Divergence analysis of atomic ionization processes and isoelectronic series

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Fisher divergences (FDs) and Jensen-Shannon divergences (JSDs) are used in this work to quantify the informational discrepancies between the one-particle electron densities of neutral atoms, singly charged ions, and isoelectronic series. These dissimilarity magnitudes, computed for a set of 319 atomic systems in both position and momentum spaces, provide relevant information concerning pattern, structure, and periodicity properties of the ionization processes. In particular an apparent correlation between extremal values of the atomic ionization potential and the divergences is found. Results are compared with those obtained by quantum similarity techniques.

I. INTRODUCTION

There is an extensive literature on measures of similarity and dissimilarity between probability densities [1–12], some of them for arbitrary dimensionality, and they have been used in a wide variety of scientific fields including, for instance, sequence analysis [13], pattern recognition [14], diversity [15], classification [16], homology [17], neural networks [18], or computational linguistics [19]. The recent explosion in knowledge-based chemical research has created a surge of interest in chemical similarity. Molecular modeling and quantitative structure activity relationship (QSAR) are simple examples of such interest [20].

Chemical similarity is often described as an inverse of a measure of distance in the appropriate space. In particular quantum similarity theory (QST) [12] was originally developed in order to establish quantitative comparisons between molecular systems by means of their fundamental structural magnitudes, i.e., electron-density functions. The obvious motivation was that studies of differences in the electronic charge densities of these species could be related to differences in their respective physical and chemical properties, according to density-functional theory and Hohenberg-Kohn theorem [21].

The simplest and most intuitive similarity measure is just an overlap integral between the two electronic densities to be compared [22–24]. On the other hand, some other similarity indices based on the concept of an information distance have been proposed and evaluated for different many-particle systems, such as, e.g., atoms, molecules, and nuclei [23,25–28].

Most of the work on quantum similarity has been done in the usual position representation r. Nevertheless, there has also been interest in extending this technique to momentum-space (p) atomic similarity. 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, where this density tends to be large. So we explore in this case the valence region in contrast to position space in which we are mainly examining behaviors near the core regions. This important result has been recently shown for the case of atomic systems [29], concluding that, when using similarity overlap measures, comparison of two many-electron systems in what concerns the shell structure requires the consideration of the momentum-space variable p through the associated one-particle density.

Therefore it is natural to be interested in searching for new divergence or similarity measures based on information theory that revealed the atomic structure and other properties not only in the momentum space but also in the position one. We adopt here this point of view by using two fundamental information measures: Shannon entropy and Fisher information, to be presented in Sec. II, and their related measures of divergence, namely, Jensen-Shannon divergence (JSD) and Fisher divergence (FD).

The main objective of this work is to study, by using the above mentioned relative measures, the dissimilarities between electronic densities corresponding to atoms and ions in both conjugated spaces. Specifically, in Sec. III we carry out a dissimilarity analysis for simple but strongly organized N-electron systems ($N \leq 54$) of neutral atoms and their singly charged ions, exploring their outer electronic layer and studying the behaviors accompanying the process of gain or loss of one electron for an atom at constant nuclear charge Z. The relationship between the atomic ionization potential (AIP) and the dissimilarity measures among neutral systems and charged species is also studied. Besides, in Sec. IV, we explore the core regions of atoms by computing the isoelectronic variation in these information divergences of over a fairly extended range of nuclear charge Z values. The results obtained by using these new divergence measures (FD and JSD) are also compared to those obtained with QSTs based on overlap measures. Conclusions and main results are collected in the last section.

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II. JENSEN-SHANNON AND FISHER INFORMATION DIVERGENCES

The main aim of this work is to study the effect of ionization processes on atoms from Li to Cs ($3 \leq Z \leq 55$) by means of their one-particle densities, $\rho(\vec{r})$ and $\gamma(\vec{p})$, in both conjugated spaces, namely, position and momentum, respectively. For the systems we are dealing with, i.e., neutral species and ions in the absence of external fields, it is sufficient to consider the spherically averaged densities $\rho(r)$ and $\gamma(p)$.

In doing so we define and compute two divergence measures, one measuring differences on the global spread of the distributions, the Jensen-Shannon divergence, and other of local character, measuring differences on intrinsic changes in the distribution, the Fisher divergence.

Several fundamental magnitudes have been introduced in the literature as measures of information for general probability densities, but the most commonly used in information theory is the Shannon entropy (S) [30,31]. It is a global measure of the spread or delocalization of a distribution being defined as the expectation value of the logarithm of the distribution:

$$S(\rho) \equiv - \int \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}. \qquad (1)$$

Information-theoretic properties based on Shannon entropy have been extensively employed in recent years for the study of quantum-mechanical and multielectronic systems. In particular, their use in atomic and molecular systems has led to an insight in these fields, providing a wide variety of results, including recent studies on complexity measures [32–39].

