

Fisher–Shannon plane and statistical complexity of atoms

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Abstract

Using the Hartree–Fock non-relativistic wave functions in the position and momentum spaces, the *statistical* measure of complexity C , due to López-Ruiz, Mancini, and Calbet for the neutral atoms as well as their monpositive and mononegative ions with atomic number $Z = 1–54$ are reported. In C , given by the product of exponential power Shannon entropy and the average density, the latter is then replaced by the Fisher measure to obtain the Fisher–Shannon plane. Our numerical results suggest that in overall the Fisher–Shannon plane reproduces the trends given by C , with significantly *enhanced* sensitivity in the position, momentum and the product spaces in all neutral atoms and ions considered.

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1. Introduction

The study complexity of the physical and biological systems is a topic of great contemporary research interest. It is difficult to define a universal measure of complexity. The quantification of complexity of real systems have led to a variety of measures, e.g., the algorithmic complexity [1,2], the *statistical* measure of complexity C , defined by López-Ruiz, Mancini, Calbet (LMC) [3,4] and the *simple* two-parameter disorder–order derived measure of complexity $\Gamma_{\alpha,\beta}$ according to Shiner, Davison, Landsberg (SDL) [5,6]. However, it is only very recently [7,8], that the studies on the electronic structural complexity of *neutral* atoms using the non-relativistic Hartree–Fock (HF) wave functions [9] for atoms with atomic number $Z = 1–54$, have been reported. Both C and $\Gamma_{\alpha,\beta}$ measures are defined as the product of two global information measures. It is interesting to explore the possibility of a statistical complexity measure which is given as the product of a global and a local information measure. In this Letter, we have examined numerically such a quantity defined by the Fisher–Shannon information plane/product (FSIP) in the

position and momentum spaces for the set of neutral atoms *as well as* their monpositive and mononegative ions with atomic number $Z = 1–54$ using the non-relativistic Hartree–Fock (HF) wave functions [10,11]. These results are compared with the corresponding estimates of C in order to ascertain the suitability of the FSIP as a possible measure of complexity. We note here that the FSIP has been earlier proposed [12] as a tool for studying the electron correlation effects in the Hookean atoms and the helium iso-electronic series. To our knowledge, the present Letter examines, for the first time, the feasibility of FSIP as measuring the complexity of atoms. Our test set is specifically chosen to include the ionized states in addition to the neutral atoms since the *extent* of ionization defines the nature of chemical bonding.

2. LMC complexity measure

The LMC measure C is given by

$$C = H \cdot D, \quad (1)$$

where H denotes a measure of information and D represents the so-called disequilibrium or the distance from equilibrium (most probable state). The form [3] of C is designed such that

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it vanishes for the two extreme probability distributions corresponding to perfect order ($H = 0$) and maximum disorder ($D = 0$), respectively.

For H in Eq. (1), we have used the exponential power Shannon entropy in the position and momentum spaces [14,15]

$$J_r = \frac{1}{2\pi e} e^{2S_r/3}, \quad (2)$$

$$J_p = \frac{1}{2\pi e} e^{2S_p/3}, \quad (3)$$

where the Shannon information entropy in position and momentum spaces are defined as

$$S_r = - \int \rho(r) \ln \rho(r) d^3r, \quad (4)$$

$$S_p = - \int \gamma(p) \ln \gamma(p) d^3p. \quad (5)$$

In Eqs. (2)–(5), $\rho(r)$ and $\gamma(p)$ denote the spherically averaged electron density distributions in the position and momentum spaces *each* normalized to unity. The Shannon entropy is a global measure of the *spread* of the probability distribution. The quantities J_r and J_p chosen to describe the entropy part, H , of statistical complexity is different from the original shape complexity [4] which uses the simple exponential Shannon entropy satisfying the desirable invariance properties [13]. We note here that all the conclusions drawn in the present work remain valid with both these choices for H . To our knowledge, numerical studies involving J_r and J_p to describe the statistical complexity for atomic and ionic systems are presented here for the first time.

