

Information entropy, information distances, and complexity in atoms

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Shannon information entropies in position and momentum spaces and their sum are calculated as functions of $Z(2 \leq Z \leq 54)$ in atoms. Roothaan-Hartree-Fock electron wave functions are used. The universal property $S = a + b \ln Z$ is verified. In addition, we calculate the Kullback-Leibler relative entropy, the Jensen-Shannon divergence, Onicescu's information energy, and a complexity measure recently proposed. Shell effects at closed-shell atoms are observed. The complexity measure shows local minima at the closed-shell atoms indicating that for the above atoms complexity decreases with respect to neighboring atoms. It is seen that complexity fluctuates around an average value, indicating that the atom cannot grow in complexity as Z increases. Onicescu's information energy is correlated with the ionization potential. Kullback distance and Jensen-Shannon distance are employed to compare Roothaan-Hartree-Fock density distributions with other densities of previous works. © 2005 American Institute of Physics. [DOI: 10.1063/1.2121610]

I. INTRODUCTION

Information-theoretic properties are used in recent years for the study of quantum mechanical systems.^{1–18} In the present work we carry out a systematic study of Shannon information S , Onicescu information energy E , order parameter Ω , and complexity $\Gamma_{\alpha,\beta}$ in atoms with $Z=2-54$. In a previous work⁵ we proposed a universal property of S for density distributions of nuclei, electrons in atoms, and valence electrons in atomic clusters. This property has the form

$$S = a + b \ln N, \quad (1)$$

where N is the number of particles of the system and the parameters a and b depend on the system under consideration. Recently⁴ we have obtained the same form for systems of correlated bosons in a trap. In the present paper we employ very accurate spin-independent atomic wave functions obtained by Bunge *et al.*,¹⁹ by applying the Roothaan-Hartree-Fock method (RHF) to calculate analytical self-consistent-field atomic wave functions. Thus we verify the above relation for atoms, which was obtained in the past^{7,8} employing another set of electron wave functions. Thus we obtain a framework to be used as a basis for further work on information-theoretic properties of atoms. An interesting question is the effect of the electron-electron correlations on S and relation(1), which could be answered in future research.

We focus our attention on the problem of similarity index based on the concept of an information distance. The concept of similarity is an old one and related to the distinction between two or more objects.²⁰ Specifically, in our paper we study two candidates connected with the concept of similarity or information distance. The first one is the Kullback-Leibler relative entropy K (and also the symmetrized Kull-

back distance SK) and the second one is the Jensen-Shannon divergence J . Thus we are able to compare various density distributions obtained using various models. It turns out that S , SK , and J measures are useful for this purpose.

The framework developed in the present work for S together with S_{\max} obtained previously⁸ with rigorous inequalities holding for S , S_r , and S_k enables us to calculate the so-called complexity measure $\Gamma_{\alpha,\beta}$ introduced in Ref. 21. Our procedure leads to the interesting result that complexity as function of Z shows shell effects at closed-shell atoms, i.e., for the above atoms complexity decreases with respect to neighboring atoms.

The outline of our paper is the following: In Sec. II we describe measures of information content of a quantum system together with information distances of two probability distributions and a complexity measure recently proposed. In Sec. III we present our formalism, while Sec. IV contains our numerical results and discussion. Section V is a summary of the paper. Finally Sec. VI contains our comments on the importance of our results on complexity.

II. MEASURES OF INFORMATION CONTENT AND INFORMATION DISTANCES

The Shannon information entropy²² S_r in position space may be defined as

$$S_r = - \int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r}, \quad (2)$$

where $\rho(\mathbf{r})$ is the electron density distribution normalized to unity. The corresponding information entropy S_k in the momentum-space representation is

$$S_k = - \int n(\mathbf{k}) \ln n(\mathbf{k}) d\mathbf{k}, \quad (3)$$

where $n(\mathbf{k})$ is the momentum density distribution normalized to unity studied in Refs. 7 and 23–25. In position space S_r determines the extent of electron delocalization, since it

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tends to a maximum as the distribution flattens out and deviates from this maximum when structure is introduced in $\rho(\mathbf{r})$. In momentum space a maximum in S_k corresponds to a delocalized distribution in momentum space.²⁶ The total information entropy is given by

$$S = S_r + S_k, \quad (4)$$

where S , S_r , and S_k obey the following rigorous inequalities:⁸

$$S_{r \min} \leq S_r \leq S_{r \max}, \quad (5)$$

$$S_{k \min} \leq S_k \leq S_{k \max}, \quad (6)$$

$$S_{\min} \leq S \leq S_{\max}. \quad (7)$$

The lower and the upper limits can be written, for density distributions normalized to one,

$$S_{r \min} = \frac{3}{2}(1 + \ln \pi) - \frac{3}{2} \ln \left(\frac{4}{3} T \right),$$

$$S_{r \max} = \frac{3}{2}(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{2}{3} \langle r^2 \rangle \right), \quad (8)$$

$$S_{k \min} = \frac{3}{2}(1 + \ln \pi) - \frac{3}{2} \ln \left(\frac{2}{3} \langle r^2 \rangle \right), \quad (9)$$

$$S_{k \max} = \frac{3}{2}(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{4}{3} T \right),$$

$$S_{\min} = 3(1 + \ln \pi), \quad (10)$$

$$S_{\max} = 3(1 + \ln \pi) + \frac{3}{2} \ln \left(\frac{8}{9} \langle r^2 \rangle T \right),$$

where $\langle r^2 \rangle$ is the mean-square radius and T is the kinetic energy.

Another measure of the information content of a quantum system is the concept of information energy E introduced by Onicescu in an attempt to define a finer measure of dispersion distribution than that of Shannon information entropy.²⁷ For a discrete probability distribution (p_1, p_2, \dots, p_k) , E is defined as

$$E = \sum_{i=1}^k p_i^2, \quad (11)$$

which is extended for a continuous density distribution $\rho(x)$ as

$$E = \int \rho^2(x) dx. \quad (12)$$

So far, only the mathematical aspects of the concept have been developed, while the physical aspects have been ignored. A recent study of E for atomic nuclei has been carried out in Ref. 28.

