

# Information planes and complexity measures for atomic systems, ionization processes and isoelectronic series

J.C. Angulo and J. Antolín

**Abstract** Within the present advanced review on the meaning, interpretation and applications of the so-called 'complexity', different order-uncertainty planes embodying relevant information-theoretic magnitudes are studied in order to analyse the information content of the position and momentum electron densities of several atomic systems, including neutral atoms, singly-charged ions and isoelectronic series. The quantities sustaining those planes are the exponential and the power Shannon entropies, the disequilibrium, the Fisher information and the variance. Each plane gives rise to a measure of complexity, determined by the product of its components. In the present work, the values of the so-called López-Ruiz, Mancini and Calbet (LMC), Fisher-Shannon (FS) and Cramer-Rao (CR) complexities will be provided in both conjugated spaces and interpreted from a physical point of view.

## 1 Introduction

There have been tremendous interests in the literature to apply information theory to the electronic structure theory of atoms and molecules [1, 2]. The concepts of uncertainty, randomness, disorder or 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.

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J.C. Angulo

Departamento de Física Atómica, Molecular y Nuclear and Instituto *Carlos I* de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain, e-mail: angulo@ugr.es

J. Antolín

Departamento de Física Aplicada, EUITIZ, Universidad de Zaragoza, 50018-Zaragoza, Spain and Instituto *Carlos I* de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain, e-mail: antolin@unizar.es

Following the usual procedures carried out within the Information Theory for quantifying the aforementioned magnitudes concerning individual distributions, some other extensions have been done in order to introduce the concepts of 'similarity' or 'divergence' between two distributions, as comparative measures. Quantum similarity theory was originally developed in order to establish quantitative comparisons between molecular systems by means of their fundamental structure magnitudes: electron density functions. Applications of this important theory have been one of the cornerstones of recent chemical research in molecules [3, 4, 5].

Some pioneering efforts relating Information Theory to electronic structure and properties of molecules can be already found in the seminal papers by Daudel in the framework of loge theory [6, 7], subsequently followed by Mezey [8] and reexamined later by Nalewajski [9]. The studies of Mezey [10] and Avnir [11] on symmetry and chirality-related problems in molecules, and in other very diverse fields (e.g. image and texture analysis), are also examples of applications of informational measures on specific aspects of shape, disorder and complexity.

This kind of measures and techniques, which in fact characterizes most of the information theory aims and tools, have been widely employed in recent years within the atomic physics framework. The present work constitutes a survey of some of those applications for obtaining relevant information on different properties of atomic systems, including structural and experimental ones. The role played by the two conjugated variables, namely position and momentum, appears fundamental for a complete description of the atomic information features. It is shown that, in spite of their simplicity among the many-body systems, the atomic ones possess a highly enough level of organization and hierarchy to be considered as an appropriate benchmark for the suggested complexity study.

The relevancy of the above concepts motivates the search for an appropriate quantification, giving rise to a variety of density functionals, each one with its own characteristics and properties which make them more or less useful attending to the specific problem we are dealing with.

Diverse information measures of probability distributions have been widely applied with the aim of describing a great variety of systems or processes in many different scientific fields. One of the pioneering and most well-known of such measures is the variance, but later on many others have been also considered for these kind of applications. Among them, it should be emphasized the role played by the Shannon entropy  $S$  [12]

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

and the Fisher information  $I$  [13, 14]

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

of a distribution  $\rho(\mathbf{r})$ . In fact,  $S$  is a basic quantity in statistical thermodynamics [15] and it is the essential tool on the application of the 'Maximum Entropy' technique based on Jaynes' principle. More recently, Fisher information appeared as a

fundamental magnitude for deriving important laws of e.g. density functional theory [16, 17] or quantum mechanics [18] by means of the extremization Frieden principle [14]. The numerous applications of tools based on both  $S$  and  $I$  suggest the relevancy of using them in a complementary way, attending to their main characteristics and properties as will be described later.

### ***1.1 Complexity: Meaning and Definitions***

Another relevant concept within information theory, in some cases strongly related to the aforementioned measures, is the so-called 'complexity' of a given system or process. There is not a unique and universal definition of complexity for arbitrary distributions, but it could be roughly understood as an indicator of pattern, structure and correlation associated to the system the distribution describes. Nevertheless, many different mathematical quantifications exist under such an intuitive description. This the case of the algorithmic [19, 20], Lempel-Ziv [21] and Grassberger [22] complexities, as well as the logical and thermodynamical depths by Bennett [23] and Lloyd and Pagels [24], respectively, all them as others with many scientific applications.

Complexity is used in very different fields (dynamical systems, time series, quantum wave functions in disordered systems, spatial patterns, language, analysis of multi-electronic systems, cellular automata, neuronal networks, self-organization, molecular or DNA analyses, social sciences, etc.) [25, 26, 27]. Although there is no general agreement about the definition of what complexity is, its quantitative characterization is a very important subject of research in nature and has received considerable attention over the past years [28, 29].

The characterization of complexity cannot be univocal and must be adequate for the type of structure or process we study, the nature and the goal of the description we want and for the level or scale of the observation that we use. In the same way it is interesting to combine the properties of the new proposals to characterize complexity and test them on diverse and known physical systems or processes. Fundamental concepts such as information or entropy are frequently present in the proposals for characterizing complexity, but some other ingredients that do not only capture uncertainty or randomness can also be searched. One wishes also to capture some other properties such as clustering, order or organization of the systems or process. Some of the definitions and relations between the above concepts are not clear; even less so is how disorder or randomness takes part in the aforementioned properties of the system and vice versa.

The initial form of complexity is designed such that it vanishes for the two extreme probability distributions (little complex ones), corresponding to perfect order (represented by a Dirac-delta) and maximum disorder (associated with a highly flat distribution). Most of those definitions take into account elements of Bayesian and information theories. Some of the more recent ones consist of the product of two factors, measuring, respectively, order and disorder on the given systems or, equiv-

alently, localization and delocalization [30, 31]. They will be referred to as product-complexities.