The relative entropy or Kullback and Leibler (KL) divergence [2] is one of the pioneering global measures of the difference between two probability distributions. It expresses the amount of information supplied by the data for discriminating among the distributions being a "directed divergence" and therefore not symmetric:

$$\mathrm{KL}(\rho_1, \rho_2) \equiv \int \rho_1(\vec{r}) \ln \frac{\rho_1(\vec{r})}{\rho_2(\vec{r})} d\vec{r}. \qquad (2)$$

Its applications for different procedures in obtaining minimum cross entropy estimations and the determination of atomic and molecular properties [40,41], among others, make it to constitute an essential tool within the information theory. Very recently, a quantum dissimilarity measure has been constructed within the aforementioned informational framework, allowing to study the relativistic effects on the electron density [42]. These kind of KL measures have been also employed to analyze molecular reaction paths [43].

Won and You [44] introduced, somewhat implicitly, a closely related information measure between two or more distributions, the JSD [45]:

$$\mathrm{JSD}(\rho_1, \rho_2) \equiv \frac{1}{2} \left[\mathrm{KL}\left(\rho_1, \frac{\rho_1 + \rho_2}{2} \right) + \mathrm{KL}\left(\rho_2, \frac{\rho_1 + \rho_2}{2} \right) \right]. \qquad (3)$$

Consequently, JSD represents the mean dissimilarity (understood in terms of the KL measure) of each density respect to the mean one. Attending to the JSD definition given above, and using Eqs. (1) and (2), the Jensen-Shannon divergence can be also expressed in terms of the Shannon entropy as

$$\mathrm{JSD}(\rho_1, \rho_2) = S\left(\frac{\rho_1 + \rho_2}{2} \right) - \frac{1}{2}[S(\rho_1) + S(\rho_2)], \qquad (4)$$

allowing to interpret also the JSD divergence as the "entropy excess" of the mean density with respect to the mean entropy of the individual densities.

Other important advantages of this divergence are that (i) does not require the condition of absolute continuity for the probability distributions involved, (ii) weights of each density can be different from 1/2 as appearing in Eq. (3), and (iii) can be generalized for an arbitrary number of distributions. During past years researchers interested toward parametric generalizations of these classical measures of information [8,10,11,46–48]. The JSD also admits other kind of generalizations as will be shown elsewhere.

This divergence has been widely applied to the analysis and characterization of symbolic sequences or series, and in concrete to the study of segmentation of DNA sequences. However its use in the framework of quantum information theory [49,50] or in the study of multielectronic systems [51,52] is very recent.

Fisher information, I, is another important information quantity [53], being originally introduced as a measure of intrinsic accuracy in statistical estimation theory. This is a measure of the gradient content of a distribution and therefore is a "local" measure which explores deeply the changes in the electronic distribution. Over the years, it has been shown to be a very useful concept; e.g., the equations of nonrelativistic quantum mechanics, the time-independent Kohn-Sham equations and the time-dependent Euler equation of DFT have been derived using the principle of minimum Fisher Information [54,55]. The Fisher information is defined as

$$I(\rho) \equiv \int \rho(\vec{r}) |\vec{\nabla} \ln \rho(\vec{r})|^2 d\vec{r}. \qquad (5)$$

This relevant magnitude is also a measure of the distribution localization, and it has not been used until very recently to investigate directly electronic densities [36,38,56–59].

Taking into account the divergence character of the symmetrized Kullback-Leibler measure, we define a similar magnitude using now Fisher information. It can be readily verified that the symmetrized relative Fisher information,

$$\mathrm{FD}(\rho_1, \rho_2) \equiv \int \rho_1(\vec{r}) \left| \vec{\nabla} \ln \frac{\rho_1(\vec{r})}{\rho_2(\vec{r})} \right|^2 d\vec{r}$$
$$+ \int \rho_2(\vec{r}) \left| \vec{\nabla} \ln \frac{\rho_2(\vec{r})}{\rho_1(\vec{r})} \right|^2 d\vec{r}, \qquad (6)$$

fulfills the basic properties of a divergence (positivity, symmetry and zero value in case of equal distributions). The local or intrinsic character of Fisher information is trans-

ferred to the FD so we have at our disposal two complementary measures of discrepancy between distributions: one of global character (JSD) and another of local one (FD). We apply in the next sections these two dissimilarity measures to the study of atomic ionization processes (in the sense of comparing the one-particle densities of the involved initial and final systems) as well as isoelectronic series.

In the computations the accurate Near-Hartree-Fock atomic wave functions of Koga *et al.* [60,61] was employed in order to calculate the atomic densities and their corresponding informational measures for all atoms and ions. Relativistic effects are not relevant for the nonheavy systems considered in this work.

III. DIVERGENCE ANALYSIS OF MONOIONIZATION PROCESSES

In this section we focus in the outer electronic layer of the atom and study the dissimilarities between the neutral systems and the singly charged ones, with identical nuclear charge, by means of their corresponding electronic densities. In doing so we calculate the Jensen-Shannon and Fisher divergences associated to the corresponding monoionization processes to analyze a set of 148 atomic systems including anions, neutral species, and cations with a number of electrons up to $N=54$. We also compute, for the sake of completeness, other information-theoretic magnitudes by using well known QSTs in order to better interpret and compare the aforementioned systems and processes. In what follows, let us keep in mind that all definitions and equations are valid for arbitrary density functions and, consequently, for both position and momentum spaces in what atomic one-particle density concerns. All computations in the present work will be also done in the two conjugated spaces.