The disequilibrium D_r in the position space is calculated as the density expectation value given by

$$D_r = \int \rho^2(r) d^3r. \quad (6)$$

Analogously, the momentum space disequilibrium D_p is given by

$$D_p = \int \gamma^2(p) d^3p. \quad (7)$$

The quantity D represents the quantum self similarity [16–18], information energy [19], or linear entropy [20,21]. Most significantly, it is also an experimentally measurable quantity [22]. It is important to note here that D , for the normal distribution, is a direct measure of the square root of inverse variance. In the following discussions, the products $J_r D_r$, $J_p D_p$ and $J_{rp} D_{rp}$, where J_{rp} and D_{rp} are given by the products $\frac{1}{2\pi e} e^{2(S_r+S_p)/3}$ and $D_r D_p$, will be used to denote the LMC complexity measures C_r , C_p and C_{rp} , respectively. We note here that in defining J_{rp} we have used the net Shannon entropy, S_T given by $S_r + S_p$, and have computed its exponential power entropy to obtain P_{rp} . Using $J_r J_p$ instead would simply scale down the numerical values by a constant term uniformly without altering any conclusions.

3. Fisher–Shannon information plane

Fisher information measure [23], I , was originally introduced as a measure of *intrinsic accuracy* in statistical estimation theory. Sears, Parr and Dinur [24] noted that the quantum mechanical kinetic energy can be considered a measure of the information distribution, and through its relation to the Weizsacker kinetic energy term, I assumes a special position in quantum mechanics and density functional theory (DFT). Over the years, I has proved to be a very useful concept, e.g., the equations of non-relativistic quantum mechanics [25] have been derived using the principle of minimum I [26]. The time-independent Kohn–Sham equations and the time-dependent Euler equation of DFT were also derived by applying the above principle [27,28]. Other applications include the studies on single-particle systems under a central potential [29], the two-electron *entangled artificial* atom proposed by Moshinsky [30], modified Thomas–Fermi atoms [31] and the derivation of analytical relationship [32] between the integrands defining S_r and I_r . In a recent paper [33], the product of inverse of atomic I with D has been found to show good correlations with the ionization potentials and static dipole polarizabilities for the neutral atoms across the periodic table. Very recently, interesting new bounds relating to the I have been derived [34,35] for the central potentials.

The Fisher information (intrinsic accuracy) measures [23] for position and momentum are

$$I_r = \int \frac{[\vec{\nabla}\rho(r)]^2}{\rho(r)} d^3r, \quad I_p = \int \frac{[\vec{\nabla}\gamma(p)]^2}{\gamma(p)} d^3p. \quad (8)$$

In position space, I_r measures the narrowness and the oscillatory nature of the probability distribution. For the normal distribution, for example, I_r is a direct measure of the inverse of variance whereas D_r measures the *square root* of the inverse variance. Such a resemblance has led us to examine the Fisher–Shannon planes for position and momentum given by $P_r = J_r I_r$ and $P_p = J_p I_p$, respectively, as a possible measure of statistical complexity similar to C in the corresponding spaces. In this Letter, we shall compare the complexity measures C_r , C_p and C_{rp} with the FSIPs given by P_r , P_p and P_{rp} , respectively, for the test set of atoms and ions as listed in the introduction. We conclude this section by noting the isoperimetric inequality in three dimensions given by [36,37]

$$P_r = J_r I_r \geq 3, \quad (9)$$

and

$$P_p = J_p I_p \geq 3. \quad (10)$$

Thus, a noteworthy feature of the measure of complexity given by FSIP is that it possesses a universal lower bound given by Eqs. (9)–(10).

4. Results and conclusions

In the present work, the non-relativistic HF densities used are identical to those employed in a recent study on atomic

