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Spreading measures of information-extremizer distributions: applications to atomic electron densities in position and momentum spaces

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Abstract. The problem of finding the information-extremizer distribution with a set of given constraints (partial information) has a relevant role from both physical and chemical points of view, specially when working within a density functional theory framework. Beyond the variance, there exist different measures of information susceptible of being extremized, such as the Fisher information and the Shannon and Tsallis entropies. Each one possesses its own properties which make their use more or less convenient according to the systems and/or the process we are dealing with. In this work, we analyze the main information measures of the electron densities of neutral atoms throughout the periodic table, in the two conjugated position and momentum spaces. It is shown how these measures display shell-filling patterns, within a level which depends on the information measure and the space considered. Additionally, the values of all these measures for the solution of various atomic information extremization problems (MaxEnt, MaxTent, MinInf), using radial expectation values as constraints, are analytically obtained, numerically evaluated and also interpreted and discussed in terms of physical characteristics of the atomic systems, such as periodicity and shell structure.

PACS. 31.15.+q – 02.30.Gp Special functions – 03.65.Db Functional analytical methods

1 Introduction

Many different methods have been considered in the literature whose main aim is to provide an *optimal* (in some sense) distribution $\rho(\vec{r})$ in a D-dimensional space, compatible with a discrete and finite set of constraints (including normalization to unity). This is the case of the orthogonal expansions or reference density methods [1], the recursion or continued fractions [2] methods, the Stieltjes-Chebyshev method [3], the moment preserving splines technique [4], and Pollaczek-polynomial-based method [5], among others.

The so-called 'maximum-entropy (MaxEnt) technique' [6,7] is one of the most popular. It is very usual [8] to deal with constraints given by expectation values (e.g. moments) and/or other density functionals of the distribution we are looking for. The resulting maximum-entropy distribution (whenever it exists) is not necessarily unique, i.e. the only optimal one determined by the finite set of constraints.

The MaxEnt technique is based on the variational problem of determining, from all those distributions compatible with the constraints, that which maximizes the 'Shannon entropy' of $\rho(\vec{r})$, defined as [9]

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

which is a well-known measure of randomness and uncertainty. For continuous distributions (as those we are going to deal with), it ranges from $-\infty$ (for $\rho(\vec{r})$ highly concentrated around a single point, approaching a Dirac-delta) to $+\infty$ (for distributions spreading almost uniformly over their domain). So, there is no solution to the MaxEnt problem for continuous distributions with an unbounded domain, unless considering a number (in principle, arbitrary) of the aforementioned constraints.

The main aim and achievement of the MaxEnt technique is the estimation of an unknown distribution when only partial data on it is available or known. The maximum entropy solution is the 'least-biased' (minimally prejudiced) one among all those compatible with the known data, which are the constraints to be imposed in the variational problem when solving it by determining the values of the associated Lagrange multipliers. Attending to the number and kind of constraints involved in the variational process, it is not guaranteed in general the existence and

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uniqueness of the solution to this problem, except for some specific cases [10,11].

The usefulness of the MaxEnt technique has been widely analyzed in many different fields, such as radioastronomy [12], parameter spectral estimation [13], particle physics [14], atomic and many-fermion physics [15] and other scientific and engineering situations [11,16,17], often providing accurate estimations of the unknown distribution. Nevertheless, there exist many cases in which the MaxEnt does not lead to an appropriate distribution [18]. Later on, this variational technique has been extended and generalized, mostly by considering other relevant information measures, such as the 'Tsallis entropy' [19,20]

$$T_q[\rho] \equiv \frac{1}{q-1}\left(1-\int[\rho(\vec{r})]^q d\vec{r}\right) \quad (q>0). \tag{2}$$

The allowed range of values of the parameter 'q' (necessarily positive) is strongly dependent on the short- and long-range behaviors of the distribution $\rho(\vec{r})$. This quantity is closely related to the 'Renyi entropy' [21],

$$R_q[\rho] \equiv \frac{1}{1-q}\,\ln\left(\int[\rho(\vec{r})]^q\,d\vec{r}\right) \quad (q>0). \tag{3}$$

In what follows, we will keep in mind that results on Tsallis entropy easily translate on Renyi entropy according to the so simple relationship between them.

Tsallis entropy can be considered as an extension or generalization of the Shannon entropy functional, as shown by the limiting relation $\lim_{q\to 1} T_q[\rho] = S[\rho]$, which is also verified by $R_q[\rho]$. The extremization of such a functional gives rise to the 'maximum-Tsallis-entropy' (MaxTent, or q-Maxent in other contexts) problem [20,22], recently found to be the basis of the modern non-extensive statistical mechanics [23]. The main characteristics of the associated variational technique can be described similarly as in the Shannon case [24].

More recently, the 'Fisher information' $I[\rho]$ has been also used as the information measure within the variational extremization technique, by determining the 'minimum-Fisher-information' (MinInf) distribution compatible with the given constraints [25]. The MinInf process is known [26,27] to provide the fundamental wave equations and/or the conservation laws of numerous natural systems at small and large scales. The Fisher information (also called Fisher channel capacity or vector Fisher information) is defined as [27,28]

$$I[\rho] = \int \frac{|\vec{\nabla}\,\rho(\vec{r})|^2}{\rho(\vec{r})}d\vec{r}, \tag{4}$$

which gives a measure of narrowness and oscillatory behavior of the distribution $\rho(\vec{r})$. It is a 'local' measure, because of its strong sensitivity to density variations over very small regions due to its gradient-functional form. The Shannon and Tsallis entropies are considered as 'global' quantities because they are much more informative on the average behavior of the density over its whole domain.

As occurs with the MaxEnt problem, it still remains open the determination, in general, of existence and uniqueness conditions for the MaxTent and MinInf problems to have a solution. The corresponding conditions are only known for some particular cases [22,25,29]. The use and extremization of the previous spreading/information measures is a subject of high current interest in many different fields such as, for instance, the study of multielectronic systems, particularly by means of density functional methods [30].

