that they are mainly dependent on the nuclear charges of the involved systems, much more than on their physical or chemical properties. However, a similar analysis based on Fig. 2(b) where the momentum space divergences are displayed for the same systems shows a strongly different behavior of the $FD_p(Z, Z')$ function even for systems with very close values of their nuclear charges. In the present example the chosen systems belong to different groups, being the outermost subshell $3p^6$ for $Z' = 18$ and $4s^2$ for $Z' = 20$. That difference between their valence subshells strongly determines the associated FD_p values according to the shell structure of the atom they are compared to. In

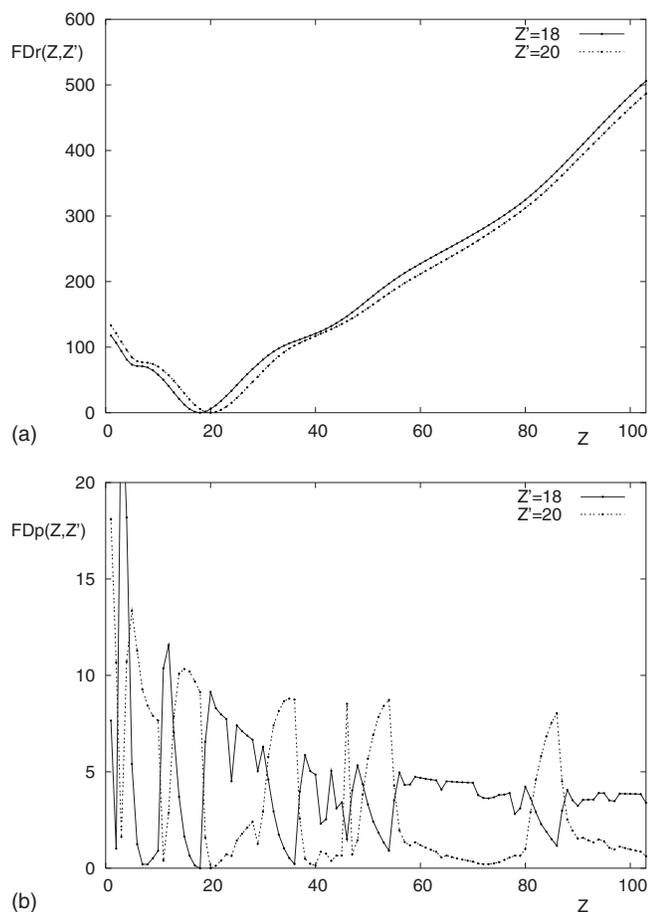


FIG. 2. $FD_r(Z, Z')$ of Ar ($Z'=18$) and Ca ($Z'=20$) for $Z=1-103$ in (a) position and (b) momentum spaces. Atomic units are used.

a similar way as explained in comments of Fig. 1(b) for the role of the momentum space divergence FD_p , it can now be also concluded that main minima correspond (with few exceptions) to systems belonging to the same group, while other extrema are mostly associated with the anomalous shell-filling process. It is clearly observed that some extrema of both curves are located at the same positions but showing an opposite character (i.e., maximum/minimum). This is, for instance, the case of extrema appearing as a consequence of the groups the atoms belong to.

A brief global conclusion obtained from the analysis of all figures discussed up to now in the present section is that the FD in momentum space $FD_p(Z, Z')$ for neutral atoms displays a structural richness which is clearly related to the shell-filling process and structure, while the same measure in position-space loses such an information content as shown by its unimodal behavior for all atomic systems.

Concerning the last conclusion, it is natural to wonder on the quality of the just analyzed FD, a measure of local character as initially discussed, as compared to the global QD given by Eq. (1). Some other works on this subject have also employed the QSI and other measures related to the QD in order to analyze the similarity on multielectronic systems. Among them, it is worthy to remark those only carried out in position space^{50,51} as well as other more complete ones just recently published involving additionally the momentum and the phase spaces.^{18,19} In the present work, we have carried