The meaning of (12) can be seen by the following simple argument: For a Gaussian distribution of mean value μ , standard deviation σ , and normalized density

$$\rho(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right], \quad (13)$$

relation (12) gives

$$E = \frac{1}{2\pi\sigma^2} \int_{-\infty}^{\infty} \exp \left[-\frac{(x-\mu)^2}{\sigma^2} \right] dx = \frac{1}{2\sigma\sqrt{\pi}}. \quad (14)$$

E is maximum if one of the p_i 's equals 1 and all the others are equal to zero, i.e., $E_{\max} = 1$, while E is minimum when $p_1 = p_2 = \dots = p_k = 1/k$, hence $E_{\min} = 1/k$ (total disorder). The fact that E becomes minimum for equal probabilities (total disorder), by analogy with thermodynamics, it has been called information energy, although it does not have the dimension of energy.²⁹

It is seen from (14) that the greater the information energy, the more concentrated is the probability distribution, while the information content decreases. Thus one can define a measure of information content analogous to Shannon's S by the relation

$$O = \frac{1}{E}. \quad (15)$$

Relation (12) is extended for a three-dimensional spherically symmetric density distribution $\rho(r)$,

$$E_r = \int_0^{\infty} \rho^2(r) 4\pi r^2 dr, \quad (16)$$

$$E_k = \int_0^{\infty} n^2(k) 4\pi k^2 dk,$$

in position and momentum spaces, respectively, where $n(k)$ is the corresponding density distribution in momentum space.

E_r has the dimension of inverse volume, while E_k of volume. Thus the product $E_r E_k$ is dimensionless and can serve as a measure of concentration (or information content) of a quantum system. It is also seen from (14) that E increases as σ decreases (or concentration increases) and Shannon's information entropy (or uncertainty) S decreases. Thus S and E are reciprocal. In order to be able to compare them, we redefine the quantity O by

$$O = \frac{1}{E_r E_k}, \quad (17)$$

as a measure of the information content of a quantum system in both position and momentum spaces.

Landsberg³⁰ defined the order parameter Ω (or disorder Δ) as

$$\Omega = 1 - \Delta = 1 - \frac{S}{S_{\max}}, \quad (18)$$

where S is the information entropy (actual) of the system and S_{\max} the maximum entropy accessible to the system. Thus the concepts of entropy and disorder are decoupled, and it is possible for the entropy and order to increase simultaneously. It is noted that $\Omega = 1$ corresponds to perfect order and pre-

dictability, while $\Omega=0$ means complete disorder and randomness.

In Ref. 21 a measure of complexity $\Gamma_{\alpha,\beta}$ was defined of the form

$$\Gamma_{\alpha,\beta} = \Delta^\alpha \Omega^\beta = \Delta^\alpha (1 - \Delta)^\beta = \Omega^\beta (1 - \Omega)^\alpha, \quad (19)$$

which is called the “simple complexity of disorder strength α and order strength β .” When $\beta=0$ and $\alpha>0$ “complexity” is an increasing function of “disorder,” and we have a measure of category I (Fig. 1 of Ref. 21). When $\alpha=0$ and $\beta>0$, complexity is an increasing function of “order” and we have a measure of category III. When both α and β are nonvanishing and positive ($\alpha>0, \beta>0$), complexity vanishes at zero disorder and zero order and has a maximum of

$$(\Gamma_{\alpha,\beta})_{\max} = \alpha^\alpha \beta^\beta / (\alpha + \beta)^{(\alpha+\beta)} \quad (20)$$

at $\Delta = \alpha / (\alpha + \beta)$ and $\Omega = \beta / (\alpha + \beta)$. This is complexity of category II according to Ref. 21.

Several cases for both α and β non-negative are shown in Fig. 2 of Ref. 21 where $\Gamma_{\alpha,\beta}$ is plotted as a function of Δ . In the present work we can find $\Delta = S/S_{\max}$ or $\Omega = 1 - \Delta$ as a function of Z . Thus we are able to plot the dependence of $\Gamma_{\alpha,\beta}$ on the atomic number Z .

The Kullback-Leibler relative information entropy K (Ref. 31) for any probability distributions $p_i^{(1)}, p_i^{(2)}$ is defined by

$$K(p_i^{(1)}, p_i^{(2)}) = \sum_i p_i^{(1)} \ln \frac{p_i^{(1)}}{p_i^{(2)}}, \quad (21)$$

which for continuous probability distributions is defined as

$$K = \int \rho^{(1)}(x) \ln \frac{\rho^{(1)}(x)}{\rho^{(2)}(x)} dx. \quad (22)$$

(21) and (22) can be easily extended for three-dimensional systems. K measures the difference of distance of $\rho_i^{(1)}$ from the reference (or *a priori*) distribution $\rho_i^{(2)}$.

It satisfies $K \geq 0$ for any distributions $\rho_i^{(1)}, \rho_i^{(2)}$. It is a measure which quantifies the distinguishability (or distance) of $\rho_i^{(1)}$ from $\rho_i^{(2)}$, employing a well-known concept in standard information theory. In other words it describes how close is $\rho_i^{(1)}$ to $\rho_i^{(2)}$ by carrying out observations or coin tossing, namely, trials L (in the sense described in Ref. 32).

However, the distance K does not satisfy the triangle inequality and in addition is (i) not symmetric, (ii) unbounded, and (iii) not always well defined.³² To avoid these difficulties Rao,³³ and Lin³⁴ introduced a symmetrized version of K ,³² the Jensen-Shannon divergence,

$$J(\rho^{(1)}, \rho^{(2)}) = H\left(\frac{\rho^{(1)} + \rho^{(2)}}{2}\right) - \frac{1}{2}H(\rho^{(1)}) - \frac{1}{2}H(\rho^{(2)}), \quad (23)$$

where $H(\rho) = -\sum_i \rho_i \ln \rho_i$ stands for Shannon's entropy. J is minimum for $\rho^{(1)} = \rho^{(2)}$ and maximum when $\rho^{(1)}$ and $\rho^{(2)}$ are two distinct distributions, when $J = \ln 2$. In our case J can be easily generalized for continuous density distributions. For J minimum the two states represented by $\rho^{(1)}$ and $\rho^{(2)}$ are completely indistinguishable, while for J maximum they are completely distinguishable. The amount of distinguishability can be further examined by using Wooters' criterion.³² Two

probability distributions $\rho^{(1)}$ and $\rho^{(2)}$ are distinguishable after L trials ($L \rightarrow \infty$) if and only if $(J(\rho^{(1)}, \rho^{(2)}))^{1/2} > 1/\sqrt{2L}$.