There also exist other information functionals which play a relevant role in the description of the spreading properties of a distribution. The most familiar one is the 'variance', which provides a measure of the averaged deviation of the distribution from the mean value (being also a 'global' measure in the sense pointed out above). It is defined as

$$V[\rho] \equiv \langle r^2\rangle - \langle r\rangle^2 \tag{5}$$

(with $r = |\vec{r}|$), expressed in terms of 'radial expectation values' of first (mean value) and second order, defined as

$$\langle r^k\rangle \equiv \int r^k \rho(\vec{r})d\vec{r}. \tag{6}$$

The integral-convergence conditions (i.e. the existence of radial expectation values) according to the kth order are determined by both the behavior of the distribution and the dimensionality D of the space.

In the present work, we will center our attention on the information provided by some of the aforementioned spreading measures when dealing with many-electron systems, as well as on analyzing the relationship between their values and relevant physical properties of those systems. Among them, specially relevant are the structural characteristics of the electron densities in position and momentum spaces, as well as the nuclear charge. For atomic systems, it is well known that different radial expectation values (in both conjugated spaces) are physically relevant and/or experimentally accessible.

To the best of our knowledge, this is the first time that such a study on information measures of extremizer distributions is carried out for many-electron systems (i.e. three-dimensional densities of atoms throughout the periodic table) in both conjugated position and momentum spaces. Recently a similar study has been performed for the D-dimensional Hydrogen atom in position space [24].

The work is structured as follows. In Section 2, the main characteristics of the extremizer distributions associated with different variational techniques will be described. In Section 3, the aforementioned distributions will be considered for the study of the electron densities of neutral atoms in the conjugated position and momentum spaces (and, consequently, for the particular dimensionality $D = 3$). This study includes the analysis of different existence conditions for the two-constraints MaxEnt problem. For each specific measure, a subsection is devoted to the interpretation of those results, including in some cases their analysis in terms of the density structure as well as the shell-filling process; moreover, the dependence of the extreme information values on both the atomic nuclear charge and the order of the radial constraints is emphasized. Finally, a brief description of related open problems and the appropriate conclusions on the present work will be also given.

2 Variational extremization of information measures

In this section we face the problem of extremizing an information measure $F[\rho]$ on a D-dimensional distribution function $\rho(\vec{r})$ when a set of M expectation values $\{g_i(\vec{r})\}$ $(i = 1, \ldots, M)$ on such a distribution is known. This problem has been recently investigated in reference [24] for the functionals $F[\rho]$ where the extremization problems were associated with Shannon's entropy $S[\rho]$ (MaxEnt), Tsallis' entropy $T_q[\rho]$ (MaxTent) and Fisher's information $I[\rho]$ (MinInf).

At this point, knowledge of existence conditions for these extremization problems appears highly relevant. The first step in the extremization process usually provides the form of the extremum information distributions subject to the given constraints. But determining the involved Lagrange multipliers from the values of the constraints is not, in general, an easy task. Even more so, the existence of a solution to that problem is not guaranteed. This is a subject on which many authors have worked as shown by the numerous articles devoted to this question [10,11,16,17,25,29,31].

Once the existence and determination of the extremizer distribution is under control, there still remains the performance of a systematical analysis of its spreading properties. This would be a relevant achievement in the study, as pointed out by many authors, of diverse systems and processes in science, finances and engineering [16,30,31].

The extremization method associated with a generic information measure $F[\rho]$ requires its maximization/minimization preserving the constraints of normalization to unity, as

$$\int \rho(\vec{r})d\vec{r} = 1, \quad (7)$$

and the expectation values $\{c_i\}$ of the functions $\{g_i(\vec{r})\}$, namely

$$\int \rho(\vec{r})g_i(\vec{r})d\vec{r} = c_i, \quad (i = 1, \ldots M), \quad (8)$$

understanding in what follows (in order to simplify notation) that $g_0(\vec{r}) \equiv 1$ (and, consequently, $c_0 = 1$). Employing the Lagrange multipliers method for the variational problem, the extremization process requires to find the solution of a coupled set of $M + 1$ equations (given by the constraints) and $M + 1$ unknowns (the Lagrange multipliers), which determine the extremum information probability density.

Let us restrict ourselves to the extremization problem involving one radial expectation value $\langle r^\alpha \rangle$ $(M = 1)$, apart from normalization. The analytical solution to this problem is known for radial expectation order $\alpha > 0$ in the MaxEnt and MaxTent problems, and for $\alpha = -1$ in the MinInf one. The corresponding extremizer distributions will be denoted by ρ_S (maximum S), ρ_T (maximum T_q) and ρ_I (minimum I). The analytical forms of all these distributions allow one [24] to determine their associated information measures, namely Shannon entropy S, Tsallis entropy T_q, Fisher information I and variance V, which are the main objects of this work. That is, these four information measures are analytically known for the three extremizer distributions described above. They will be denoted so that, for example, V_I gives the variance V of the minimum-Fisher-information distribution $\rho_I(\vec{r})$, the subscript denoting the extremized measure, and similarly for the other measures and distributions.

Taking into account that the applications of the present study will be carried out by considering the three-dimensional $(D = 3)$ one-particle atomic distributions in position and momentum spaces, we will discuss in what follows, for the sake of simplicity, the expressions corresponding to that particular dimensionality.

Also in order to avoid a too high number of equations, and considering the main purposes of this work, we will omit the detailed analytical expressions describing the variational solutions and their associated information measures (which can be found in Ref. [24]).

Attending to the strong relationship between Shannon and Tsallis entropies, which allows one to *roughly* (but not strictly) consider the Shannon entropy as a particular case of the Tsallis one (according to the limiting value as $q \to 1$), we will firstly discuss the MaxTent problem, because, as will be checked later, many of the conclusions obtained from the analysis of this problem will be also valid in the MaxEnt one, especially those associated with the global character of both measures. Nevertheless, it is worthy to remark that there also exist relevant differences between them, mainly due to the functional form of the extremizer distribution. And finally, as should be expected according to the strongly different characteristics of the Fisher information measure, such a difference will be also clearly displayed when studying the associated MinInf problem, which deals with a local measure, in an opposite way to the previous entropy maximization problems. For the sake of simplicity, we will restrict ourselves in this case to the particular order $\alpha = -1$, due to the involvement of the problem for any other value.