A. Quantum similarity techniques

First of all, let us show the results concerning QST. As we have pointed out before, these techniques are based on overlap integrals and use the quantum similarity index (QSI) to measure the proximity of two electronic distributions $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$. The QSI is defined as

$$\mathrm{QSI}(\rho_1,\rho_2) \equiv \frac{\int \rho_1(\vec{r})\rho_2(\vec{r})d\vec{r}}{\int \rho_1^2(\vec{r})d\vec{r}\int \rho_2^2(\vec{r})d\vec{r}}. \tag{7}$$

It is clear that a closely related divergence, the quadratic distance (QD), can also be defined by simply integrating the square of the difference between these two densities. In fact it can be also expressed in terms of the same three overlap integrals:

$$\mathrm{QD}(\rho_1,\rho_2) \equiv \int [\rho_1(\vec{r}) - \rho_2(\vec{r})]^2 d\vec{r}$$

$$= \int \rho_1^2(\vec{r})d\vec{r} + \int \rho_2^2(\vec{r})d\vec{r} - 2\int \rho_1(\vec{r})\rho_2(\vec{r})d\vec{r}. \tag{8}$$
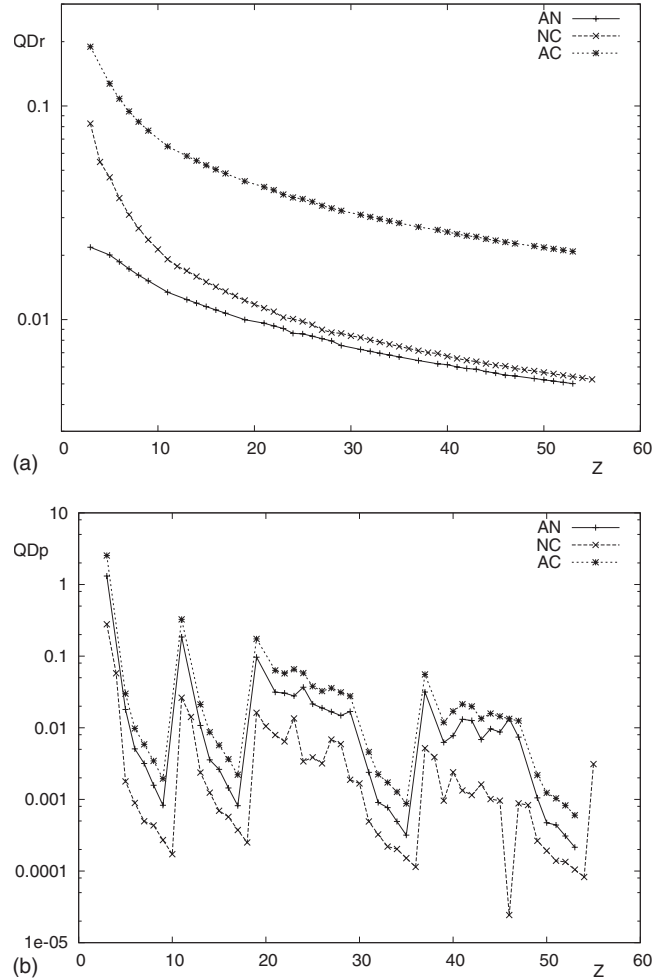
We have computed, in r and p spaces, QD and QSI between

FIG. 1. Quadratic distance QD among neutral atoms (N) and singly charged anions (A) and cations (C) with nuclear charge Z in (a) position and (b) momentum spaces. Atomic units are used.

neutral species ($N=1$–54) and their singly charged cations (NC pairs) or anions (AN pairs) and also between anions and cations (AC). The results confirm and expand some basic and preliminary results obtained for these charged systems [62].

Concerning position space, all computed values of QD_r, for the aforementioned pairs of atomic systems as shown in Fig. 1(a), provide a very smooth curve versus Z, whatever the type of process suffered by the atom might be. The monotonic decreasing behavior of the curves shows how QD_r between atoms and ions are simply smaller as the nuclear charge, Z, grows. Therefore QD in position space masks any information concerning periodicity properties, groups which the systems belong to and so on.