The present work is a first step to examine the problem of comparison of probability distributions (for atoms and various models) which is an area well developed in statistics, known as information geometry.³³

III. FORMALISM

The key quantities in our work are the density distribution $\rho(\mathbf{r})$ and the momentum distribution $n(\mathbf{k})$. In general the calculation of $\rho(\mathbf{r})$ and $n(\mathbf{k})$ presuppose the knowledge of the one-body density matrix $\rho(\mathbf{r}_1, \mathbf{r}'_1)$ which is defined as

$$\begin{aligned} \rho(\mathbf{r}_1, \mathbf{r}'_1) &= \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) \Psi(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_Z) d\mathbf{r}_2 \dots d\mathbf{r}_Z, \end{aligned} \quad (24)$$

where $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$ is the wave function that describes the system under consideration (in the present work the atom). $\rho(\mathbf{r})$ is just the diagonal part of the $\rho(\mathbf{r}_1, \mathbf{r}'_1)$, i.e.,

$$\rho(\mathbf{r}_1) = \rho(\mathbf{r}_1, \mathbf{r}'_1)|_{\mathbf{r}_1=\mathbf{r}'_1},$$

while $n(\mathbf{k})$ is the Fourier transform of the one-body density matrix, i.e.,

$$n(\mathbf{k}) = \int \rho(\mathbf{r}_1, \mathbf{r}'_1) \exp[-i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}'_1)] d\mathbf{r}'_1 d\mathbf{r}_1.$$

In the framework of the Hartree-Fock approximation, which is applied in the present work, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$ has the well-known form of a Slater determinant (electrons of the atoms consist a system which obeys the Fermi-Dirac statistics). It is easy to prove that in this case $\rho(\mathbf{r}_1, \mathbf{r}'_1)$ takes the following simple form:

$$\rho(\mathbf{r}_1, \mathbf{r}'_1) = \sum_i \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}'_1), \quad (25)$$

where $\phi_i(\mathbf{r})$ is the single-particle wave function describing the electrons in an atom. The index i runs over all Z single-particle states. Now $\rho(\mathbf{r})$ and $n(\mathbf{k})$ are written as

$$\rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}), \quad (26)$$

$$n(\mathbf{k}) = \sum_i \tilde{\phi}_i^*(\mathbf{k}) \tilde{\phi}_i(\mathbf{k}), \quad (27)$$

where

$$\tilde{\phi}_i(\mathbf{k}) = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \phi_i(\mathbf{r}) d\mathbf{r}. \quad (28)$$

The wave functions $\phi_i(\mathbf{r})$ and $\tilde{\phi}_i(\mathbf{k})$ are decomposed in the usual form,

$$\phi_i(\mathbf{r}) = \phi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\Omega_r)$$

and

$$\tilde{\phi}_i(\mathbf{k}) = \tilde{\phi}_{nlm}(\mathbf{k}) = \tilde{R}_{nl}(k) Y_{lm}(\Omega_k).$$

The radial momentum wave function $\tilde{R}_{nl}(k)$ is related to the radial wave function in coordinate space through

$$\tilde{R}_{nl}(k) = 4\pi \int_0^\infty r^2 R_{nl}(r) j_l(kr) dr, \quad (29)$$

where $j_l(kr)$ is a spherical Bessel function.

In the present work we consider very accurate spin-independent atomic wave functions obtained by Bunge *et al.*¹⁹ by applying the Roothaan-Hartree-Fock method to calculate analytical self-consistent-field atomic wave function. In this approach the radial atomic orbitals R_{nl} are expanded as a finite superposition of primitive radial functions,

$$R_{nl}(r) = \sum_j C_{jnl} S_{jl}(r), \quad (30)$$

where the normalized primitive basis $S_{jl}(r)$ is taken as a Slater-type orbital set,

$$S_{jl}(r) = N_{jl} r^{n_{jl}-1} e^{-Z_{jl}r}, \quad (31)$$

where the normalization factor N_{jl} is given by

$$N_{jl} = (2Z_{jl})^{(n_{jl}+1/2)} / [(2n_{jl})!]^{1/2} \quad (32)$$

and n_{jl} is the principal quantum number, Z_{jl} is the orbital exponent, and l is the azimuthal quantum number.

In general $\rho(\mathbf{r})$ is not spherically symmetric and depends in addition on the angle θ . In the present work we consider $\rho(\mathbf{r})$ averaged spherically [the same holds also for $n(\mathbf{k})$].

The Shannon information entropy in position space, momentum space, and in total are given in Eqs. (2)–(4), respectively.

Another quantity which gives information about the localization (delocalization) of the atomic systems is the local Shannon entropy defined (in position and momentum spaces, respectively) as follows:

$$S_r^{\text{loc}}(\mathbf{r}) = -4\pi r^2 \rho(\mathbf{r}) \ln \rho(\mathbf{r}), \quad (33)$$

$$S_k^{\text{loc}}(\mathbf{k}) = -4\pi k^2 n(\mathbf{k}) \ln n(\mathbf{k}).$$

In order to formulate the concept of the similarity or information distance between two atomic systems with $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ the corresponding density distributions, the Kullback-Leibler relative entropy is defined as

$$K = \int \rho_A(\mathbf{r}) \ln \frac{\rho_A(\mathbf{r})}{\rho_B(\mathbf{r})} d\mathbf{r}, \quad (34)$$

which may be interpreted as a measure of deviation of $\rho_A(\mathbf{r})$ from $\rho_B(\mathbf{r})$. The corresponding symmetrized Kullback distance SK is

$$SK = \int \rho_A(\mathbf{r}) \ln \frac{\rho_A(\mathbf{r})}{\rho_B(\mathbf{r})} d\mathbf{r} + \int \rho_B(\mathbf{r}) \ln \frac{\rho_B(\mathbf{r})}{\rho_A(\mathbf{r})} d\mathbf{r}. \quad (35)$$

The physical meaning of the Kullback distance is very clear. K is equal to zero for two identical species and approaches infinity as the difference between $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ increases. K and SK in momentum space are defined using $n_A(\mathbf{k})$ and $n_B(\mathbf{k})$ in the same way.

The Jensen-Shannon divergence entropy is defined as follows:

$$J = - \int \left(\frac{\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})}{2} \right) \ln \left(\frac{\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})}{2} \right) d\mathbf{r} + \frac{1}{2} \int \rho_A(\mathbf{r}) \ln \rho_A(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho_B(\mathbf{r}) \ln \rho_B(\mathbf{r}) d\mathbf{r}. \quad (36)$$

The physical meaning of J is similar to SK , while the definition in momentum space is defined using $n(\mathbf{k})$ in the same way.