These product complexity measures have been criticized and consequently modified leading to powerful estimators successfully checked in a wide variety of fields [32, 33, 34, 35, 36, 37]. Fundamental concepts such as entropy or information are frequently present in the proposals for characterizing complexity, but it is known that other ingredients capturing not only randomness are also necessary. In fact one would wish also to detect, for instance, clustering or pattern.

Even restricting ourselves to the aforementioned factorization, there is no unique definition for complexity. The reason is that there exist different candidates for being one of the coupled factors which give rise to complexity. The most popular ones are well-known to play a relevant role in an information-theoretic framework. Among them, let us mention the Shannon entropy  $S$ , the disequilibrium  $D$ , the Fisher information  $I$  and the variance  $V$ .

Much work has been done using those quantities as basic measures, not only for quantifying the level of spreading of distributions but also for many other applications, such as, for instance, maximum-entropy estimation and reconstruction of an unknown distribution from very limited information on it.

Other authors have recently dealt with some particular factors of the complexity measures. In particular, Shannon entropy has been extensively used in the study of many important properties of multielectronic systems, such as, for instance, rigorous bounds [38], electronic correlation [39], effective potentials [40], similarity [41] and minimum cross entropy approximations [42].

More recently, Fisher information has been studied as an intrinsic accuracy measure for concrete atomic models and densities [43, 44] and also for quantum mechanics central potentials [45]. Also, the concept of phase space Fisher information, where position and momentum variables are included, was analyzed for hydrogen-like atoms and the isotropic harmonic oscillator [46]. The net Fisher information measure is found to correlate well with the inverse of the ionization potential and dipole polarizability [44].

Quantum similarities and self-similarities  $D$  for neutral atoms were computed for nuclear charges  $Z=1-54$  only in the position space [47, 48], but afterwards a more complete analysis including  $Z=1-103$  neutral systems and singly charged ions has been done in position and momentum spaces [49].

Some studies on atomic similarity, using magnitudes closely related to  $D$  or to relative Shannon entropies, have been also reported [50, 51]. Very recently a comparative analysis of  $I$  and  $D$  shows that they both vary similarly with  $Z$  within the neutral atoms, exhibiting the same maxima and minima, but Fisher information presents a significantly enhanced sensitivity in the position and momentum spaces in all systems considered [52]

### 1.1.1 LMC Complexity

Among the more recent and successful definitions of complexity, usually built up as a product of two factors quantifying, respectively, order/disequilibrium and disorder/uncertainty, specially remarkable is the one provided by López-Ruiz, Mancini and Calbet [30], to be denoted by  $C(LMC)$  due to its pioneering authors, which satisfies as others do the condition of reaching minimal values for both extremely ordered and disordered limits. Additional relevant properties are the invariance under scaling, translation and replication.

The initial definition of the LMC complexity has been criticized [28] and modified [35] in order to the aforementioned properties be verified, giving rise to the expression

$$C(LMC) \equiv D \cdot e^S = D \cdot L, \quad (3)$$

of a distribution  $\rho(\mathbf{r})$ . It is built up as the product of two relevant quantities within an information-theoretic framework: the 'disequilibrium'  $D$  [53],

$$D(\rho) \equiv \int \rho^2(\mathbf{r}) d\mathbf{r} \quad (4)$$

which quantifies the departure of  $\rho(\mathbf{r})$  from equiprobability, and the aforementioned Shannon entropy  $S$  as measure of randomness or uncertainty on the distribution. The usefulness of  $C(LMC)$  has been shown in different fields, allowing detection of periodic, quasiperiodic, linear stochastic and chaotic dynamics [30, 36, 37].

### 1.1.2 Fisher-Shannon Complexity

It appears also interesting to look for statistical complexities involving also a local information measure, as can be done by replacing one of the LMC global factors by a 'local' measure of intrinsic accuracy. In this sense, the main properties of Fisher information  $I$  make this quantity to be an appropriate candidate with the aim of defining a complexity in terms of complementary global and local factors. Very recently, the Fisher-Shannon complexity  $C(FS)$  has been defined [52, 54] in terms of both Fisher information and Shannon entropy and, consequently, providing a measure combining the global and local characters, and also preserving the desirable properties for any complexity as previously described. The Fisher information  $I$  itself plays a fundamental role in different physical problems, such as the derivation of non-relativistic quantum-mechanical equations by means of minimum  $I$  principle, as also done for the time-independent Kohn-Sham equations and the time-dependent Euler equation [17, 55].

The FS is defined in terms of the power Shannon entropy  $J \equiv \frac{1}{2\pi e} e^{2S/3}$  and the Fisher information  $I$  as

$$C(FS) \equiv I \cdot J \quad (5)$$

where definition of  $J$  is chosen in order to preserve general complexity properties. As compared to LMC complexity, and apart from the explicit dependence on Shannon entropy,  $C(\text{FS})$  replaces the disequilibrium global factor by the Fisher local one. The  $C(\text{FS})$  expression arises from the isoperimetric three-dimensional inequality  $I \cdot J \geq 3$  [56, 57, 58] providing a universal lower bound to FS complexity. Among the main applications carried out, it should be remarked those concerning atomic distributions in position and momentum spaces where FS complexity is shown to provide relevant information on atomic shell structure and ionization processes [52, 54, 59, 60].

### 1.1.3 Cramer-Rao Complexity

In the present work, we will also analyze, apart from  $C(\text{LMC})$  and  $C(\text{FS})$ , the 'Cramer-Rao' complexity  $C(\text{CR})$ , also as the product of a local and a global measure, keeping the first one as the Fisher information  $I$ , and replacing the Shannon entropy exponential by the variance  $V$ , giving rise to

$$C(\text{CR}) \equiv I \cdot V, \quad (6)$$

product which has been considered in different contexts [61, 60, 59]. Specially remarkable is the existence of a lower bound, in spite of the factors being of very different origin as well as their definition in terms of the distribution, emphasizing again the strong connection between both the local and global level of uncertainty.