However, results are completely different in momentum space where the shell structure of the periodic table is clearly displayed in Fig. 1(b). The ranges of values for QD_p are strongly dependent on the orbital angular momentum "l" of the subshells affected by the change in the number of electrons, and the great structure of the curves in this space contrasts deeply with the monotonous behavior displayed in position space. These very different trends in the conjugated spaces are shown in Fig. 1 for the three studied processes: $A\rightarrow N$, $N\rightarrow C$, and $A\rightarrow C$. It is worthy to note also that (i)
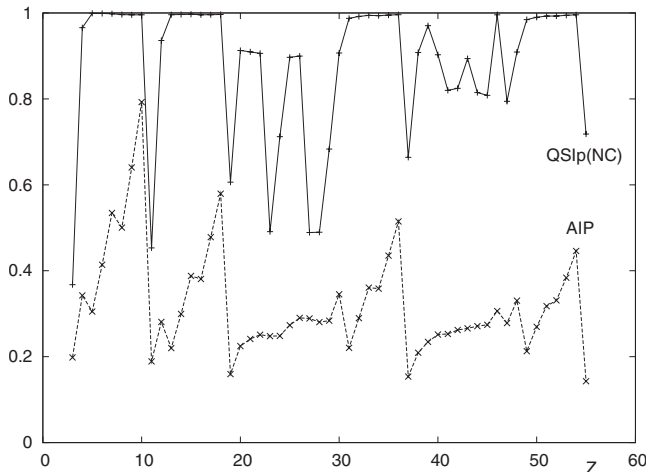
FIG. 2. Quantum similarity index $QSI_p(NC)$ between neutral atoms (N) and singly charged cations (C), and atomic ionization potential AIP of neutral atoms with nuclear charge Z. Atomic units are used.

the three curves in momentum space [Fig. 1(b)] are completely fitted, in spite of their picked structure, (ii) distances between these three couples are always increasing when Z is fixed in the sense that $QD(AN) < QD(NC) < QD(AC)$ in both spaces, and (iii) an average decreasing trend, with the size of the atom, modulates this rich structure, i.e., changes in the ionization processes of heavy atoms are, overall, smaller than those suffered by light atoms.

Analogous results are found for the corresponding QSI, where all computed values, in position space, almost reach the maximum value 1, whereas a much richer structure is shown in p space, as displayed in Fig. 2, for illustration, in the NC process. As expected, minimum values of QSI_p correspond, overall, with maximum ones of QD_p. Besides the AIP, which is the basic experimental magnitude to be compared with the divergences we have computed, is also displayed in the figure. It is worthy to mention here the coincidence of minima for QSI_p with relevant ones for AIP (corresponding to ionization related to "s" subshells) and also the apparent constant (almost equal to 1) values of QSI_p for atoms suffering ionizations in "p" subsells.

The strong differences found concerning the level of structure for both the QD and QSI measures in the two conjugated spaces are understood by analyzing their definitions as well as the short- and long-range behaviors of the one-particle densities. The exponential decreasing of the position space density $\rho(r)$ makes the values of the three overlap integrals to be mainly quantified by the region around the nucleus, where the nuclear charge Z determines the value of the density. Consequently, both QD_r and QSI_r are strongly dependent on the nuclear charge of the compared systems, much more than the outermost regions where the valence subshell determine the shell-filling pattern. On the other hand, such a valence region corresponds to the low-speed electrons, i.e., those associated with the momentum density around the origin and, consequently, to the main contributions on evaluating the overlap integrals and the corresponding QD_p and QSI_p measures.
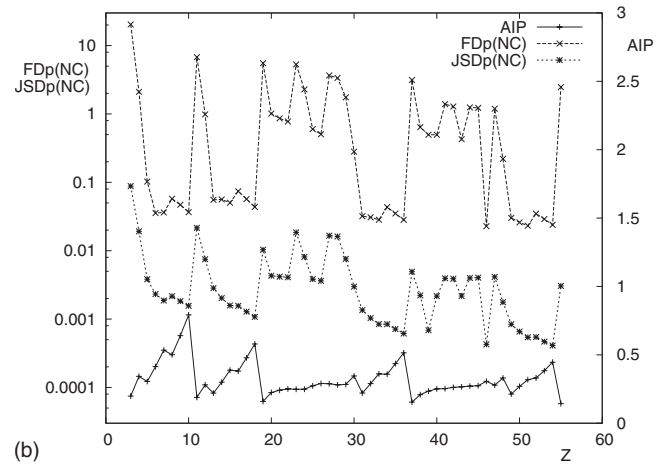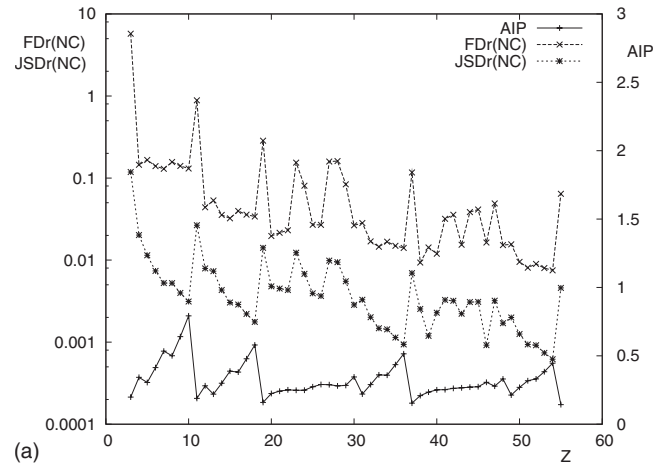

FIG. 3. Fisher and Jensen-Shannon divergences, FD (NC) and JSD (NC), between neutral atoms (N) and singly charged cations (C), in (a) position and (b) momentum spaces, and atomic ionization potential AIP of neutral atoms with nuclear charge Z. Atomic units are used.