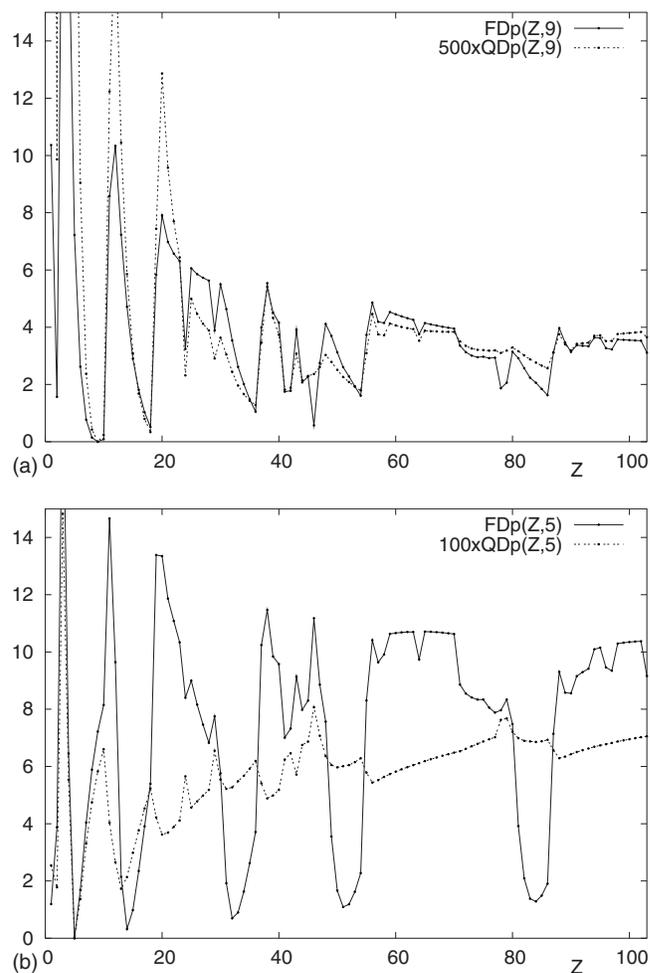


FIG. 3. $FD_p(Z, Z')$ and $QD_p(Z, Z')$ in momentum space for $Z=1-103$ of (a) F ($Z'=9$) and (b) B ($Z'=5$). Atomic units are used.

out for the QD distance a similar analysis as that performed with the FD. Again, the previously mentioned unimodal shape for the $QD_r(Z, Z')$ curves is displayed in position space, a richer structure being obtained in momentum space. So, and for comparison purposes, we will restrict ourselves to the FD_p and QD_p quantities, in order to analyze the characteristic structural patterns of both them.

From a systematic comparison of the curves $FD_p(Z, Z')$ and $QD_p(Z, Z')$ as functions of Z for a fixed Z' , it is concluded that their resemblances and differences are strongly determined by the specific Z' atomic value chosen for comparing them, as well as by the region specified by a Z range. This can be clearly observed in Figs. 3(a) and 3(b), corresponding to $Z'=9$ and $Z'=5$, respectively. The main structure of both curves in Fig. 3(a) for $Z'=9$ (properly scaled in order to carry out a useful comparison) is very similar over almost the whole Periodic Table. All peaks appear to be of the same kind (maximum or minimum), whether for cases corresponding to atoms of the same group as $Z'=9$ whether for those associated with the anomalous shell filling. However, a strongly different behavior is observed in Fig. 3(b) for the $Z'=5$ atom. It is clearly observed how the $FD_p(Z, 5)$ displays an enhanced sensitivity associated with the shell structure as compared to that shown by the $QD_p(Z, 5)$.