## 1.2 Numerical Analysis

The main aim of the present work is to analyze the above defined LMC, FS and CR complexities associated to the one-particle densities in both conjugated spaces, namely position  $\rho(\mathbf{r})$  and momentum  $\gamma(\mathbf{p})$  densities, as well as the product or phase-space distribution  $f(\mathbf{r}, \mathbf{p}) \equiv \rho(\mathbf{r})\gamma(\mathbf{p})$ , for a great amount of atomic systems including neutral atoms (Section II), singly charged ions (Section III) and isoelectronic series (Section IV).

Analyzing the main information-theoretic properties of many-electron systems has been a field widely studied by means of different procedures and quantities, in particular for atomic and molecular systems in both position and momentum spaces. It is worthy to remark the pioneering works of Gadre et al [62, 63] where the Shannon entropy plays a fundamental role, as well as the more recent ones concerning electronic structural complexity [27, 64], the connection between information measures (e.g disequilibrium, Fisher information) and experimentally accessible quantities such as the ionization potentials or the static dipole polarizabilities [44], interpretation of chemical phenomena from momentum Shannon entropy [65, 66], applications of the LMC complexity [36, 37] and the quantum similarity measure

[47] to the study of neutral atoms, and their extension to the FS and CR complexities [52, 60] as well as to ionized systems [39, 54, 59, 67].

The applications in the present work on a global of 370 systems will be carried out in order to gain insight not only on the information content of those systems, but also to interpret the complexity values in terms of physical properties and processes, such as shell-structure and ionization. Also the associated informational planes subtended by the factors composing each complexity will allow to obtain relevant interpretations on the main physical processes and characteristics of the distributions here studied. In doing so, Near-Hartree-Fock wavefunctions [68, 69] will be employed to compute the densities and the associated information measures and planes as well as complexities. For atomic systems in the absence of external fields (as is the case of this work) it is sufficient to deal with the spherically averaged densities  $\rho(r)$  and  $\gamma(p)$ . Main conclusions on the results will be given in Section V.

## 2 Complexity and Atomic Shell Structure

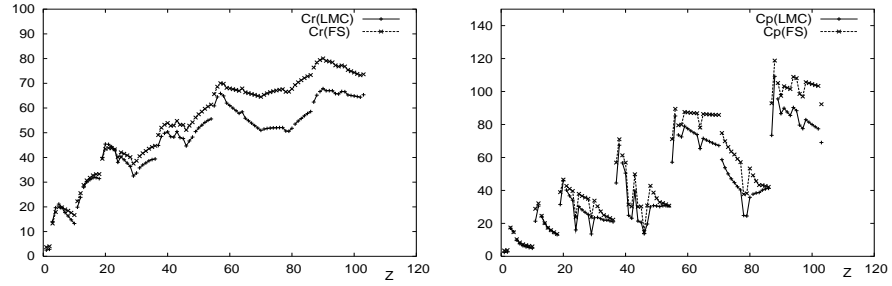
Complexity studies for atoms have also been carried out, but most of them are only for  $Z=1-54$  [27, 64]. Recent complexity computations, using relativistic wave functions in the position space, were also done [70]. Some other complexity works simply take the position density, not the momentum one, as basic variable [71]. In this sense, it is worthy to point out the different behaviors displayed by some of these quantities in position and momentum spaces for atomic systems, as we have recently shown [50, 52].

In particular, it has been shown that it is not sufficient to study the above measures only in the usual position space, but also in the complementary momentum space, in order to have a complete description of the information theoretic internal structure and the behaviour of physical processes suffered by these systems. Some other new proposals of product-type complexity measures (e.g., Cramer-Rao complexity) have been also constructed and computed for multielectronic systems [60].

This section is devoted to the analysis and interpretation, from a physical point of view, of the LMC, FS and CR complexity values and information planes corresponding to all neutral atoms throughout the Periodic Table, within the range of nuclear charges  $Z = 1 - 103$ . Such a study is carried out in position, momentum and phase/product spaces, which corresponding distributions and their complexities are obtained by means of the accurate wavefunctions provided in Ref. [68].

### 2.1 Comparison between Atomic LMC and FS Complexities

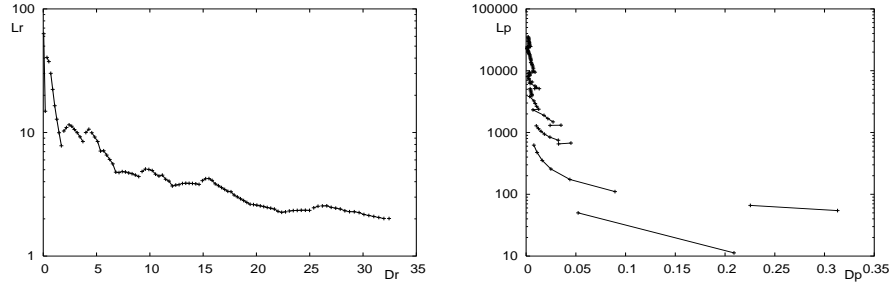
First, let us compare the LMC and FS complexities for those systems, as done in Fig. 1 for position and momentum spaces (1(a) and 1(b), respectively). It is remarkable, attending to the curves displayed in these figures, the similar structure of LMC



**Fig. 1** LMC and FS complexities for neutral atoms with nuclear charge  $Z$  in position (left) and momentum (right) spaces. Atomic units (a.u.) are used.

and FS complexities in both spaces, in spite of their strongly different definition, mainly due to the information measure accompanying the Shannon factor, namely the 'global' disequilibrium for LMC and the 'local' Fisher information for FS. It is worthy to point out not only the almost identical magnitude orders of both complexities, but also the strong correlation between their structure, characterized by the number and location of extrema, and the shell-filling process as well as the groups the atoms belong to. Last comment is supported by the fact that both complexities in the two conjugated spaces display local minima for noble gases as well as for some atoms involved in the so-called 'anomalous shell-filling' (being specially relevant the systems  $Z = 24, 29, 46$ ). Similar comments can be done concerning maximal values.