B. Fisher and Jensen-Shannon divergences

Figures 3(a) and 3(b) show, in r and p spaces, respectively, the results obtained by comparing the informational divergences defined in Sec. II, namely, FD and JSD, when an electron is removed from the neutral species ($N \rightarrow C$), as well as the atomic ionization potential AIP needed for performing such process. We note first that both divergences show in position space a notable structure in contrast to QD (Fig. 1) or QSI measures, and second that, in spite of being of very different character [local (FD) or global (JSD) ones], both divergences not only follow similar general trends in the two conjugated spaces, but each one also belong to a similar range of values independently of the considered space. These are important facts that reveal the power of these two divergences over those computed by QST.

Carrying out the same analysis for other ionization processes, namely, those in which the compared systems are a singly charged anion and the resulting one after removing one ($A \rightarrow N$) or two ($A \rightarrow C$) electrons (the neutral atom of the singly charged cation, respectively) provide similar conclusions.

TABLE I. Nuclear charge Z of local extrema for the atomic ionization potential AIP of neutral atoms and/or the Fisher and Jensen-Shannon divergences in position (FD$_r$ and JSD$_r$) and momentum (FD$_p$ and JSD$_p$) spaces and the quadratic distance QD$_p$ and the quantum similarity index QSI$_p$ in momentum space for ionization processes among neutral atoms (N) and singly charged anions (A) and cations (C). Atomic units are used.

Measure		$N \rightarrow C$	$A \rightarrow N$	$A \rightarrow C$
AIP	(s)	3,11,19,23,28,37,47,55		
	(p,d)	5,8,13,16,31,34,49		
FD$_r$	(s)	3,11,19,23,28,37,42,45,47,55	3,11,19,24,37,41,45	3,11,19,24,29,37,42,47
	(p,d)	5,8,13,16,31,34,39,49	6,14,32,50,53	8,16,34,52
JSD$_r$	(s)	3,11,19,23,27,37,41,45,47,55	3,11,19,24,29,37,42,44,46	3,11,19,23,27,37,41,44
	(p,d)	31,49		
FD$_p$	(s)	3,11,19,23,27,37,41,44,47,55	3,11,19,37,46	3,11,19,23,27,37,41,44
	(p,d)	25,33,40,43,51	33,51	
JSD$_p$	(s)	3,11,19,23,27,37,41,45,47,55	3,11,19,24,29,37,42,44,46	3,11,19,23,27,37,41,44
	(p,d)	8,52	7,15,33,51	
QD$_p$	(s)	3,11,19,23,25,27,37,40,43,47,55	3,11,19,24,29,37,41,44,46	3,11,19,23,27,37,41,44
	(p,d)			
QSI$_p$	(s)	3,11,19,23,27,37,41,45,47,55	3,11,19,24,29,37,42,44,46	3,11,19,24,29,37,42,47
	(p,d)	16,34,52	7,15,33,51	8,15

However it is important to note and analyze the pointed and fluctuant structure of these divergences in each period comparing their extremal values to those of AIP. In Table I, values of the nuclear charge Z for which all divergences considered in this work display local extrema are given. In addition, minimum values of the AIP are associated to systems with a single electron in the valence subshell, making consequently such a subshell to disappear after ionization and the resulting system to strongly differ from the initial one. This relevant difference is usually revealed in terms of a high divergence and dissimilarity between the initial and the final systems.

Attending to the above discussion, Table I contains the values of Z for which both the AIP and the QSI$_p$ display local minima and also those corresponding to local maxima of momentum space QD$_p$ as well the divergences FD and JSD in both position and momentum spaces. Let us remember at this point the structureless of both QD and QSI in position space, being consequently not included in the table. Additionally, two cases have been distinguished according to the involvement of any s electron on the ionization process or else only p and d ones. This is done due to the relevant role played by the first ones in conditioning the associated divergence and similarity values.

However, there is only one exception for the rules previously given in order to choose the kind of extrema (maxima or minima) to be considered: instead of maxima, the Z values provided for the FD$_r$(AN) divergence correspond to its minima. The fact that this particular quantity displayed such a behavior can be explained attending to the long-range behavior of the position space atomic densities. Denoted by ϵ the AIP of a given system (for the sake of simplicity) is well known [63,64] that the charge density behaves as $\rho(r) \sim e^{-\sqrt{8\epsilon}r}$ for large r. The FD definition given by Eq. (6) allows to assert that FD$(\rho_1, \rho_2) \sim (\epsilon_1 - \epsilon_2)^2$. For alkaline-earth

metals, the AN process makes a completely filled s valence subshell to be half filled, while the other two processes (NC and AC) completely remove the initial nonempty s subshell, giving rise to a final closed-shell system (namely, the singly charged cation) with a much higher AIP than the final system (neutral atom with s^1 valence subshell) in the AN process. So, the difference between their AIPs, which determines the behavior of the FD divergence, is much higher when the final system is a cation than a neutral atom. In this analysis it has been essential the presence of the logarithmic derivative in the FD definition, which provides the aforementioned dependence on the ionization potential in position space. This is not the case of neither the momentum space nor the other measures.