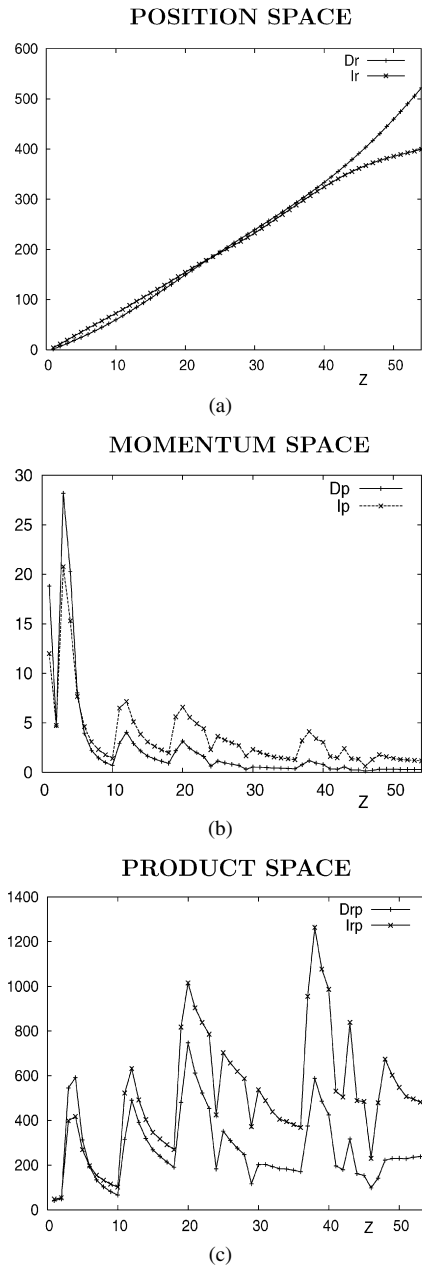


Fig. 1. A comparison of (a) $35 \times D_r$ with I_r , (b) $90 \times D_p$ with I_p , and (c) $5000 \times D_r p$ with $I_r p$ corresponding to the neutral atoms as a function of Z .

quantum similarity [18] wherein the spherically averaged densities are generated using Koga–Roothaan–Hartree–Fock wave functions [10,11]. The momentum space wave functions were computed using analytic expressions given in terms of the linear expansions of the Slater type functions describing the position space HF wave functions. All the necessary integrals have been estimated by means of the numerical quadrature using the spherically averaged electron density.

In the discussion which follows, first we shall be specifically displaying the variations in disequilibrium, D , and I with the nuclear charge for the neutral atoms $Z (= 1-54)$. In Fig. 1(a), we have compared the estimates of D_r (35 times) with I_r corresponding to the neutral atoms as a function of Z . It is observed that while D_r increases monotonically with Z ,

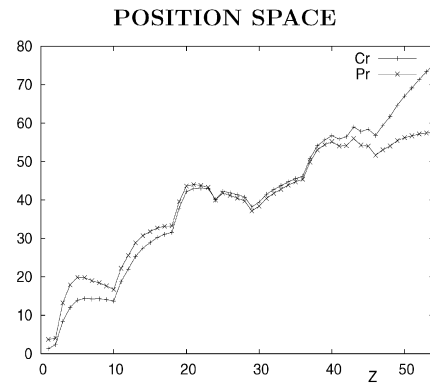


Fig. 2. A comparison of $35 \times C_r$ and P_r corresponding to neutral atoms as a function of Z .

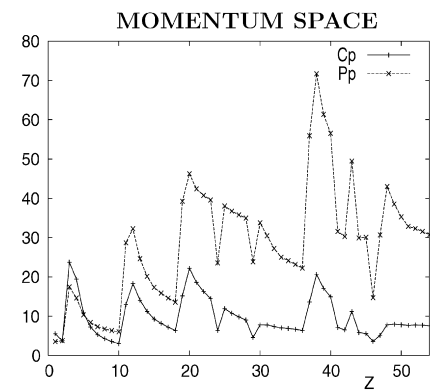


Fig. 3. A comparison of $90 \times C_p$ and P_p corresponding to the neutral atoms as a function of Z .

I_r goes down at $Z = 5, 46$, then relatively less pronounced at $Z = 11$, and decreases from 51 to 53. Over most of the region, otherwise, I_r follows the D_r curve. In Fig. 1(b), we have similarly displayed the variation of D_p (90 times) with I_p for the neutral atoms wherein it is found that the two quantities show similar trends. More significantly, the locations of extrema in both D_p and I_p are observed at the identical values of Z . For example, minima occur at $Z = 2, 10, 18, 36, 54$ (noble gases) as well as $Z = 24, 29, 46$ (anomalous shell-filling), while the maxima are located at $Z = 3, 12, 20, 30, 38, 43$, and 48 , respectively. As compared to the position space, it is observed that the shell structure is revealed more clearly in the momentum space through out for all atoms. The observations concerning D_p and I_p in Fig. 1(b) also hold good when $D_r D_p$ (5000 times) and $I_r I_p$ are plotted, as in Fig. 1(c). We shall now consider the numerical comparison between C and P values in the position, momentum and the product spaces for the neutral atoms. In Fig. 2, we have plotted C_r and P_r for the neutral atoms as a function of Z . It is observed that the shell structure is more clearly delineated through P_r . Further, the increase in complexity at the onset of a new shell originating at the alkali metal atoms is more sensitively reflected in P_r . The overall similarity between C_r and P_r is found to be excellent. These observations are also found to hold good in the momentum space as displayed in Fig. 3, wherein we have plotted C_p and P_p for the neutral atoms. Here, the appearance of the extrema are even