Another aspect of our work is to compare RHF densities with those of the work³⁵ in the framework of SK and J . More specifically we compare the density distributions of the electrons originating from the paper of Bunge *et al.*¹⁹ (used in the present work) with the phenomenological one of Sagar *et al.*³⁵ who employed the phenomenological form

$$\rho(r) = \frac{(2I_1)^{3/2}}{\pi} e^{-2(2I_1)^{1/2}r}, \quad (37)$$

where I_1 is the first ionization potential of the system. We also compare RHF densities with those of the well-known Thomas-Fermi model. For the density distribution we use the simple form obtained by Sommerfeld³⁶ where

$$\rho(r) = C_{\text{norm}} \frac{2^{3/2} Z^{3/2}}{3\pi^2 r^{3/2}} \left(1 + \left(\frac{r}{\mu\alpha} \right)^d \right)^{-(3/2)c}, \quad (38)$$

where $\alpha = 12^{2/3}$, $d = 0.772$, $c = 3.886$, and $\mu = 0.885341/Z^{1/3}$. The normalization constant C_{norm} is calculated from the normalization condition $\int \rho(\mathbf{r}) d\mathbf{r} = 1$.

IV. NUMERICAL RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b) we plot the Shannon information entropy both in coordinate space (S_r) and momentum space (S_k) as functions of the electron number Z . In S_r coexist an average increasing behavior and also an obvious shell effect structure around fully filled shells, such as He, Ne, Ar, and Kr, where there are minima of the curve $S_r(Z)$. The physical meaning of that behavior is that $\rho(r)$ for these atoms is the most compact one when compared to the neighboring atoms. The values of S_k [Fig. 1(b)] show a monotonic increase with Z . However, there is also in the behavior of S_k a local shell effect.

In Fig. 2(a) we plot the total Shannon information entropy S . S is a strictly monotonic increasing function of Z with only two exceptions for Ni and Pd. These exceptions are due to the fact that S_r and S_k depend on the arrangement of the electrons in shells. There is a delicate balance between S_r and S_k resulting in the general rule that $S = S_r + S_k$ is a monotonic increasing function of Z except in Ni and Pd where the electron arrangement in shells is such that the decrease of the value of S_r cannot be balanced by a corresponding increase of S_k . Thus the monotonicity of S is slightly violated. A shell effect is also obvious in the behavior of S , i.e., minima at closed shells. Figure 2(b) illustrates the trend of S as a function of $\ln Z$. The best linear fit is also plotted in the same figure where $S = 6.257 + 1.069 \ln Z$. It is noted that this result is not new but has been already ob-

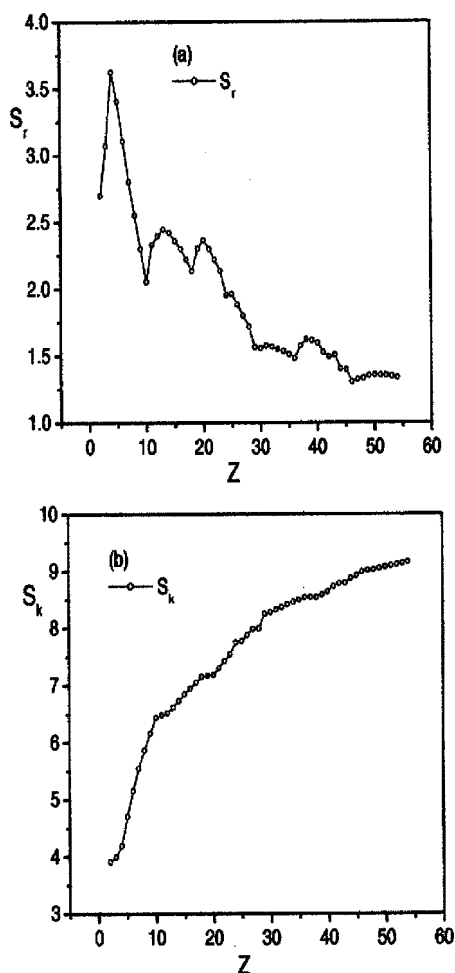


FIG. 1. Shannon information entropy (a) in coordinate space S_r and (b) in momentum space S_k , as a function of the electron number Z .

tained using other wave functions in Refs. 7 and 8. In the present work we verify this result with RHF electron wave functions¹⁹ and we employ this framework for new calculations.

In Figs. 3(a)–3(d) we plot the complexity measure $\Gamma_{\alpha,\beta}$ in atoms for various values of parameters α and β . It is seen that for all sets of α and β , $\Gamma_{\alpha,\beta}$ shows qualitatively the same trend as a function of Z , i.e., it fluctuates around an average value and shows local minima for atoms with closed shells. These results compare favorably with intuition, i.e., complexity is less at closed shells which can be considered more compact than neighboring nuclei and consequently less complex. It is noted that this result comes from a procedure which is not trivial, i.e., first we calculate $\rho(\mathbf{r})$ and $n(\mathbf{k})$, second we find $S=S_r+S_k$ from the Shannon definition and S_{\max} employing rigorous inequalities, and third we obtain the complexity measure introduced in Ref. 21.

Figure 4(a) displays the values of the Onicescu information content O versus Z . The first three maxima correspond to the fully closed shells (He, Ne, and Ar) where in the case of the next closed shell (Kr) a local maximum exists. In Fig. 4(b) we plot in the same footing the Onicescu information content O and the ionization potential I_1 . It is indicated that O and I_1 are correlated in the sense that there is a similarity in the trend of the values of O and I_1 as functions of Z . This