### 2.1.1 LMC and FS Information Planes



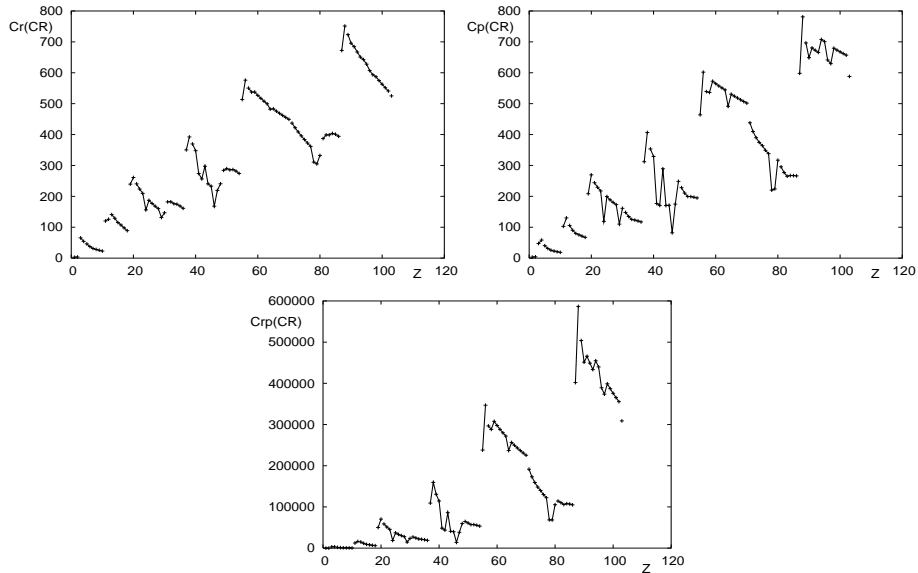
**Fig. 2** Disequilibrium-Shannon plane (D,L) for neutral atoms with nuclear charge  $Z$  in position (left) and momentum (right) spaces. Atomic units (a.u.) are used.

Attending to the factors which compose complexities, it is also interesting to analyze the individual contribution of each one to the total complexity. For illustration,



the 'disequilibrium-Shannon plane' is shown in Fig. 2, drawn in terms of  $(D,L)$ , as components of the LMC complexity, in position and momentum spaces (Figs. 2(a) and 2(b), respectively). Both figures again reveal the shell-filling patterns, much clearly in momentum than in position space. In fact, the different pieces of curves in momentum space belong to disjoint exponential entropy ( $L_p$ ) values. Adding a new subshell makes  $L_p$  to increase, the disequilibrium  $D_p$  decreasing within each subshell. Opposite behaviors are displayed in position space concerning not only monotonicity, but also location of regions within the planes where heavy atoms concentrate around: high disequilibrium in position space and high disorder (entropy) in the momentum one.

## 2.2 Atomic CR Complexity

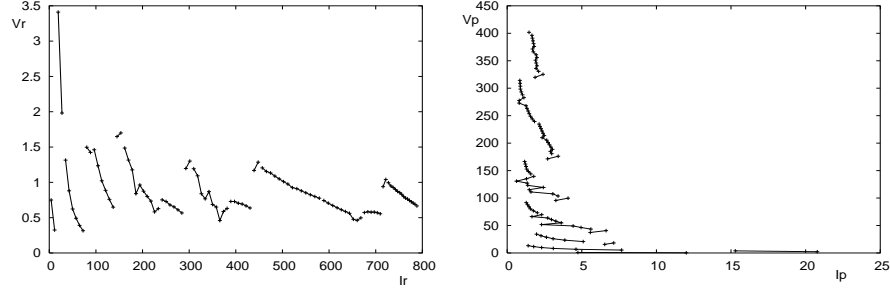


**Fig. 3** CR complexity for neutral atoms with nuclear charge  $Z$  in position (upper left), momentum (upper right) and product (lower) spaces. Atomic units (a.u.) are used.

Concerning Cramer-Rao complexity  $C(CR)$ , main numerical results for atomic systems are displayed in Fig. 3 for position, momentum and product spaces. In analyzing their structure as functions of the nuclear charge  $Z$  it is interesting to observe that most minima of  $C_r(CR)$  and all of  $C_p(CR)$  are the same of the LMC and FS complexities, previously specified. In fact, shell structure patterns are very similar for the three complexities, in spite of being determined by four quantities ( $S$ ,  $D$ ,  $I$  and  $V$ ) of very different character. The same also occurs for some of those isolated

factors in all spaces, such as e.g. the exponential entropy  $L$  and the variance  $V$ , which figures are not shown for the sake of shortness.

### 2.2.1 CR Information Plane



**Fig. 4** Cramer-Rao plane ( $I,V$ ) for neutral atoms with nuclear charge  $Z$  in position (left) and momentum (right) spaces. Atomic units (a.u.) are used.

The Cramer-Rao ( $I,V$ ) information plane is shown in Fig. 4 for the two conjugated spaces, in order check to which extent each composing factor is responsible of the shell-filling pattern displayed. In position space (Fig. 4(a)), adding a new subshell makes Fisher information  $I_r$  to appreciably increase, its values belonging to disjoint intervals determined by the valence subshell. However, the variance  $V_r$  ranges over a unique interval for all systems without distinguishing their shell structure, but displaying a monotonically decreasing behavior (with few exceptions) within each specific subshell. Just the opposite behaviors for the corresponding momentum quantities  $I_p$  and  $V_p$  are observed in Fig. 4(b), in what concerns ranges of values and monotonicity.

It is worthy to notice how the three complexity measures here considered are able to provide information not only on randomness or disorder, but also on the structure and organization of the atomic systems. The same is not always true for the individual factors, appearing relevant to deal simultaneously with the localization and randomness factors, as well as the complementary conjugated spaces, in order to have a more complete description of the information content of atomic systems.