Let us briefly describe the main characteristics of the three-dimensional $(D = 3)$ extremizer distributions subject to the normalization and the α-order constraints:

- *MaxTent distribution*: the solution is a power-like function, with a finite-size support (a sphere which radius depends on $\langle r^\alpha \rangle$).
- *MaxEnt distribution*: the solution has an exponentionally decreasing behavior over the non-negative real line $r \geq 0$, namely on the distance 'r' from the origin. As pointed out just before discussing the extremizer solutions, the functional form of the MaxEnt solution (i.e. exponential over the whole space) strongly differs from

that of MaxTent problem (i.e. power-like over a finite radius support), in spite of the limiting relationship between the involved entropies.
It is worthy to mention that, also in reference [24], the existence conditions for the MaxEnt problem when adding an additional constraint $\langle r^\beta \rangle$ (i.e. $M = 2$) were also obtained. We will also check those conditions in Section 3 for atomic systems.

- *MinInf distribution*: as remarked above, we restrict now the problem, for the sake of simplicity, to the particular case $\alpha = -1$. The solution is (in a similar fashion as in the MaxEnt problem) an exponentially decreasing function.

Next section is devoted to the study, in these three extremization problems, of the information measures for atomic systems throughout the periodic table by means of their one-particle densities $\rho(\vec{r})$ and $\gamma(\vec{p})$ (position and momentum spaces, respectively), by applying the aforementioned results (which are valid for any distribution function), to those specific densities.

3 Atomic spreading measures in position and momentum spaces

The measures described in previous sections are defined (whenever being possible) for normalized-to-one distributions $\rho(\vec{r})$ defined over the three-dimensional space $\mathbb{R}^3$. Consequently, the vector $\vec{r}$ consists of 3 components, which can be expressed equivalently in Cartesian or spherical coordinates, namely $\vec{r} = (x, y, z) = (r, \theta, \phi)$, where $r = |\vec{r}|$.

In principle, it is not guaranteed that those information measures be well-defined for any arbitrary distributions, because their definition requires the involved integral to be convergent and, for the Fisher information, the distribution to be differentiable. For illustration, the definition of the variance V requires appropriate short- and long-range behaviors of the distribution for the involved first- and second-order radial expectation values to be finite, namely $r^4\rho(r) \to 0$ as $r \to 0$ and $r^5\rho(r) \to 0$ as $r \to \infty$. Similar requirements need also to be verified in the Tsallis entropy case (determined by the considered value of the T_q parameter), as well as the aforementioned differentiability over the whole domain when considering Fisher information I. Nevertheless, all these convergence and differentiability conditions are verified by the atomic distributions analyzed in the present work.

One of the basic ingredients in the study of many-fermion systems (e.g. atoms, molecules) is the one-particle density $\rho(\vec{r})$ on the three-dimensional space, as revealed by the so-called 'density functional theory' (DFT). Such a density describes the distribution of the electron cloud around each position $\vec{r}$ in $\mathbb{R}^3$, and it plays the main role within the DFT for describing many different properties of the system, such as kinetic, exchange and correlation energies, among others [32].

It is very usual to deal additionally with the corresponding distribution in the so-called *conjugated space*. This is the case in which the $\vec{r}$-space distribution of a N-particle system is defined from an initial wavefunction $\Psi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)$ by integrating $|\Psi|^2$ on all variables except $\vec{r}$, giving rise to $\rho(\vec{r})$. If one considers the Fourier transform $\tilde{\Psi}(\vec{p}, \vec{p}_2, ..., \vec{p}_N)$ to build up the associated distribution $\gamma(\vec{p})$ (preserving normalization), many properties and characteristics of both densities $\rho(\vec{r})$ and $\gamma(\vec{p})$ are well-known to be strongly related. As mentioned above, this is the case, for instance, of the so-called *one-particle densities* of many-particle systems (e.g. atoms, molecules). Similarly as $\rho(\vec{r})$ (position space density, in what follows) provides the mass density around location $\vec{r}$, the 'momentum space density' $\gamma(\vec{p})$ quantifies the linear momentum distribution around the momentum vector $\vec{p}$. Different relationships involving quantities associated with both complementary densities are of capital importance through the concept of *uncertainty* of the system.

In what follows, atomic units (a.u.) will be considered for variables, densities and functionals (i.e. $\hbar = m_e = e = 1$ and, consequently, also the Bohr radius $a_0 = 1$) when carrying out the numerical analysis for atoms. Fixing the system of units is essential for a proper description of different quantities, according to their definition.

It is worthy to point out that, for atomic systems in the absence of external fields, it is sufficient to deal with the spherically averaged densities $\rho(r)$ and $\gamma(p)$ for a complete description, the independent variable (r or p) ranging over the non-negative real line $[0, \infty)$.

Some radial moments (in both spaces) are specially relevant for atomic systems from a physical point of view. It is well known, for instance that $\langle r^{-1} \rangle$ is essentially the electron-nucleus attraction energy, $\langle r^2 \rangle$ is related to the diamagnetic susceptibility, $\langle p^{-1} \rangle$ is twice the height of the peak of the Compton profile, and $\langle p^2 \rangle$ is twice the kinetic energy and $\langle p^4 \rangle$ its relativistic correction. So, those physically relevant and/or experimentally accessible quantities provide also information on the spreading measures of the system.

The previously introduced notation on extremum information measures will refer to the position-space density $\rho(\vec{r})$, adding above the symbol '$\sim$' (in a similar fashion as done for the wavefunction in the conjugated space) when dealing with the momentum or $\vec{p}$-space density $\gamma(\vec{p})$ (e.g. $\tilde{I}_S$ is the Fisher information I of the distribution $\gamma_S(\vec{p})$ which maximizes Shannon entropy S).