In all the aforementioned cases there exist a strong correlation also with the structure displayed by the atomic ionization potential AIP in the NC ionization process in which an s electron is removed, as shown in the corresponding column of the table, as well as in Figs. 3(a) and 3(b). However, the same is not true when the removed electron is of p or d type, where such a connection with the AIP extrema only remains for the position space Fisher divergence FD$_r$. Concerning the QST and divergence measures, these comments are also valid for the AN and AC ionization processes.

The above-mentioned goodness of the Fisher divergence in position space FD$_r$ on displaying such a richer structure as compared to the other measures as well as the Fisher itself in momentum space can be better understood by turning up to the long-range behavior of the charge density in terms of the atomic ionization potential, being the connection between the extrema of FD$_r$ and AIP the closest one within the magnitudes enclosed in Table I.

In order to better interpret the number and location of extrema of these quantities, the corresponding ionization processes are detailed in Table II for all systems considered

TABLE II. Initial and final occupation numbers of outermost atomic subshells for some ionization processes among neutral atoms (N) and singly charged anions (A) and cations (C).

Z	$A \rightarrow N \rightarrow C$
3–4	$2s^{j+1} \rightarrow 2s^j \rightarrow 2s^{j-1}$
5–10	$2p^{j+1} \rightarrow 2p^j \rightarrow 2p^{j-1}$
11–12	$3s^{j+1} \rightarrow 3s^j \rightarrow 3s^{j-1}$
13–18	$3p^{j+1} \rightarrow 3p^j \rightarrow 3p^{j-1}$
19–20	$4s^{j+1} \rightarrow 4s^j \rightarrow 4s^{j-1}$
21–22,25–26,30	$4s^2 3d^{j+1} \rightarrow 4s^2 3d^j \rightarrow 4s^1 3d^j$
23,27–28	$4s^2 3d^{j+1} \rightarrow 4s^2 3d^j \rightarrow 4s^0 3d^{j+1}$
24,29	$4s^2 3d^j \rightarrow 4s^1 3d^j \rightarrow 4s^0 3d^j$
31–36	$4p^{j+1} \rightarrow 4p^j \rightarrow 4p^{j-1}$
37–38	$5s^{j+1} \rightarrow 5s^j \rightarrow 5s^{j-1}$
39	$5s^2 4d^1 5p^1 \rightarrow 5s^2 4d^1 \rightarrow 5s^2 4d^0$
40,43,48	$5s^2 4d^{j+1} \rightarrow 5s^2 4d^j \rightarrow 5s^1 4d^j$
41–42,44–45,47	$5s^2 4d^j \rightarrow 5s^1 4d^j \rightarrow 5s^0 4d^j$
46	$5s^2 4d^9 \rightarrow 5s^0 4d^{10} \rightarrow 5s^0 4d^9$
49–54	$5p^{j+1} \rightarrow 5p^j \rightarrow 5p^{j-1}$
55	$6s^1 \rightarrow 6s^0$

in the present section. It is observed the systematic presence of the alkaline atoms ($Z=3,11,19,37,55$) for which only s electrons are removed from the initial system. Additionally, many of the other extrema shown in Table I correspond to systems involved in the so-called "anomalous shell filling" as well as for ionizations concerning nonvalence subshells (see Table II). Sometimes there appear extrema for processes concerning p subshells when they become half filled or completely removed after the ionization.

Let us remark here that some recent works have dealt previously with the correlation between information measures and the atomic ionization potential, according to its role in describing the single ionization processes. The net Fisher information measure, defined as the product of both the position and momentum Fisher information, is found to be correlated, at least qualitatively, with the inverse of the experimental ionization potential [65], as similarly shown to occur with Onicescu information energy [37]. However, those and other works only deal with pairs of neutral systems within a given model or a unique system described within different models [40] contrary to the case considered in the present work, namely, the correlation with dissimilarities between neutral and charged species.