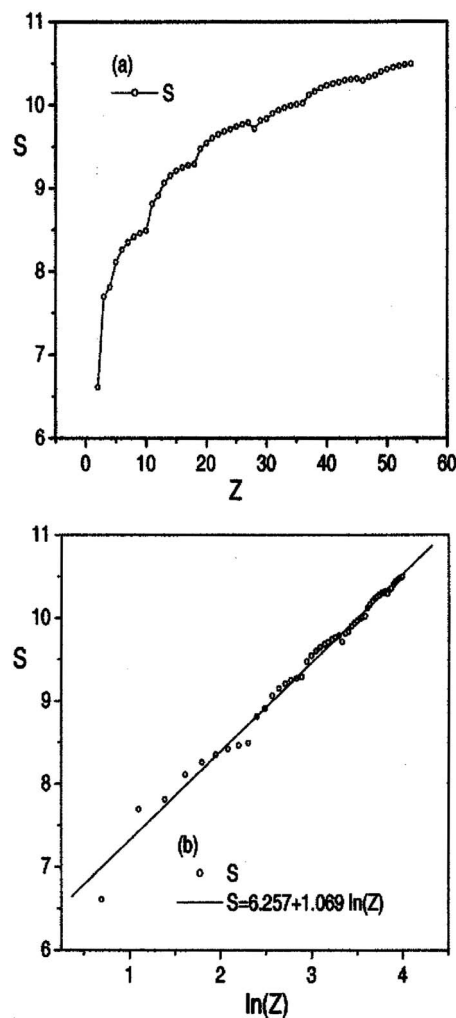


FIG. 2. (a) Total Shannon information entropy S . (b) S as a function of $\ln Z$ and linear fit.

similarity is more obvious in regions of small Z where linear relations $O=a+b \ln Z$ can be extracted for regions Li–Ne and Na–Ar. However, it seems that, there is no universal relation between them. There are many entropic measures of spread of probability densities, e.g., S , E , etc., but researchers prefer S because of its unique properties, while E was introduced by Onicescu as a sensitive measure of information. However, S and E are different functionals of the density and their relation is difficult to find.

In Fig. 5(a) we display the symmetrized Kullback distance between the RHF density distributions and the approximate one given by relation (37). It is obvious that the symmetrized Kullback distance SK becomes minimum in the case of the fully closed-shell atoms. This physically means that the approximate $\rho(\mathbf{r})$ (37) works better in closed-shell atoms than the open shells. In addition there is an increasing trend with Z . That means that in general $\rho(\mathbf{r})$ (37) fails to describe the structure of heavier atoms. Figure 5(b) displays the Jensen-Shannon divergence entropy J as a function of Z . The behavior is almost similar to SK and the comments are the same. In Fig. 5(c) we display J vs SK . There is a linear relation of the two information distances.

In Fig. 6(a) we display SK as an information distance

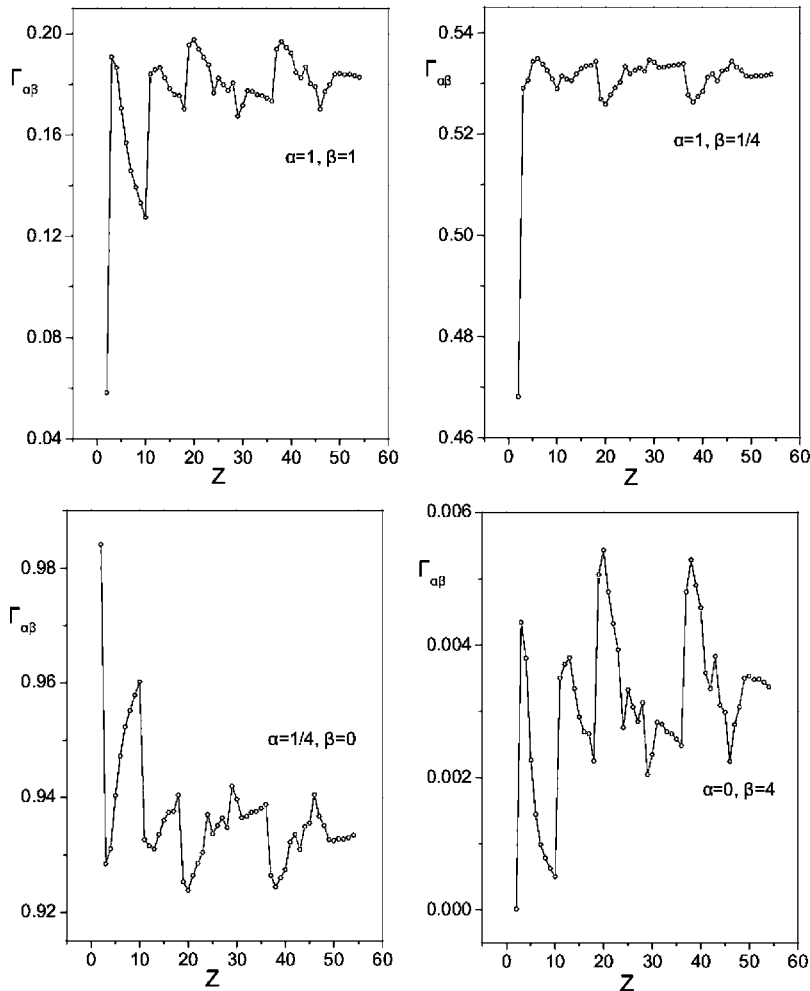


FIG. 3. Complexity measure $\Gamma_{\alpha\beta}$ for various sets of parameters α and β as a function of Z .

between the RHF density distribution and the Thomas-Fermi density distribution given by relation (38). It is seen that the values of SK decrease with Z . This is expected because the Thomas-Fermi approximation works well in heavier atoms. So the two distributions are closer in heavier atoms than in the light ones. The local maxima of the values of SK correspond to the closed-shell atoms. This deviation is due to the absence of shell effect character of the Thomas-Fermi distribution compared to the realistic RHF density distribution. Figure 6(b) displays J as a function of Z . The behavior is almost similar to SK . In Fig. 6(c) we display J vs SK .

The local Shannon entropy (33) both in position and momentum spaces is presented in Fig. 7 for various atoms. As it is pointed out in Ref. 37 in systems with density $\rho(\mathbf{r}) > 1$ near the nucleus the local Shannon entropy in position space S_r^{loc} will be negative, thus the contribution to the integral from this region will serve to lower its value (localization) while in the region where $\rho(\mathbf{r}) < 1$, such as the valence, contribution to the Shannon entropy in position space will be positive which leads to delocalization. In contrast the local Shannon entropy in momentum space S_k^{loc} is always positive. This is due to the fact that $n(\mathbf{k}) < 1$ for all k . So, there is no negative contribution to the Shannon entropy in momentum space.

It is worth, discussing the behavior of the momentum distribution and as a consequence the local Shannon entropy,

to mention that the precise knowledge of the electron momentum distribution is important for atoms used as a dark matter or neutrino detector. In such a kind of experiment the single-particle wave function in momentum space or in general the momentum density of the electrons are the main ingredients of the relative cross sections. The trend (localization, delocalization, etc.) of the electron wave function or momentum distribution affects considerably the values of the cross sections, especially in experiments where the production of electrons in neutralino-nucleus or neutrino-nucleus collisions are investigated.^{38–40}

Finally in Table I we tabulate for the sake of reference the quantities S_r , S_k , S , S_{max} , Ω , and O for each atom as functions of Z . We include the results for Hydrogen which are known exactly, i.e., $S_r = 3 + \ln \pi$ and $S_k = \ln 32\pi^2 - 10/3$.