The main aim in the present section is the study for ground-state neutral atoms throughout the periodic table, with nuclear charge $Z = 1{-}103$, of the information-theoretic measures S, T_q, I and V for the extremizer distributions (i.e. the solutions of the MaxEnt, MaxTent and MinInf problems), constrained by normalization and an α-order expectation value, in position and momentum spaces. For carrying out the numerical calculations, the accurate near-Hartree-Fock wavefunctions of Koga et al. [33] will be employed. Such a study will be done by analyzing the dependence of the measures in both the nuclear charge Z and the constraint order α for each conjugated space. The associated radial expectation values are defined for $\alpha > -3$ in position space and within the range $-3 < \alpha < 5$ in the momentum one, due to the rigorously known short- and long-range behaviors of the densities. Concerning the information measures, all them are finite-valued for these systems (taking into account the differentiability of the densities at any point as well as the aforementioned behaviors at zero and infinity), with the only constraint $q > 3/8$ in momentum space as a consequence (in order to the integral appearing in the definition of T_q be convergent) of the long-range behavior of the one-particle density $\gamma(p)$ as p^{-8} [34].

For completeness, the existence conditions for the two-moment (α, β)-MaxEnt problem will be also checked for these systems by means of their radial expectation values obtained with the aforementioned near-Hartree-Fock framework.

3.1 The MaxTent atomic problem

As mentioned in the introduction, Tsallis entropy T_q definition constitutes an extension or generalization of Shannon entropy S, or equivalently, S can be considered as a particular value of T_q having in mind the limiting equality $S = T_1$. In spite of this equality, the maximizer distributions of both entropies are significantly different, as described in Section 2. For the MaxEnt problem, it has an exponential-like decreasing behavior as increasing the distance from the origin over the whole space, while the MaxTent solution (for $q \neq 1$) has a finite-size support, being a sphere centered at the origin. So, the MaxEnt problem cannot be seen as a mere particular case of the MaxTent one, but a very special case as described later on.

This is the reason for being so interesting to carry out, for the spreading measures associated with both the MaxTent and the MaxEnt problems, a similar study concerning the dependence on the nuclear charge Z and the constraint order α of the corresponding information measures, in both conjugated spaces. For illustration, the $q = 1.7$ value of Tsallis parameter will be considered in order to perform the numerical calculations, but similar conclusions are derived from the results obtained considering other values. Additionally, when dealing with a fixed constraint order α, most comments are also valid independently of its value.

In Figure 1, variance, Fisher information and Shannon and Tsallis entropies of the MaxTent distributions are displayed (employing some scaling factors in order to better compare among themselves) for the ground-state neutral atoms with nuclear charge $Z = 1{-}103$ in position (Fig. 1a) and momentum (Fig. 1b) spaces, with constraint order $\alpha = 1$ (the expectation value being calculated within the aforementioned Hartree-Fock framework, employing the wavefunctions provided in Ref. [33]). Some comments are in order:

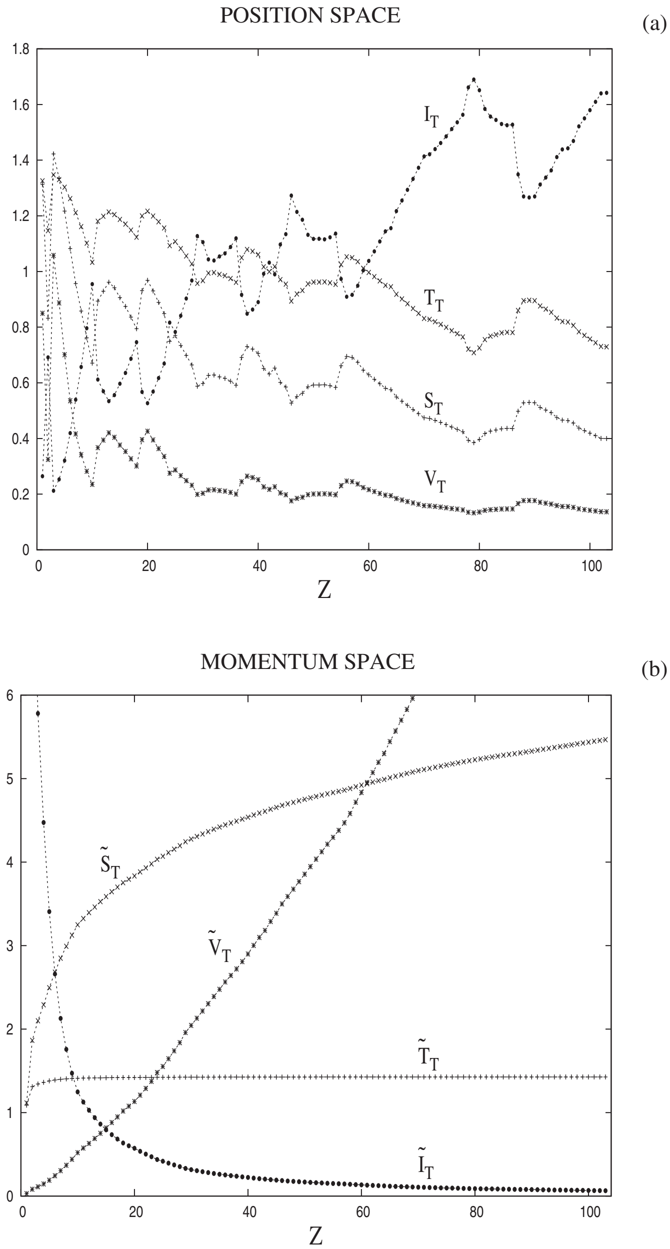

Fig. 1. Variance, Fisher information and Shannon and Tsallis entropies of the MaxTent (maximum Tsallis entropy) solution for $q = 1.7$ with radial constraint order $\alpha = 1$ in (a) position ($3 \times V_T$, $I_T/26$, $S_T/3$ and $T_T(q = 1.7)$), and (b) momentum ($\tilde{V}_T/3$, $\tilde{I}_T$, $\tilde{S}_T/2$ and $\tilde{T}_T(q = 1.7)$) spaces, for all ground-state neutral atoms with nuclear charge $Z = 1{-}103$. Atomic units are used.