IV. DIVERGENCE ANALYSIS OF ISOELECTRONIC SERIES

The isoelectronic series provide a well-known benchmark for the study of atoms and molecules. In this section results concerning the application of the informational divergences defined previously are presented. We have analyzed nine isoelectronic series of neutral atoms and some of their cations. Each series consists of 21 systems, all of them with equal number of electrons N and their nuclear charge running from
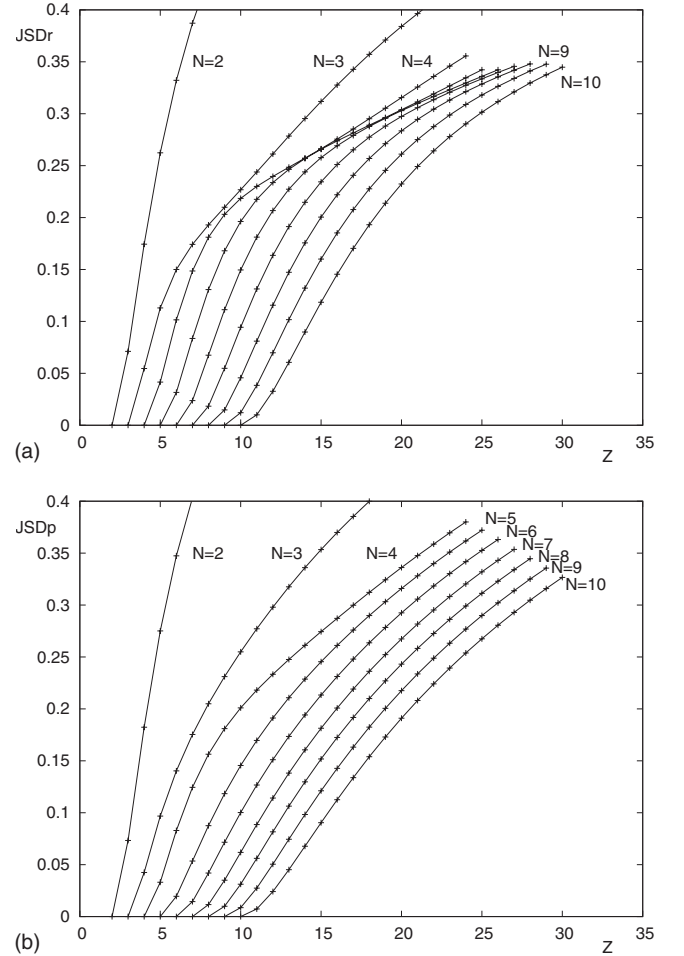

FIG. 4. Jensen-Shannon divergence JSD between N-electron neutral atoms and cations for the isoelectronic series with N $=2-10$ and nuclear charge Z within the range $N \leq Z \leq N+20$ for each series, in (a) position and (b) momentum spaces. Atomic units are used.

$Z=N$ to $Z=N+20$. In this form we study how these divergence measures characterize, from the informational point of view, this set of 189 different systems, corresponding to the series with $N-2-10$. On one hand, the effect of increasing/decreasing the nuclear charge can be studied and on the other the electronic organization of each isoelectronic series can be investigated. In doing so, all the divergences (QSI, QD, FD, and JSD) between the neutral species ($Z=N$) and each member of the isoelectronic series ($Z=N+1,\ldots,N+20$) have been computed.

Double Fig. 4 shows the global JSD in r and p spaces. This global divergence works equally well in position and momentum space and results in both spaces are not very different.

Some monotonic trends are also shown in these figures: (i) the divergence between the neutral system and each member of the isoelectronic series increases with Z as it could be expected, showing that distances increase when the nuclear charge is larger; (ii) this increasing behavior with the size of the nucleus is progressively less notable; and (iii) the location of each isoelectronic curve is ordered according to N so that divergences decrease with the number of electrons N. In
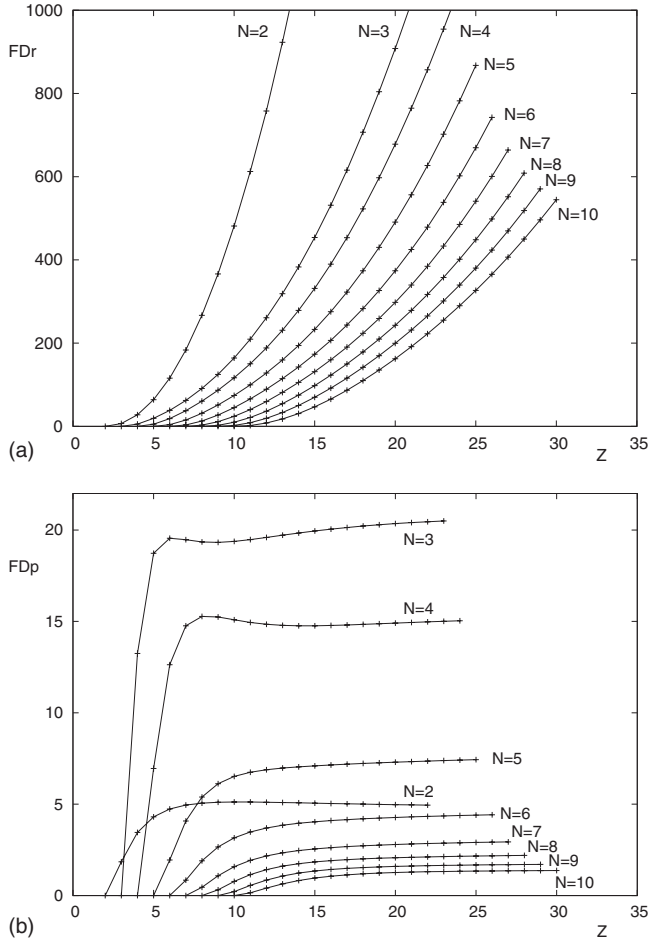
FIG. 5. Fisher divergence FD between N-electron neutral atoms and cations for the isoelectronic series with $N=2-10$ and nuclear charge Z within the range $N \le Z \le N+20$ for each series, in (a) position and (b) momentum spaces. Atomic units are used.