Summarizing the results of this section, (i) a complete description of the information-theoretic characteristics of atomic systems requires the complementary use of position and momentum spaces, (ii) LMC and FS complexities provide similar results (qualitatively and quantitatively) for all neutral atoms in both spaces, displaying periodicity and shell-filling patterns as also CR complexity does, and (iii) such patterns of the localization-delocalization planes in one space are inverse to those of the conjugated space.

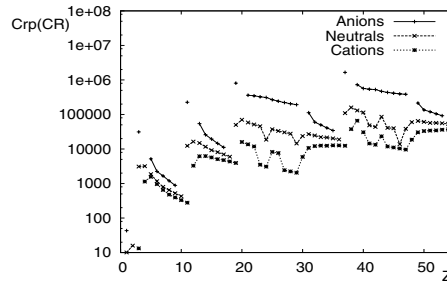
### 3 Effects of the Ionization on Complexity

In this section the LMC, FS and CR complexities are analyzed for singly charged ions with a number of electrons up to  $N = 54$ , that is with a global charge  $Q = Z - N = \pm 1$ ,  $Z$  being the nuclear charge. These quantities, together with the previously discussed values for neutral atoms within such  $N$  range, provide us with information on how complexity progresses in mono-ionization processes [54, 59]. In doing, we are considering a global of 150 systems (53 cations, 43 anions and 54 neutral atoms), the computations on ions being performed by employing the accurate wavefunctions of Ref. [69].

#### 3.1 LMC and FS Complexities of Singly-Charged Ions

A similar comparison between LMC and FS complexities as done previously for neutral atoms in both conjugated spaces has been also carried out for anions and cations in the two spaces. Conclusions raised by the analysis of these quantities for ions are almost identical to those provided when discussing the Fig. 1 for neutral atoms, in what concerns similarity between  $C(\text{LMC})$  and  $C(\text{FS})$  values as well as their connection with the shell-filling process by means of the location of their extrema, most minima of complexity corresponding to noble gases or the anomalous shell-filling set of atoms.

#### 3.2 CR Complexity of Singly-Charged Ions and Neutral Atoms

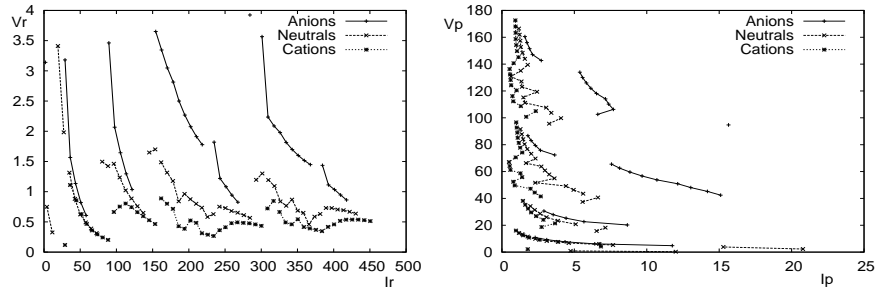


**Fig. 5** CR complexity in product space neutral atoms and singly charged ions with nuclear charge  $Z$ . Atomic units (a.u.) are used.

Concerning the Cramer-Rao complexity  $C(\text{CR})$ , its evolution throughout the ionization is clearly displayed in Fig. 5, where its value is provided for the three considered species (anions, cations and neutrals) in order to determine to which extent the ionization processes (by adding or removing electrons keeping fixed the nuclear charge  $Z$ ) modify the atomic complexity. For illustration, this comparison is

carried out for the Cramer-Rao complexity  $C_{rp}(CR)$  in the product space as shown in Fig. 5. Again, it is clearly observed the correlation of complexity with the atomic shell structure for all species. Additionally, it is appreciated that (i) complexity increases as the system loses an electron, and (ii) maxima are clearly associated to 's' valence subshells (those involved in ionization) while minima correspond to noble gases or some anomalous 'd' subshells filling.

### 3.2.1 CR Information Plane for Monoionization Processes



**Fig. 6** Cramer-Rao plane (I,V) in position (left) and momentum (right) spaces, for neutral atoms and singly charged ions with nuclear charge  $Z$ . Atomic units (a.u.) are used.

The Cramer-Rao informational plane subtended by the constituting factors (I,V) also provides interesting results interpreted according to the atomic shell structure. Fig. 6 displays this plane in both conjugated spaces (6(a) for position and 6(b) for momentum) for the systems here considered. Apart from the faithful reproduction of shell structure, it is worthy to remark that, as shown in Fig. 6(a), systems of large  $Z$  are highly localized and organized in position space while the light ones appear much more delocalized. Location at the position  $(I_r, V_r)$  plane after an ionization process slightly changes for heavy atoms as to the light ones. Additionally, for fixed nuclear charge  $Z$  complexity  $C_r(CR)$  decreases following the sequence anion-neutral-cation, that is as losing electrons, being the changes associated to 's' electrons considerably higher to those of 'p' or 'd' subshells.

Exactly the opposite trends to those discussed in position space are observed in the momentum one, as shown in Fig. 6(b): large  $Z$  systems are now less localized and with a greater variance than the light ones, and losing electrons makes the variance to increase and Fisher information to decrease, just the reciprocal that happens in position space.

## 4 Isoelectronic Series: Dependence of Complexity on the Nuclear Charge

After carrying out the analysis of complexity dependence on the outermost subshells, as done in the previous section by considering ionization processes, let us now focus in the atomic core as source of the attractive forces and their effects on complexity values.