1. A first comparison between Figures 1a and 1b reveals the strong structural differences according to the space we deal with. There appears a very *rich* piecewise structure on curves corresponding to information measures in position space (Fig. 1a), while much softer shapes are displayed in momentum space (Fig. 1b). Centering our attention upon position space, the spatial relationship among the atoms is checked for the locations of extrema and for the process of filling atomic subshells. In this sense, different periods throughout the periodic table are represented by apparent pieces of the curves. Within each period, the global measures decrease (in overall) when adding an electron while, on the other hand, the local Fisher information increases.

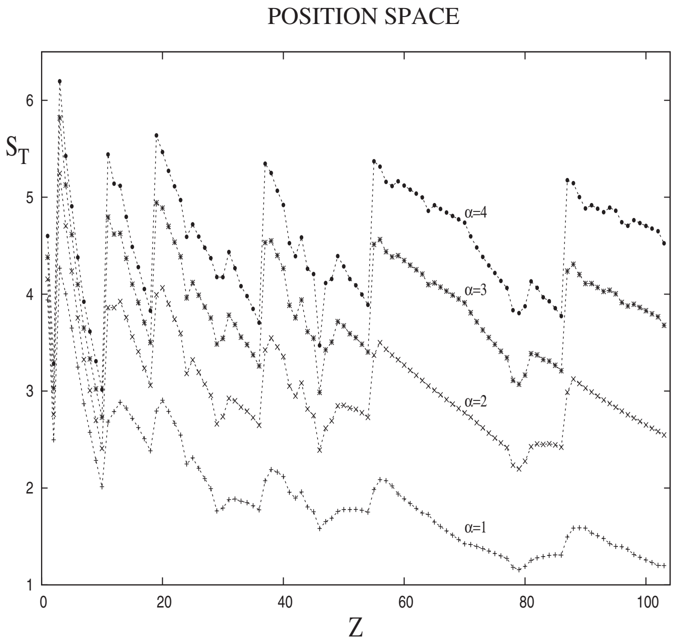

Fig. 2. Shannon entropy (S_T) of the MaxTent (maximum Tsallis entropy) solutions in position space with radial constraint orders $\alpha = 1, 2, 3, 4$, for all ground-state neutral atoms with nuclear charge $Z = 1{-}103$. Atomic units are used.

Moreover, other structural properties, such as the *anomalous* shell-filling, are also revealed by the additional peaks associated with the corresponding elements. This is the case, for instance of systems with $Z = 24, 29$ ($3d$ subshell), $Z = 41{-}42$, $44{-}47$ ($4d$ subshell) and $Z = 78, 79$ ($5d$ subshell).

2. As mentioned in the Introduction, the Fisher functional is a *local* measure of information, contrary to the variance and Shannon and Tsallis entropies, which are quantities of *global* character. This fact is clearly appreciated in Figure 1a, where local maxima of the global measures appear at the same position as local minima of the local measure, and conversely (e.g. maxima of global measures occur, with very few exceptions, for noble gases, namely systems with completely filled valence orbitals). Such a behavior indicates that a higher spreading of the distribution raises the global measures but decreases the local one, as should be expected according to the meaning and the definitions of the different information quantities.
3. A similar comment can also be done by analyzing Figure 1b (momentum space), now in terms of monotonicity properties instead of location of extrema. In this sense, it is worthy to remark that curves corresponding to global measures are monotonically increasing with the nuclear charge Z as well as concave, while the behavior in the Fisher case is just the opposite one, namely it decreases with Z displaying a convex shape.

It is also interesting to consider the dependence of the information measures on the constraint order α of the chosen constraint, as illustrated by Figure 2 for the Shannon entropy S_T of the Tsallis extremized distribution in position space, again for $Z = 1{-}103$. As clearly observed, the quantity S_T provided by the particular values $\alpha = 1, 2, 3, 4$ behaves in a similar fashion independently of the constraint order, differing among themselves only (roughly) by a scaling factor. According to the global character of Shannon entropy and its relation with the Tsallis one, most comments concerning location of extrema and its interpretation in terms of periodicity and shell structure, as well as the relevant structural differences between the position and the momentum space studies, can be also obtained from those of Figure 1, being valid for any α.

3.2 The MaxEnt atomic problem

Having in mind, as previously mentioned, the similar interpretation of the Z dependence for both the MaxTent and the MaxEnt problems, let us now analyze in more detail the dependence of the measures associated with the MaxEnt distribution on the constraint order α in both conjugated spaces, by considering the maximal Shannon entropy in position space (S_S) and Fisher information in momentum space ($\tilde{I}_S$), that is, a global and a local measure. Nevertheless, additional comments will be also done concerning other quantities in both spaces, apart from those appearing in the figure. Specially interesting is the different behavior displayed by these quantities (the other global measures behaves in a similar way as Shannon entropy) attending to the space we are dealing with, not only in the level of structure but also in the way the global measures appear ordered.

For illustration, a comparison of these quantities as functions of α is carried out for different ground-state atomic systems ($Z = 10, 19, 25, 33, 38, 48, 70, 83$) in Figure 3. The selection of those systems is not arbitrary, but made in order to include a variety of valence subshells and occupation numbers. It is worthy to remark that (i) the 'global' position space Shannon entropy S_S monotonically increases while the 'local' momentum space Fisher information $\tilde{I}_S$ monotonically decreases; and (ii) both quantities also differ on higher order monotonicity properties, namely the position space Shannon entropy S_S is a concave function of α, the Fisher information $\tilde{I}_S$ (momentum space) being convex. Concerning other information measures in the two conjugated spaces, let us also point out that, except for very small values of α, (i) the three global measures here considered (variance and Shannon and Tsallis entropies) monotonically increase in the two conjugated spaces, the local one (Fisher information) being monotonically decreasing in both them; and (ii) the four measures in momentum space, as well as the variance and the Fisher information in position space, display convex shapes, while Shannon and Tsallis entropies in position space are (in overall) concave functions of the constraint order α.