V. SUMMARY

In previous works the universal relation $S = a + b \ln N$ was proposed for the information entropy S as function of the number of particles N in atoms, nuclei, atomic clusters, and correlated bosons in a trap, i.e., systems of various sizes, with various interactions, obeying different statistics (fermions and bosons). In this paper we verify the above relation employing RHF electron density distributions for atoms. Thus we construct a basis in order to study some information-theoretic properties of atoms. Specifically, we

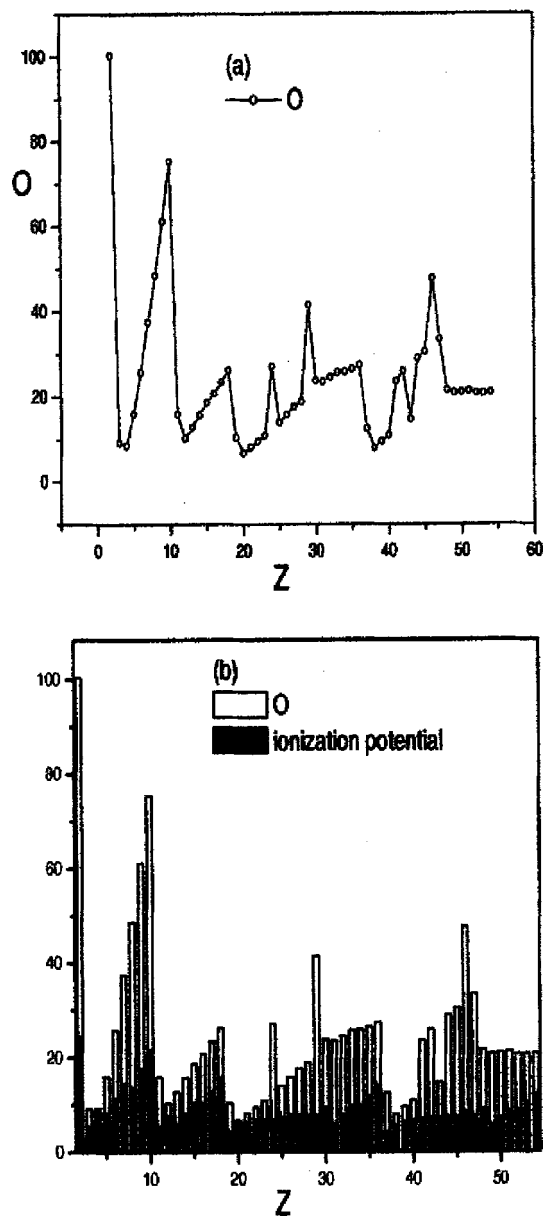


FIG. 4. (a) Onicescu information content O vs Z , (b) Onicescu information content O , and ionization potential I_1 (in Hartree units) vs Z .

calculate the symmetrized Kullback-Leibler relative entropy SK and the Jensen-Shannon divergence J which serve as measures of information distance of probability distributions and are useful to compare electron distributions according to various models. Two examples are given. We compare RHF density distributions first with an asymptotic density depending on the ionization potential and second with the well-known Thomas-Fermi approximation.

We also obtain Onicescu's information energy E and its corresponding information measure, which correlates with the ionization potential. Finally, we calculate a recently proposed complexity measure $\Gamma_{\alpha,\beta}$ inspired by Landsberg's order parameter Ω . It turns out that the function $\Gamma_{\alpha,\beta}(Z)$ shows the interesting feature that for closed-shell atoms it is smaller than neighboring ones. This indicates that closed-shell atoms are less complex than neighboring ones, which compares favorably with expectations according to intuition.

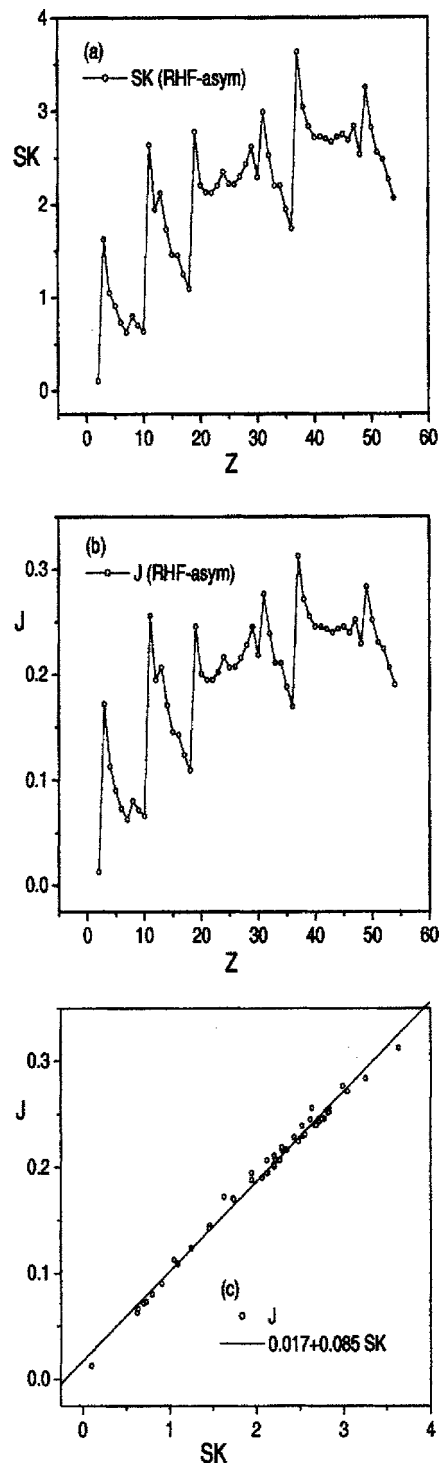


FIG. 5. (a) Symmetrized Kullback distance between the RHF density distribution and the approximate (asymptotic) one [Eq. (37)]. (b) Corresponding Jensen-Shannon divergence entropy vs Z . (c) Jensen-Shannon divergence vs the symmetrized Kullback distance.