### 4.1 Composition and Number of Isoelectronic Series

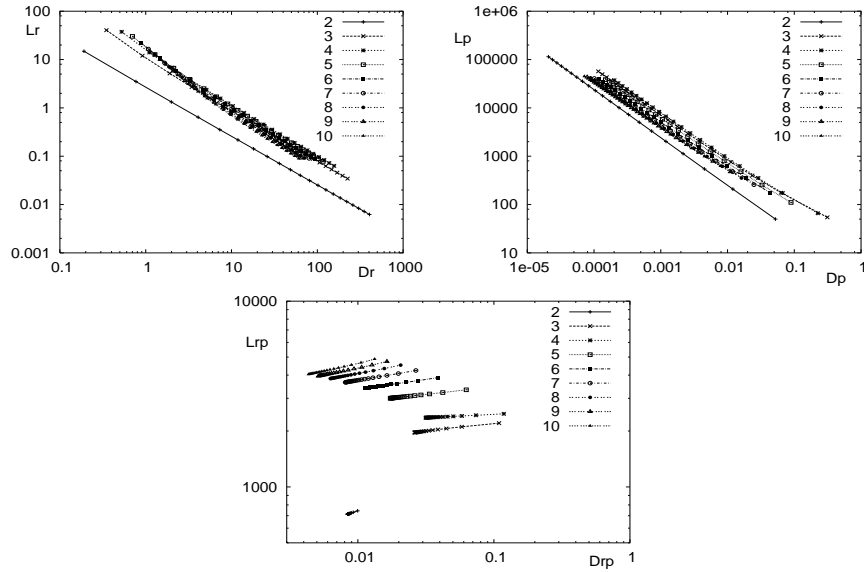
We start by considering a neutral atom, that is a system with identical values of the nuclear charge  $Z$  and the number of electrons  $N$ , from which we give rise to a set of cations by progressively increasing one-by-one the nuclear charge  $Z$  keeping fixed the number of electrons (or, equivalently, starting from a global charge  $Q \equiv Z - N = 0$  until reaching a maximum positive value, being  $Q_{max} = 20$  in the numerical application here considered). Such a set of cations together with the neutral atom is known as an 'isoelectronic series', characterized by the fixed number of electrons  $N$  as well as the maximum value  $Q_{max}$ . Studying the previously considered complexity measures for a given isoelectronic series provides information on their dependence on the nuclear charge  $Z$  for fixed  $N$  electrons. In this section, such a study will be carried out for nine isoelectronic series, namely those corresponding to  $N = 2 - 10$ , within a Hartree-Fock framework [69]. Each series consists of 21 members (a neutral atom and 20 cations), giving rise consequently to analyze complexities of a global of 189 atomic systems.

### 4.2 Complexities and Information Planes of Isoelectronic Series

As in Section III, we consider here (i) LMC, FS and CR complexities, (ii) the associated information planes (D,L), (I,J) and (I,V), and (iii) distributions in position, momentum and product spaces.

#### 4.2.1 LMC Complexity and Information Plane

In Fig. 7 the disequilibrium-Shannon plane (D,L) is shown in position, momentum and product spaces (Figs. 7(a), 7(b) and 7(c), respectively) for the isoelectronic series  $N = 2 - 10$ . For the individual spaces (position and momentum), each series roughly follows a linear trajectory in a double logarithmic scale. In fact, the Helium series ( $N = 2$ ) displays an almost constant  $C(LMC) = D \cdot L$  line in both spaces, what means that increasing the nuclear charge produces, as should be expected, a higher



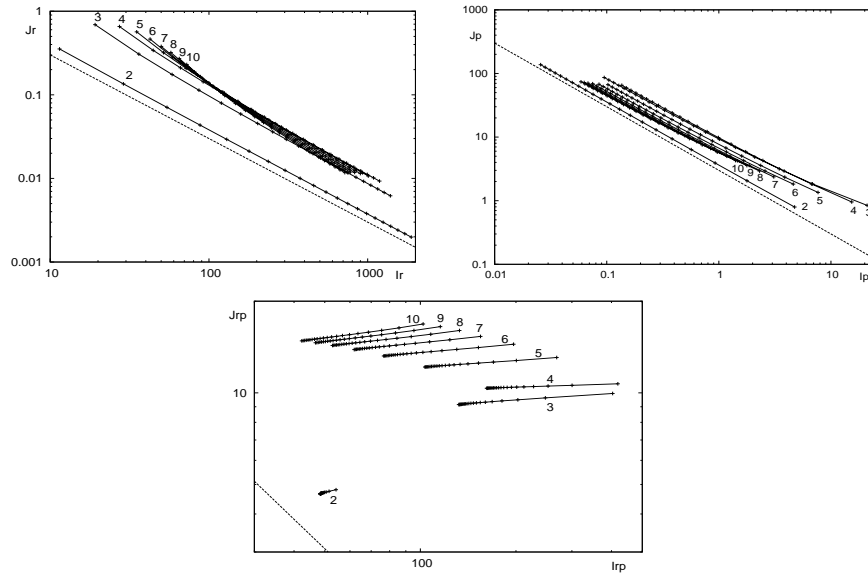
**Fig. 7** Disequilibrium-Shannon plane (D,L) in position (upper left), momentum (upper right) and product (lower) spaces, for isoelectronic series with  $N = 2 - 10$  electrons. Atomic units are used.

localization  $D$  and a lower uncertainty, both effects compensating each other proportionally and providing an almost constant product which defines LMC complexity. Concerning product space, the corresponding Disequilibrium-Shannon plane (D,L) is shown in Fig. 7(c). It is worthy to notice the strong changes in the slopes of all series as compared to those of the isolated spaces. While product entropy does not suffer drastic changes, localization appears very different within each series. Additionally, shell-filling patterns are clearly displayed, with systems having  $2s$  as valence subshell having a higher complexity than those filling the  $2p$  one. It is also remarkable that the  $N = 2$  series displays a very different behavior as compared to the other series. This can be interpreted by taking into account that those systems are the unique ones here considered consisting only on a core shell. From all these comments it should be concluded that the product space plane is relevant in order obtain an interpretation of the Disequilibrium-Shannon plane values in terms of shell structure.