Another relevant difference between Figures 3a and 3b concerns ordering of curves (from above to below) attending to the space considered. While in momentum space

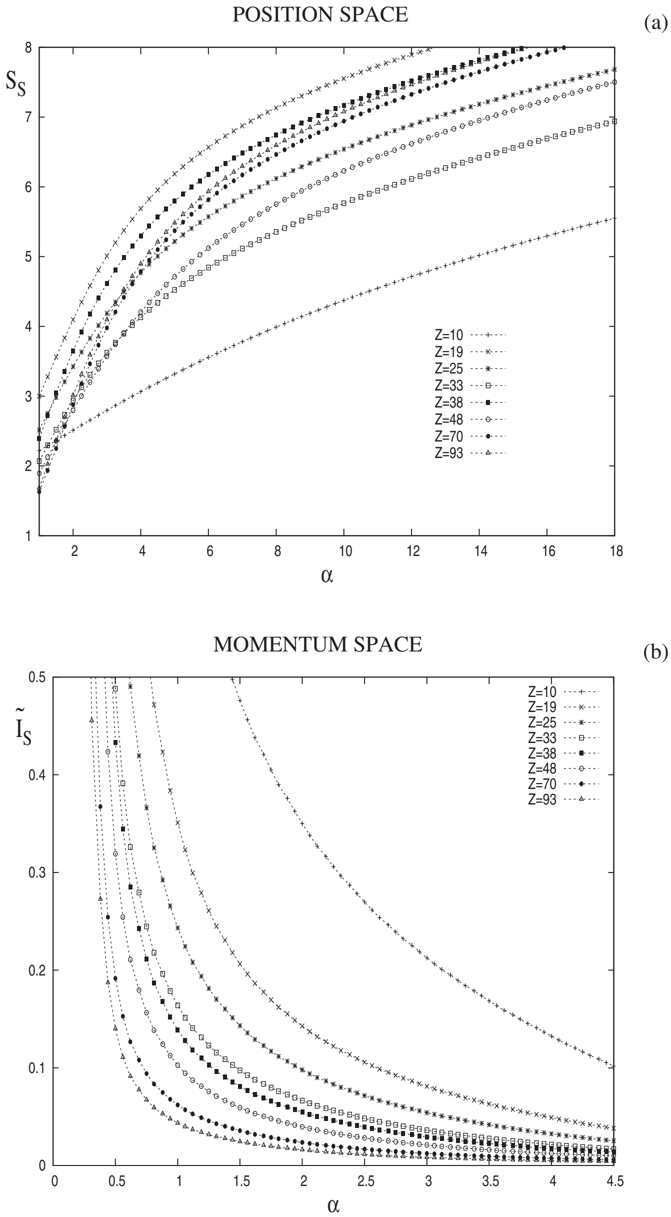

Fig. 3. (a) Shannon entropy in position space (S_S), and (b) Fisher information in momentum space ($\tilde{I}_S$), of the MaxEnt (maximum Shannon entropy) solution with the radial constraint $\langle r^\alpha \rangle$ as a function of α, for ground-state neutral atoms with nuclear charge $Z = 10, 19, 25, 33, 38, 48, 70, 83$. Atomic units are used.

they are ordered according to the nuclear charge Z, ordering in position space is governed by the electronic configuration of the valence subshell. The same comment is also valid for all other information measures considered in this work.

Finally, and for completeness, let us mention that we have checked the existence conditions of MaxEnt solutions (provided in Ref. [24]) when adding a second radial constraint (i.e. with $M = 2$). In doing so, we have considered radial expectation values of integer-order within the range -2 to 4. The analysis carried out reveals that they are not verified neither in position nor in momentum space, independently of the pair of constraints considered. Consequently, there does not exist MaxEnt solution under those conditions for atomic charge and momentum densities, at least for those systems.

3.3 The MinInf atomic problem

As compared to the previous variational problems, the minimization of Fisher information under some given constraints presents different characteristics from the conceptual and mathematical points of view. As its own name indicates, now the aim is to find a minimizer information distribution instead of a maximizer one. The reason is the kind of functional to extremize, namely the Fisher information which, contrary to the convex functionals T_q and S (Tsallis and Shannon entropies), is a concave one. This rigorous property has been previously pointed out when discussing the maximization problems.

Also the local character of I, opposite to the global one of S and T_q, justifies the replacement of a maximization by a minimization problem. The fact that the gradient of the distribution appears in the definition of I makes that minimum values to be reached for highly spread distributions, according to the concept of 'least-biased' functions.

Affording the associated variational problem mathematically is more involved than the previous ones, mainly due to the above mentioned gradient operator in the Fisher information definition. The only case (to the best of our knowledge) for which an analytical solution has been obtained is that corresponding to a unique constraint (apart from normalization) of order $\alpha = -1$. Nevertheless, for our present purposes (namely the application of the MinInf information measures to the study of atomic systems), such an order is specially relevant and meaningful from a physical point of view in both position and momentum spaces, because the associated constraints in conjugated spaces, namely $\langle r^{-1} \rangle$ and $\langle p^{-1} \rangle$ are proportional (as previously mentioned) to the electron-nucleus attraction energy and to the height of the peak of the Compton profile, respectively.

The analysis of the information measures associated with the minimizer distributions is carried out below according to their dependence on the atomic nuclear charge Z for both the position and momentum spaces, as displayed in Figure 4 (employing some scaling factors in Fig. 4a for a better comparison of the position spaces quantities). For illustration, the value $q = 0.9$ has been chosen for the characteristic parameter of the Tsallis entropy T_q.