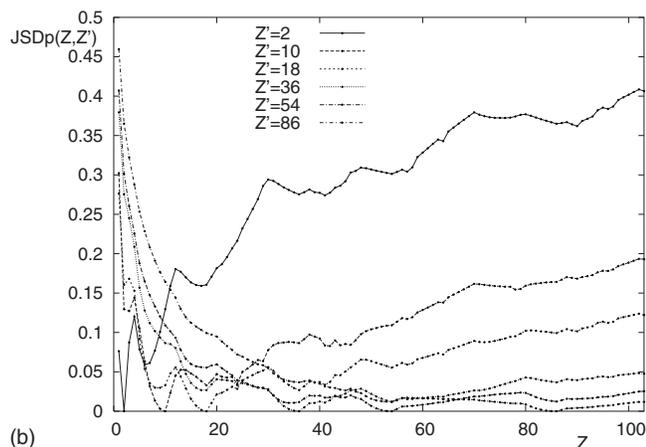
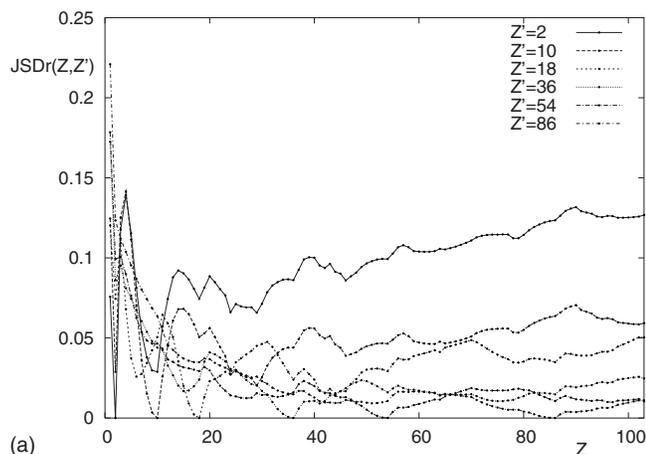


FIG. 4. JSD(Z, Z') of noble gases ($Z'=2, 10, 18, 36, 54, 86$) for $Z=1-103$ in (a) position and (b) momentum spaces. Atomic units are used.

III. JSD IN ATOMIC SYSTEMS

One of the most popular ways (apart from the QD) of defining global quantitative measures of dissimilarity among distribution functions is based on the concept of Shannon entropy because of its well-known global character as indicator of the density information content. In this sense, it is worthy to remember both the definitions of the JSD and the symmetrized KLS, as provided by Eqs. (4) and (3), respectively. In both cases, the global character of the Shannon entropy translates into the associated JSD and KLS measures.

Attending to the aim of the present work, namely the analysis of different measures in order to compare atomic electron densities in both position and momentum spaces as well as the interpretation of the corresponding results from a physical point of view, it appears natural to carry out a similar study to that developed in Sec. II for the FD, now in terms of the above mentioned quantities of global character, opposite to the local one of the FD.

In doing so, let us first analyze the JSD(Z, Z') curves (as functions of Z) for each value Z' corresponding again (for comparison purposes) to noble gases in position [Fig. 4(a)] and momentum [Fig. 4(b)] spaces, in a similar fashion as done for FD. Now it is worthy to remark the roughly similar structure of the JSD measure for any Z' through the whole Periodic Table independently of the space considered. This

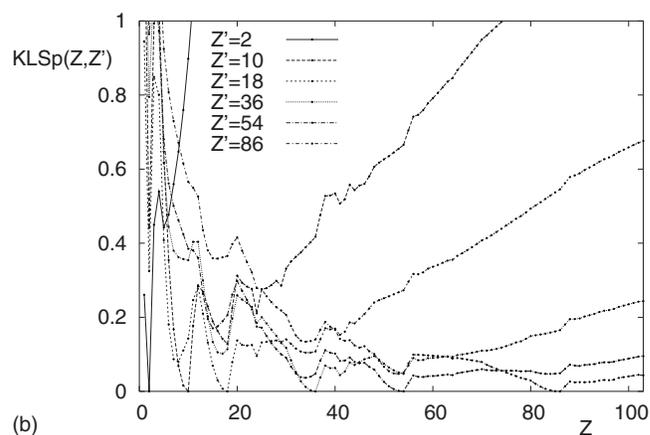
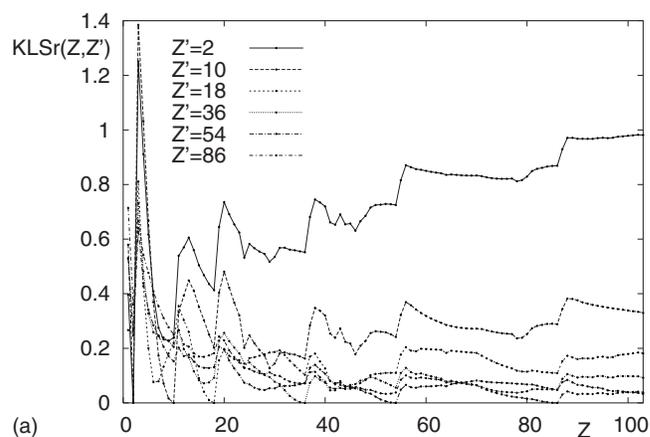