VI. FINAL COMMENTS

There is a long debate in the literature on order, disorder, complexity, and organization for physical, biological, and other systems. A generally accepted quantitative definition of complexity does not exist so far. More work has been carried out in classical systems and much less in quantum ones. Our aim is to contribute in this debate examining complexity in atoms (for the first time to our knowledge) adopting a par-

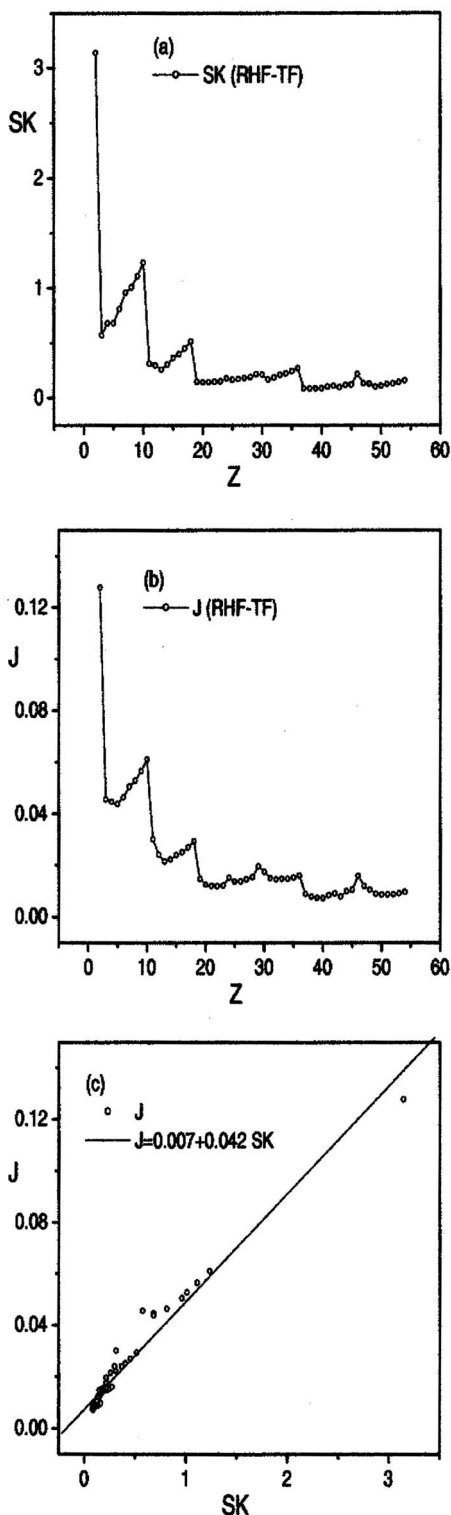


FIG. 6. (a) Symmetrized Kullback distance between the RHF density distribution and the Thomas-Fermi density distribution as functions of Z . (b) Corresponding Jensen-Shannon divergence entropy vs Z . (c) Jensen-Shannon divergence vs the symmetrized Kullback distance.

ticular definition of complexity measure according to Shiner *et al.*²¹ The reason for our choice is that we can easily calculate it for atoms (and we intend to calculate it for other quantum systems as well), because our previous experience with information entropy facilitates this. More work is needed in the future by using the so called statistical measure of complexity of Lopez-Ruiz *et al.*⁴¹

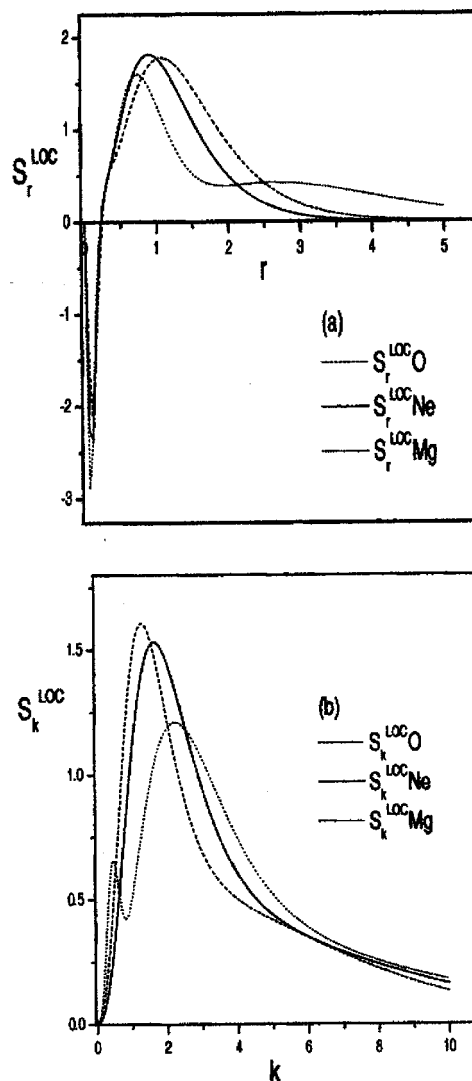


FIG. 7. Local Shannon information entropy (a) in coordinate space S_r^{loc} and (b) in momentum space S_k^{loc} , as a function of the electron number Z .

In Ref. 42 the authors studied disorder and complexity in an ideal Fermi gas of electrons. They observed that for a small number of electrons Landsberg's order parameter Ω is small, while Ω increases as one pumps electrons into the system and the energy levels fill up. This result is in a way counterintuitive and indicates that as particles are added in a quantum-mechanical system, the system becomes more ordered. This result was further corroborated in Ref. 43 by calculating Ω as function of the number of particles N for realistic quantum systems, i.e., atomic nuclei and atomic clusters. In Ref. 4 $\Omega(N)$ was obtained for bosonic systems as well (correlated atoms in a trap). All cases show the same trend for $\Omega(N)$, i.e., Ω is an increasing function of N . However, if one is interested how complex (or organized) is a system, the information entropy S (sometimes used as a measure of disorder) or the order parameter Ω (or disorder $\Delta = 1 - \Omega$) are not suitable measures of complexity or organization. We note that these terms are interrelated from a semantic point of view. $\Gamma_{\alpha,\beta}$ has the advantage of being a convex measure of order (or disorder), i.e., it vanishes for highly

TABLE I. The values of various quantities in our systematic study.