As in preceding maximization problems, the different structures displayed in the given space by all the information measures of the minimized Fisher information are clearly revealed. However, the most remarkable point is that momentum space is now the one which provides a higher level of structure, again displaying a high number of local extrema whose location is determined by the shell-filling process and showing periodicity patterns.

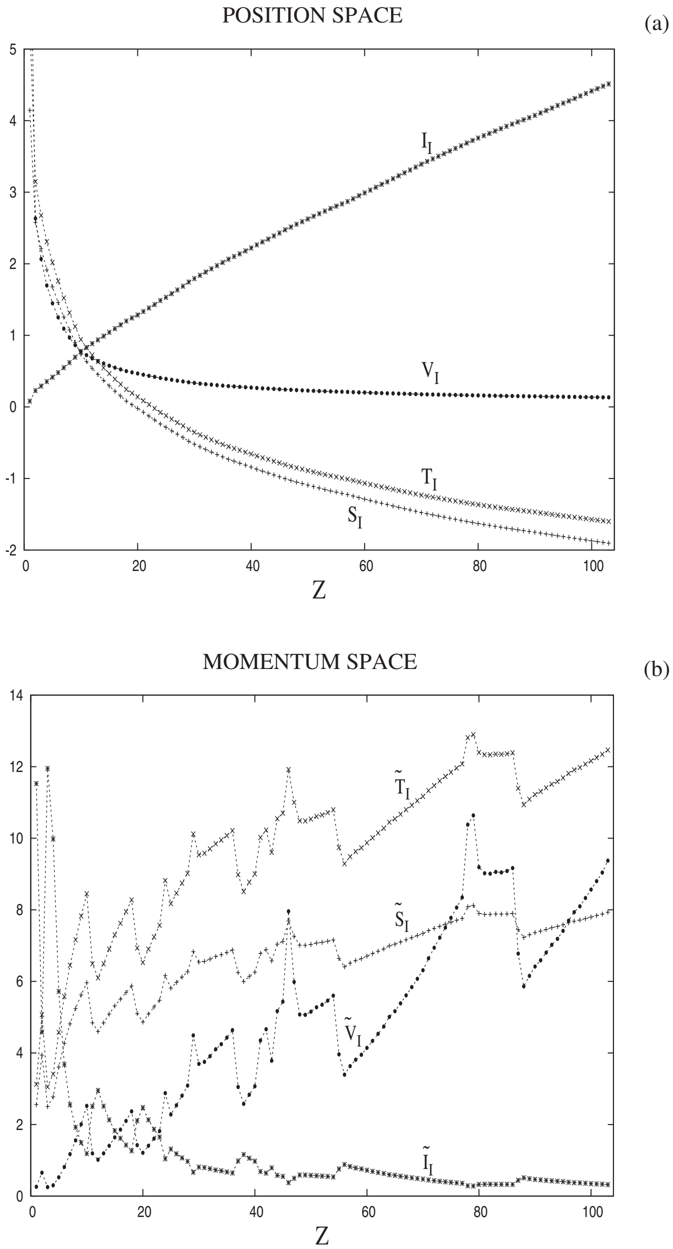

Fig. 4. Variance, Fisher information and Shannon and Tsallis entropies of the MinInf (minimum Fisher information) solution with radial constraint order $\alpha = -1$ in (a) position ($10 \times V_I$, $I_I/50$, S_I and $T_I(q = 0.9)$), and (b) momentum ($\tilde{V}_I$, $\tilde{I}_I$, $\tilde{S}_I$ and $\tilde{T}_I(q = 0.9)$) spaces, for all ground-state neutral atoms with nuclear charge $Z = 1-103$. Atomic units are used.

The shell-structure properties of atomic systems are mainly characterized by the valence orbital, usually the outermost subshells. The aforementioned results on all extremization problems allow one to conclude that the information-theoretic apport of the valence orbital to the global measures is much more significant in position space, while Fisher information appears to be more sensitive to valence contribution in momentum space.

Summarizing, it has been clearly revealed the complementary usefulness of global and local information measures, as well as their values in both conjugated spaces (position and momentum), in order to get a complete description of the information content of the atomic systems, as well as its interpretation in terms of relevant physical properties and their main structural characteristics.

4 Conclusions and open problems

After clarifying the role played by different information measures on an arbitrary distribution, and the associated extremization problems (MaxEnt, MaxTent and MinInf) when a given set of constraints (expectation values) is known, we have analyzed the mutual dependence among the one-constraint solutions and the values of their information-theoretic measures for real physical systems, namely neutral atoms throughout the periodic table. The behavior in terms of the nuclear charge Z and the constraint order α has been studied in both conjugated spaces, displaying in some cases the shell-structure patterns (including anomalous shell-filling) according to the global or local character of the involved spreading measure. The characteristic atomic periodicity appears strongly related to the location of maxima and minima in the information curves. In this sense, it is worthy to remark that, while the information measures of the MinInf solution are much more sensitive to valence orbital occupation number for the momentum space density $\gamma(\vec{p})$, the same is true for the MaxEnt and MaxTent ones but in the conjugate space, i.e. for the charge density $\rho(\vec{r})$. Other properties, such as ordering among themselves, monotonicity (strict or piecewise) and convexity on the Z and α variables have been considered. Additionally, for the MaxEnt case it has been checked that, in the present Hartree-Fock framework, the existence conditions for the two-constraint problem, which has been recently determined analytically in reference [24], do not hold for any neutral atom neither in position nor in momentum space, at least for integer-order constraints.

For future work, it is expected (i) to afford the three (and higher) constraints problem; (ii) to establish uncertainty-like relationships for the extremization problems, working within the product or phase space; (iii) to study the dependence of the aforementioned measures on additional physical and chemical properties (ionization potential, electron affinities); (iv) to impose different kinds of constraints, such as short- and long-range behaviors; and (v) to deal with other many-fermion systems (e.g. molecules) and distributions (e.g. form factors and Compton profiles, whose moments are strongly related to the one-particle densities in position and momentum spaces).