FIG. 5. Symmetrized KL entropy KLS(Z, Z') of noble gases ($Z'=2, 10, 18, 36, 54, 86$) for $Z=1-103$ in (a) position and (b) momentum spaces. Atomic units are used.

similarity strongly differs from the corresponding behavior of the FD as remarked in Sec. II. An important conclusion on this result is that the position-space JSD_r divergence provides much more information on the atomic structural properties than the QD or the FD, being far from the position-space unimodality. Location of main extrema of JSD(Z, Z') still remains determined by the shell-filling process following similar patterns to those of the FD_p divergence in momentum space, but also appearing now in position space for the JSD_r divergence, in spite of not being so ordered, narrow and deep as in the FD_p case.

Restricting ourselves to the momentum space, it is clearly revealed the higher content of information of the FD on the atomic shell-filling process than that provided by the JSD, being again better displayed in momentum space the structural richness of atomic systems by means of the local divergence FD as compared to the global one JSD.

Similar comments are also valid for all other groups in the Periodic Table, as well as for the symmetrized KL entropy KLS(Z, Z') in both spaces. In order to have an idea of the behavior of the KLS relative measure, the corresponding values are displayed in Figs. 5(a) and 5(b) in position and momentum spaces, respectively. Similarly as occurred with the JSD divergence, the shell-filling pattern is clearly displayed in both spaces, even more clearly in position space when dealing with heavy systems. In any case, location of extrema in both cases appears again determined by the shell

structure of the involved atoms. The present analysis widely generalizes and improves the only previous one, to the best of our knowledge, carried out in order to compare atomic distributions,³⁰ where the KLS relative entropy, as well as the quadratic and L^1 distances, were employed to the study of consecutive atoms.

The reason of JSD and KLS displaying relevant structure in both conjugated spaces, as opposite to the FD case where only in momentum space was observed, arises from their global character, being consequently determined by the behavior of the compared densities over the whole domain with a balanced quantification on short- and long-range regions.

So, it can be concluded that the measures of global character JSD_r and KLS_r in position space provide more information than the local-character measure FD_r , while the level of structure of the same quantities in momentum space appears appreciably higher for the FD_p than for the global Jensen–Shannon and KLS ones.

IV. CONCLUSIONS

Exploring quantitatively the level of similarity/dissimilarity between two different systems in terms of meaningful distributions appears actually as a very interesting field. The general validity of the techniques proposed and employed in the present work allows their use for studying any multielectronic or quantum-mechanical system, e.g., atoms, molecules, clusters, and many others.

Different divergence measures are here proposed, including local- and global-character ones, with the aim of analyzing the similarity and discrepancy among neutral atoms throughout the whole Periodic Table. These systems have been considered as an appropriate benchmark due to their strong hierarchical organization. The studied divergences have been shown to provide relevant information on the atomic shell structure.

In particular, the FD, in spite of its local character, is almost insensitive (as also happens with the QD and the QSI measures) to the atomic shell structure when dealing with the corresponding position-space distributions, constituting only, in fact, a measure of how close the compared systems are located at the Periodic Table, independently of the groups they belong to be different or the same. On the other hand, the situation absolutely differs from that one when dealing within the momentum space, where both the QD and the FD measures clearly show the complex organization and the shell-filling patterns at the Periodic Table. Now a strong similarity among members of the same atomic group is displayed, as well as relevant differences among systems owning different valence subshells. Higher resolution is displayed by FD as compared to QD, especially for large Z systems.

Concerning the global divergences KLS and JSD, both related to the concept of Shannon entropy as information measure, they are shown to be quantities displaying a non-trivial structure in position space, at a similar level to that provided in momentum space. Nevertheless, such a structure is much softer as compared to that of the momentum space FD. Attending to the last comment, it appears much better to

consider the simultaneous analysis in both conjugated spaces of all divergences here studied in order to exploit the information content and structural richness of the atomic systems.

As an immediate consequence of the above discussed characteristics, it appears strongly relevant to consider the complementary use of both spaces attending to the chosen divergence or comparative measure between atomic densities, especially for interpreting the results according to relevant physical and/or chemical properties such as those related to their shell structure.

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