Z	Atom	S_r	S_k	S	S_{\max}	Ω	O
1	H	4.144 73	2.421 86	6.566 59	7.9054	0.211 13	120.267 00
2	He	2.698 51	3.913 42	6.611 93	7.0493	0.062 04	100.361 00
3	Li	3.071 44	3.996 82	7.698 26	10.3578	0.256 77	9.157 13
4	Be	3.623 86	4.190 19	7.814 05	10.3950	0.248 29	8.454 34
5	B	3.405 45	4.705 90	8.111 35	10.3738	0.218 10	15.965 30
6	C	3.106 02	5.156 58	8.262 60	10.2624	0.194 92	25.712 10
7	N	2.801 69	5.549 34	8.351 03	10.1520	0.177 40	37.432 00
8	O	2.550 54	5.867 37	8.417 91	10.1113	0.167 47	48.483 40
9	F	2.298 83	6.163 33	8.462 15	10.0533	0.158 27	61.145 00
10	Ne	2.055 14	6.437 07	8.492 21	9.9908	0.149 99	75.244 70
11	Na	2.330 09	6.483 10	8.813 19	11.6463	0.243 26	15.869 00
12	Mg	2.395 40	6.514 40	8.910 38	11.8296	0.246 77	10.194 80
13	Al	2.445 69	6.619 28	9.064 97	12.0615	0.248 43	12.765 90
14	Si	2.419 14	6.733 80	9.152 94	12.0500	0.240 42	15.636 00
15	P	2.359 03	6.848 65	9.207 67	11.9954	0.232 40	18.624 90
16	S	2.299 32	6.949 39	9.248 71	11.9769	0.227 79	20.803 80
17	Cl	2.221 74	7.052 43	9.274 18	11.9315	0.227 16	23.368 30
18	Ar	2.133 83	7.155 41	9.289 24	11.8758	0.217 80	26.210 00
19	K	2.301 77	7.172 42	9.474 19	12.9220	0.266 82	10.375 40
20	Ca	2.363 09	7.182 50	9.543 34	13.0994	0.271 47	6.669 98
21	Sc	2.298 14	7.303 29	9.601 43	13.0334	0.263 32	8.120 90
22	Ti	2.218 55	7.426 93	9.645 48	12.9721	0.256 44	9.487 93
23	V	2.135 12	7.547 17	9.682 29	12.9160	0.250 36	10.915 40
24	Cr	1.955 89	7.751 35	9.707 24	12.5913	0.229 05	27.029 60
25	Mn	1.962 57	7.776 88	9.739 45	12.8162	0.240 07	13.942 20
26	Fe	1.882 13	7.882 65	9.764 78	12.7697	0.235 32	15.780 50
27	Co	1.800 01	7.986 12	9.786 13	12.7264	0.231 04	17.652 10
28	Ni	1.718 26	7.992 94	9.711 20	12.7198	0.236 53	18.836 70
29	Cu	1.563 25	8.250 76	9.814 01	12.4646	0.212 65	41.475 10
30	Zn	1.556 25	8.278 67	9.834 93	12.6106	0.220 11	23.743 00
31	Ga	1.574 44	8.323 88	9.898 32	12.8676	0.230 76	23.527 80
32	Ge	1.567 46	8.371 50	9.938 96	12.9098	0.230 12	24.532 50
33	As	1.549 80	8.418 28	9.968 08	12.9082	0.227 77	25.682 80
34	Se	1.534 25	8.458 51	9.992 76	12.9298	0.227 15	25.812 20
35	Br	1.510 64	8.499 58	10.010 20	12.9230	0.225 40	26.440 50
36	Kr	1.481 46	8.540 92	10.022 40	12.9026	0.223 23	27.337 00
37	Rb	1.576 26	8.544 30	10.120 60	13.7376	0.263 29	12.459 70
38	Sr	1.621 44	8.542 28	10.163 70	13.9159	0.269 63	7.918 95
39	Y	1.614 38	8.590 46	10.204 80	13.8772	0.264 63	9.571 34
40	Zr	1.594 62	8.640 54	10.235 20	13.8304	0.259 95	10.940 10
41	Nb	1.524 86	8.732 36	10.257 20	13.5780	0.244 57	23.598 20
42	Mo	1.491 17	8.782 33	10.273 50	13.5247	0.240 39	25.895 50
43	Tc	1.507 62	8.790 74	10.298 40	13.7087	0.248 77	14.737 30
44	Ru	1.403 05	8.875 61	10.306 10	13.4876	0.235 88	28.971 20
45	Rh	1.396 35	8.922 06	10.318 40	13.4670	0.233 80	30.466 70
46	Pd	1.304 82	8.989 08	10.293 90	13.1570	0.217 61	47.724 20
47	Ag	1.323 46	9.013 91	10.337 40	13.4264	0.158 16	33.399 90
48	Cd	1.331 32	9.026 13	10.357 40	13.5464	0.235 41	21.517 40
49	In	1.351 91	9.048 92	10.400 80	13.7432	0.243 20	20.891 60
50	Sn	1.357 01	9.072 95	10.430 00	13.7921	0.243 77	21.007 20
51	Sb	1.354 83	9.096 83	10.451 70	13.8039	0.242 85	21.248 80
52	Te	1.353 45	9.117 19	10.470 60	13.8313	0.242 97	20.804 00
53	I	1.346 58	9.138 32	10.484 90	13.8349	0.242 14	20.742 70
54	Xe	1.335 82	9.160 22	10.496 00	13.8264	0.240 87	20.893 80

ordered and disordered systems. In other words, it satisfies the “one-hump” criterion for statistical complexity measures. Thus $\Gamma_{\alpha,\beta}$ is obtained by multiplying a measure of “order” by a measure of “disorder.” A simple example is a perfect crys-

tal which has perfect order and an ideal gas with complete disorder. Both have zero complexity and fit well with the definition of $\Gamma_{\alpha,\beta}$.

In the present paper we find that complexity is less at

closed-shell atoms. This satisfies our intuition, at least does not contradict common sense and indicates that our procedure from electron densities to information entropy and maximum entropy to complexity measure $\Gamma_{\alpha,\beta}$ is reasonable. The fact that $\Gamma_{\alpha,\beta}$ fluctuates around an average value is new and interesting, because it shows that complexity of atoms does not increase as the atomic number Z increases. In other words, as one pumps electrons into the atom, the atom has not the ability to grow in complexity. The question is open what happens if atoms form molecules, molecules form more complex systems, etc. We mention that the question whether physical or biological systems have the ability for organized complexity without the intervention of an external factor or agent is a hot subject in the community of scientists interested in complexity and can be extrapolated even in philosophical questions.

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