In position space, systems with large nuclear charge  $Z$  for any isoelectronic series display a highly localized structure (large  $D$ ) as shown in Fig. 7(a). In such a large  $D$  area, trajectories are almost linear which correspond to an almost constant product measure. Deviations from this linear shapes are better observed for low nuclear charge systems, possessing a greater complexity. Biggest position space complexities correspond to neutral systems, with a relatively lower lower localization and greater uncertainty as compared to its cations. All those comments are just the opposite ones in momentum spaces, as can be readily realized by observing Fig. 7(b). Heavy systems are characterized by a low localization and high entropy in mome-

tum space, and neutrals deviate from isoproduct lines as possessing a higher level of structure. It is worthy to remark also that spacing between consecutive systems within each isoelectronic series decreases as increasing  $Z$ , because of a higher similarity between systems with large nuclear charge as compare to those with low  $Z$ , which progressively separate among themselves.

#### 4.2.2 FS Complexity and Information Plane



**Fig. 8** Fisher-Shannon plane ( $I, J$ ) in position (upper left), momentum (upper right) and product (lower) spaces, for isoelectronic series with  $N = 2 - 10$  electrons. Atomic units are used.

A similar analysis has been also carried out for the Fisher-Shannon plane ( $I, J$ ) in position, momentum and product spaces (Fig. 8). It is worthy to remember the rigorous lower bound to the associated FS complexity  $C(FS) = I \cdot J \geq \text{constant}$  (the constant being 3 for the conjugated spaces and  $18\pi e$  for the product space) in order to verify such a bound for the systems here considered. The straight line  $I \cdot J = \text{constant}$  drawn in the plane by using a double logarithmic scale divides it into an 'allowed' (upper) and a 'forbidden' (lower) parts. Parallel lines to that one represent isocomplexity points, and higher deviations from this frontier are associated to greater FS complexities. Such a parallel shape is roughly displayed by all isoelectronic series in both position and momentum spaces, as shown respectively in Figs. 8(a) and 8(b). Similar comments to those provided on discussing Fig. 7 in what concerns location areas of systems at the plane, distances within a series between consecutive systems, deviation from minimal complexity values and opposite

behaviors in conjugated spaces are also valid for the position and momentum (I,J) planes as concluded by analyzing Figs. 8(a) and 8(b).

For the sake of brevity, results on the Cramer-Rao plane (I,V) are not displayed, but conclusions obtained from their values are the same as those just discussed for disequilibrium-Shannon and Fisher-Shannon planes.

## 5 Concluding Remarks

Different information-theoretic quantities as well as complexities defined as the product of a couple of localization-delocalization factors have been shown to provide relevant information not only on the shell structure and organization of a great variety of atomic systems, but also on ionization processes and their dependence on both the nuclear charge and the number of electrons. In doing so, it appears necessary to deal simultaneously with the conjugated position and momentum space electron densities, being also important to consider the product space in order to get a more detailed and complete description of such systems. The method here employed for carrying out the present study is also applicable to the analysis of additional multifermionic systems, as is the case of molecules and many others, as well as physical or chemical processes, such as reactions or polarization among others. Some of these subjects are now being studied and will be presented hopefully elsewhere.

It has been also shown the interest of studying the associated information planes subtended by two information functionals, which for the atomic case clearly display the characteristic shell-filling patterns throughout the whole periodic table. It still remains open the question of the existence of additional functionals, planes and complexities providing further information on the atomic structure and the ionization processes, among others

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## References

1. S.B. Sears, S.R. Gadre, *J. Chem. Phys.* **75**, 4626 (1981).
2. R.F. Nalewajski, R.G. Parr, *J. Phys. Chem. A* **105**, 7391 (2001).
3. R. Carbó-Dorca, X. Girones, P.G. Mezey (eds.), *Fundamentals of Molecular Similarity* (Kluwer Academic, Dordrecht/Plenum, New York, 2001).
4. J. Cioslowski, A. Nanayakkara, *J. Am. Chem. Soc.* **115**, 11213 (1993).
5. R. Carbó-Dorca, L. Amat, E. Besalu, X. Girones, D. Robert, *J. Mol. Struct. (Theochem)* **504**, 181 (2000).
6. R. Daudel, *C.R. Acad. Sci. (Paris)* **237**, 601 (1953).
7. C. Aslangul, R. Constanciel, R. Daudel, P. Kottis, *Adv. Quantum Chem.* **6**, 94 (1972).