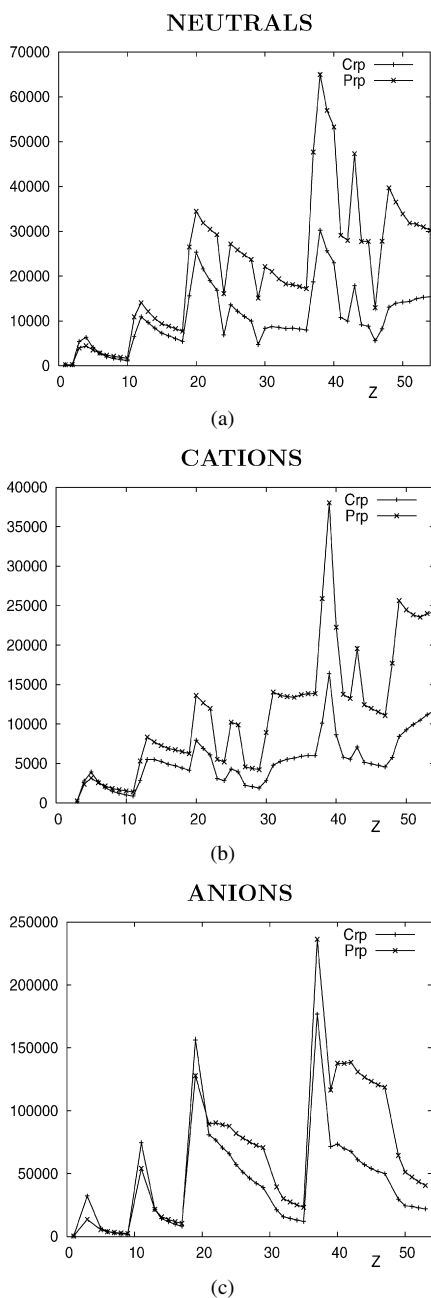


Fig. 4. A comparison of $5000 \times C_{rp}$ with P_{rp} corresponding to the neutral atoms, positive ions, and negative ions as a function of Z .

more profoundly displayed through P_p in comparison with P_r noted earlier in Fig. 2. The trends in D , I , C and P for the positive and negative ions in the position and momentum spaces are found to be similar as in the neutral atoms. In order to avoid repetitions these variations are not displayed separately. However, in the product space we shall now consider all the systems together. Thus, in Fig. 4(a)–(c) we have plotted the quantities C_{rp} and P_{rp} for the neutral, positive and negative ions, respectively. In view of the essential similarity between C_{rp} and P_{rp} it is finally concluded from Fig. 4 that in comparison to the LMC measure, FSIP presents itself as an alternative measure of complexity for electron probability density of atoms and ions with the notable characteristics that (a) it includes a global informa-

tion (J) and a local statistical measure (I), and (b) the variation in complexity with Z is revealed more sensitively.

5. Future work

Some possibilities of future work that follow from the present study will be briefly mentioned now. The well-known relative Shannon entropy [38] of the density $\rho_1(r)$ with respect to a prior distribution $\rho_2(r)$ is defined as

$$S_r^{1,2} = \int_0^\infty 4\pi r^2 \rho_1(r) \log\left(\frac{\rho_1(r)}{\rho_2(r)}\right) dr, \quad (11)$$

which is zero in case of $\rho_1(r)$ as equal to $\rho_2(r)$ and otherwise positive, under the same condition of normalization. Analogously, the relative Fisher information measure of the density $\rho_1(r)$ with respect to a prior distribution $\rho_2(r)$ may be defined as

$$I_r^{1,2} = \int_0^\infty 4\pi r^2 \rho_1(r) \left[\frac{d}{dr} \log\left(\frac{\rho_1(r)}{\rho_2(r)}\right) \right]^2 dr, \quad (12)$$

which is zero in case of $\rho_1(r)$ as equal to $\rho_2(r)$ and otherwise positive. Choosing the prior as constant or unity, I_r has the significance of a measure of disorder. In general, $I_r^{1,2}$ offers itself as a new quantum similarity measure [16]. It would be also useful to analyze the isoelectronic variations of C_{rp} and P_{rp} by including a larger set of multiply charged positive ions [12] and study, e.g., the Z dependence of the statistical complexity measures. Finally, a more detailed analysis of the variation of statistical complexity with the process of ionization, e.g., the variation in $[\frac{dC}{dN}]_Z$ as a function of Z and the active sub-shell in atoms would be useful. The results of such studies will be reported elsewhere.

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