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References

1. C.T. Corcoran, P.W. Langhoff, Chem. Phys. Lett. **41**, 609 (1976)
2. R. Haydock, V. Heine, M. Kelly, J. Phys. C **5**, 2845 (1972)
3. C.T. Corcoran, P.W. Langhoff, J. Math. Phys. **18**, 651 (1977)
4. M. Frontini, V. Gautschi, G.V. Milovanovic, Numer. Math. **50**, 503 (1987)
5. E. Escalas, G.A. Viano, J. Math. Phys. **34**, 5781 (1993)
6. E.T. Jaynes, Phys. Rev. **106**, 620 (1957); E.T. Jaynes, Phys. Rev. **108**, 171 (1957)
7. E.T. Jaynes, in *The Maximum Entropy Problem*, edited by R.D. Levine, M. Tribus (MIT Press, Cambridge, 1978)
8. J. Antolín, J. Math. Phys. **31**, 791 (1990); M.J. Leasenburg, L.R. Mead, J. Math. Phys. **34**, 6009 (1993); I. Csizsar, Ann. Probab. **3**, 146 (1975); A. Zarzo, J.C. Angulo, J. Antolín, R.J. Yáñez, Z. Phys. D **37**, 295 (1996)
9. C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication* (University of Illinois Press, Urbana, 1949)
10. D.C. Dowson, A. Wragg, IEEE Trans. Inf. Theory **19**, 689 (1973); A. Kociszewski, J. Phys. A **19**, L823 (1986); J.M. Einbu, IEEE Trans. Inf. Theory **23**, 772 (1977); M. Frontini, A. Tagliani, Appl. Math. Comput. **97**, 183 (1998)
11. P. Ishwar, P. Moulin, IEEE Trans. Inf. Theory **51**, 3322 (2005)
12. J. Skilling, R.K. Bryan, Mon. Not. R. Astr. Soc. **211**, 111 (1984)
13. D.M. Liu, E.K. Wong, Phys. Rep. **193**, 41 (1990)
14. J. Antolín, Phys. Rev. D **43**, 1532 (1991)
15. T. Koga, Theor. Chim. Acta (Berlin) **64**, 249 (1984); J. Antolín, A. Zarzo, J.C. Angulo, Phys. Rev. A **50**, 240 (1994); J.C. Angulo, R.J. Yáñez, J. Antolín, A. Zarzo, Int. J. Quantum Chem. **56**, 747 (1995)
16. J.N. Kapur, *Maximum Entropy Models in Science and Engineering* (Wiley, New York, 1993)
17. M. Grendar Jr, M. Grendar, in *Bayesian Inference and Maximum Entropy Methods in Science and Engineering*, edited by G. Erickson, Y. Zhai (AIP, Melville, 2004), pp. 97–109
18. B.R. Frieden, Phys. Rev. A **41**, 4265 (1990)
19. J. Havrda, F. Charvat, Kybernetika **3**, 30 (1967)
20. C. Tsallis, J. Statist. Phys. **52**, 479 (1988)
21. A. Renyi, *On measures of entropy and information*, in Proc. 4th Berkley Symposium on Mathematics of Statistics and Probability **1**, 547 (1961)
22. C. Tsallis, R.S. Mendes, A.R. Plastino, Physica A **261**, 534 (1998); S. Martínez, F. Nicolas, F. Pennini, A. Plastino, Physica A **286**, 489 (2000)
23. *Nonextensive Statistical Mechanics*, edited by J.P. Boon, C. Tsallis, Europhysics News **36** (2005)
24. S. López-Rosa, J.C. Angulo, J.S. Dehesa, R.J. Yáñez, Physica A **387**, 2243 (2008); erratum, Physica A **387**, 4729 (2008)
25. M. Reginatto, Phys. Rev. A **58**, 1775 (1998); B.R. Frieden, A. Plastino, A.R. Plastino, B.H. Soffer, Phys. Rev. E **60**, 48 (1999); B.R. Frieden, Physica A **198**, 262 (1993)
26. B.R. Frieden, A. Plastino, A.R. Plastino, B.H. Soffer, Phys. Rev. E **66**, 046128 (2002)
27. B.R. Frieden, *Science from Fisher information* (Cambridge University Press, Cambridge, 2004)
28. B.R. Frieden, W.J. Cocke, Phys. Rev. E **54**, 257 (1996)
29. L. Rebollo-Neira, A. Plastino, J. Fernández-Rubio, Physica A **258**, 458 (1998); E. Romera, J.S. Dehesa, Phys. Rev. A **50**, 256 (1994)
30. A. Nagy, J. Chem. Phys. **119**, 9401 (2003); R.F. Nalewajski, R.G. Parr, Proc. Natl. Acad. Sci. USA **97**, 8879 (2000); J.C. Angulo, J.S. Dehesa, J. Chem. Phys. **97**, 6485 (1992); erratum, J. Chem. Phys. **98**, 1 (1993); B.R. Frieden, B.H. Soffer, Found. Phys. Lett. **13**, 89 (2000); S. Luo, Found. Phys. Lett. **32**, 1757 (2002); R.J. Hawkins, B.R. Frieden, Phys. Lett. A **322**, 126 (2004)
31. M. Junk, Math. Mod. Meth. Appl. Sci. **10**, 1001 (2000); J.C. Cuchí, Ph.D. Thesis, Universidad de Zaragoza, 2005; L.R. Mead, N. Papanicolau, J. Math. Phys. **5**, 2404 (1984); A. Plastino, A.R. Plastino, Brazilian J. Phys. **29**, 50 (1999); V. Zivojmovic, Signal Processing **65**, 297 (1998)
32. R.G. Parr, W. Yang, *Density-functional Theory of Atoms and Molecules* (Oxford University Press, 1989)
33. T. Koga, K. Kanayama, S. Watanabe, A.J. Thakkar, Int. J. Quantum Chem. **71**, 491 (1999)
34. R. Benesch, V.H. Simith Jr, *Wave Mechanics: the First Fifty Years* (Butterworth, London, 1973)