8. P.G. Mezey, R. Daudel, I.G. Csizmadia, *Int. J. Quantum Chem.* **16**, 1009 (1979).
9. R.F. Nalewajski, *Chem. Phys. Lett.* **375**, 196 (2003).
10. L. Wang, L. Wang, S. Arimoto, P.G. Mezey, *J. Math. Chem.* **40**, 145 (2006).
11. D. Avnir, A.Y. Meyer, *J. Mol. Struct. (Theochem)*, **226**, 211 (1991).
12. C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication* (University of Illinois Press, Urbana, 1949).
13. R.A. Fisher, *Proc. Cambridge Phil. Sec.* **22**, 700 (1925).
14. B.R. Frieden, *Science from Fisher Information* (Cambridge University Press, 2004).
15. E.T. Jaynes, *Phys. Rev. A* **106**, 620 (1957).
16. A. Nagy, *Chem. Phys. Lett.* **425**, 157 (2006).
17. R. Nalewajski, *Chem. Phys. Lett.* **372**, 28 (2003).
18. M. Reginatto, *Phys. Rev. A* **58**, 1775 (1998).
19. A.N. Kolmogorov, *Prob. Inf. Transm.* **1**, 1 (1965).
20. G.J. Chaitin, *J. ACM* **13**, 547 (1966).
21. A. Lempel, J. Ziv, *IEEE Trans. Inform. Theory* **22**, 75 (1976).
22. P. Grassberger, *Int. J. Theory Phys.* **25**, 907 (1986).
23. C.H. Bennett, *Logical Depth and Physical Complexity*, pp. 227-257 in *The Universal Turing Machine: A Half Century Survey* (Oxford University Press, Oxford, 1988).
24. S.S. Lloyd, H. Pagels, *Ann. Phys. NY* **188**, 186 (1988).
25. C.R. Shalizi, K.L. Shalizi, R. Haslinger, *Phys. Rev. Lett.* **93**, 118701 (2004).
26. O.A. Rosso, M.T. Martin, A. Plastino, *Physica A* **320**, 497 (2003).
27. K.Ch. Chatzisavvas, Ch.C. Moustakidis, C.P. Panos, *J. Chem. Phys.* **123**, 174111 (2005).
28. D.P. Feldman, J.P. Crutchfield, *Phys. Lett. A* **238**, 244 (1998).
29. P.W. Lambert, M.P. Martin, A. Plastino, O.A. Rosso, *Physica A* **334**, 119 (2004).
30. R. López-Ruiz, H.L. Mancini, X. Calbet, *Phys. Lett. A* **209**, 321 (1995).
31. J.S. Shiner, M. Davison, P.T. Landsberg, *Phys. Rev. E* **59**, 1459 (1999).
32. C. Anteonodo, A. Plastino, *Phys. Lett. A* **223**, 348 (1996).
33. R.G. Catalán, J. Garay, R. López-Ruiz, *Phys. Rev. E* **66**, 011102 (2002).
34. M.T. Martin, A. Plastino, O.A. Rosso, *Phys. Lett. A* **311**, 126 (2003).
35. R. López-Ruiz, *Biophysical Chemistry* **115**, 215 (2005).
36. T. Yamano, *J. Math. Phys.* **45**, 1974 (2004).
37. T. Yamano, *Physica A* **340**, 131 (2004).
38. J.C. Angulo, *Phys. Rev. A* **50**, 311 (1994).
39. N.L. Guevara, R.P. Sagar, R.O. Esquivel, *Phys. Rev. A* **67**, 012507 (2003).
40. E. Romera, J.J. Torres, J.C. Angulo, *Phys. Rev. A* **65**, 024502 (2002).
41. M. Ho, V.H. Smith Jr., D.F. Weaver, C. Gatti, R.P. Sagar, R.O. Esquivel, *J. Chem. Phys.* **108**, 5469 (1998).
42. J. Antolín, J.C. Cuchí, J.C. Angulo, *J. Phys. B* **32**, 577 (1999).
43. A. Nagy, K.D. Sen, *Phys. Lett. A* **360**, 291 (2006).
44. K.D. Sen, C.P. Panos, K.Ch. Chtzisavvas, Ch.C. Moustakidis, *Phys. Lett. A* **364**, 286 (2007).
45. E. Romera, P. Sánchez-Moreno, J.S. Dehesa, *J. Math. Phys.* **47**, 103504 (2006).
46. I. Hornyak, A. Nagy, *Chem. Phys. Lett.* **437**, 132 (2007).
47. A. Borgoo, M. Godefroid, K.D. Sen, F. de Proft, P. Geerlings, *Chem. Phys. Lett.* **399**, 363 (2004).
48. F. de Proft, P.W. Ayers, K.D. Sen, P. Geerlings, *J. Chem. Phys.* **120**, 9969 (2004).
49. J. Antolín, J.C. Angulo, *Eur. Phys. J. D* **46**, 21 (2008).
50. J.C. Angulo, J. Antolín, *J. Chem. Phys.* **126**, 044106 (2007).
51. A. Borgoo, M. Godefroid, P. Indelicato, F. De Proft, P. Geerlings, *J. Chem. Phys.* **126**, 044102 (2007).
52. J.C. Angulo, J. Antolín, K.D. Sen, *Phys. Lett. A* **372**, 670 (2008).
53. O. Onicescu, *C.R. Acad. Sci. Paris A* **263**, 25 (1966).
54. K.D. Sen, J. Antolín, J.C. Angulo, *Phys. Rev. A* **76**, 032502 (2007).
55. A. Nagy, *J. Chem. Phys.* **119**, 9401 (2003).
56. T.M. Cover, J.A. Thomas, *Elements of Information Theory* (Wiley-Interscience, New York, 1991).

57. A. Dembo, T.A. Cover, J.A. Thomas, *IEEE Trans. Inf. Theory* **37**, 1501 (1991).
58. J.M. Pearson, *Proc. Amer. Math. Soc.* **125**, 3335 (1997).
59. J. Antolín, J.C. Angulo, *Int. J. Quantum Chem.* **109**, 586 (2009).
60. J.C. Angulo, J. Antolín, *J. Chem. Phys.* **128**, 164109 (2008).
61. J.S. Dehesa, P. Sánchez Moreno, R.J. Yáñez, *J. Comp. Appl. Math.* **186**, 523 (2006).
62. S.R. Gadre, *Phys. Rev. A* **30**, 620 (1984).
63. S.R. Gadre, R.D. Bendale, *Curr. Sci. (India)* **54**, 970 (1985) **17**, 138 (1985).
64. C.P. Panos, K.Ch. Chatzisavvas, Ch.C. Moustakidis, E.G. Kyhou, *Phys. Lett. A* **363**, 78 (2007).
65. S.R. Gadre, R.D. Bendale, S.P. Gejji, *Chem. Phys. Lett.* **17**, 138 (1985).
66. R.P. Sagar, N.L. Guevara, *J. Chem. Phys.* **124**, 134101 (2006).
67. E. Romera, J.S. Dehesa, *J. Chem. Phys.* **120**, 8906 (2004).
68. T. Koga, K. Kanayama, S. Watanabe, A. J. Thakkar, *Intl. J. Quantum Chem.* **71**, 491 (1999).
69. T. Koga, K. Kanayama, S. Watanabe, S. Imai, A. J. Thakkar, *Theor. Chem. Acc.* **104**, 411 (2000).
70. A. Borgoo, F. de Proft, P. Geerlings, K.D. Sen, *Chem. Phys. Lett.* **444**, 186 (2007).
71. J.B. Szabo, K.D. Sen, A. Nagy, *Phys. Lett. A* **372**, 2428 (2008).