form (near the origin, asymptotic behavior, etc.) of the densities we are comparing. In particular, it is worthy to remember the hydrogenlike behavior of the position space density around the nucleus, which translates into the so-called "cusp condition" [66], valid for any atomic system:

$$\frac{\rho'(0)}{\rho(0)} = -2Z, \tag{9}$$

which reveals a proportionality of the logarithmic derivative at the nucleus and the nuclear charge. Taking into account that the main contribution to the integrals defining FD_r comes from the region surrounding the nucleus (due to the fast exponential decay of the density), the aforementioned condition translates into a dependence of such a divergence between these systems on their nuclear charges as

$$FD(\rho_1, \rho_2) \sim (Z_1 - Z_2)^2, \tag{10}$$

which makes, as expected, the Fisher divergence to considerably increase as comparing the neutral system with a highly charged one. In fact, increasing the nuclear charge makes the slope of the logarithmic derivative of the density around the nucleus to proportionally increase and, consequently, also the Fisher information itself due to the high "content of gradient" in that region. Additionally, it is worthy to point out how both divergences behave in a strongly different or similar fashion according to the space we are dealing with, namely, position or momentum, respectively.

Similar comments on the QD and QSI measures can be done concerning monotonicity and ordering of the curves. In fact, the shape of the quadratic distance QD is found to be very similar to that of the Fisher divergence, sharing also the previously discussed opposite trends in both conjugated spaces. In what concerns the quantum similarity index QSI, it displays a monotonically decreasing behavior as increasing the nuclear charge. This means that the similarity index along a given isoelectronic series mainly depends on the difference between the nuclear charges of the compared systems.

V. CONCLUSIONS

The comparison of ionized and neutral atomic systems by means of quantum similarity techniques provides only relevant information on periodicity properties and shell structure when dealing with one-particle densities in momentum space. However, the corresponding values in position space are only concerned by, at most, how large the nuclear charge is.

On the contrary the divergences measures defined and computed in this work, one of local character (FD) and other of global one (JSD) explore deeply, in both conjugated spaces, the changes suffered by the atoms on their shell structure after the ionization by changing either the number of electrons or the nuclear charge.

In this work we report the variation in such dissimilarity measures for a comprehensive set of neutral atoms, singly charged ions, and isoelectronic series using the numerical data generated on 319 atomic systems in position and momentum spaces.

other words divergences are less relevant when the size of the electronic cloud is bigger.

Double Fig. 5 shows the FD for the same isoelectronic series studied above. In this case it is important to note a very different behavior than JSD shows. First of all the trends of this local divergence, FD, in r and p spaces are very different as FD_r displays a clearly increasing behavior with Z, but FD_p tends toward a constant value when the size of the nucleus grows. Besides FD_r has the following characteristics: (i) inside each series, it increases with Z as JSD_r does, but now this increasing is more and more notable according to the size of the nucleus and (ii) a monotonic decreasing ordering of the isoelectronic curves with N is once again observed. On the contrary the most important characteristics of FD_p are the following: (i) it increases at lesser extent as the nucleus becomes larger, and at the end of the series it is almost insensitive to the size of the nucleus, and (ii) the monotonic behavior of the curves with N is broken by the $N=2$ isoelectronic series.

This much more sensitive trend of FD versus JSD can be understood if we look at the local character of this divergence in comparison with the much more global one of JSD. Therefore this divergence is much more sensible to the local

These dissimilarity measures clearly show the complex organization and the shell-filling patterns at the periodic table. Specially remarkable is the correlation found between extrema of the atomic ionization potential and those of the divergences. Besides a thorough analysis of changes suffered on the subshells from which an electron is removed is done and they are also related to the values of the divergence measures. Characteristic features in the divergences accompanying the ionization process are identified, and the physical reasons for the observed patterns are described. In particular, it has been shown the relevant role played, among other characteristics, by the angular momentum quantum number of the removed electrons in the ionization process, the significance in many cases of the anomalous shell filling, as well as the value of the atomic ionization potential as related to the Fisher and Jensen-Shannon divergences and the QST measures.

Concerning the similar study of the dependence on the nuclear charge Z when keeping the number of electrons N fixed along different isoelectronic series, the divergence among neutral atoms and cations increases as the difference between the nuclear charges of both systems becomes larger. In this case, no shell-filling properties are displayed since both atomic systems under comparison have identical occupation numbers.

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