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Information-theoretical complexity for the hydrogenic identity S_N2 exchange reaction

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Abstract   We investigate the complexity of the hydrogenic identity S_N2 exchange reaction by means of information-theoretic functionals such as disequilibrium (D), exponential entropy (L), Fisher information (I), power entropy (J) and joint information-theoretic measures, i.e., the I–D, D–L and I–J planes and the Fisher–Shannon (FS) and López-Mancini-Calbet (LMC) shape complexities. The several information-theoretic measures of the one-particle density were computed in position (r) and momentum (p) spaces. The analysis revealed that the chemically significant regions of this reaction can be identified through most of the information-theoretic functionals or planes, not only the ones which are commonly revealed by the energy, such as the reactant/product (R/P) and the transition state (TS), but also those that are not present in the energy profile such as the bond cleavage energy region (BCER), the bond breaking/forming regions (B–B/F) and the charge transfer process (CT). The analysis of the complexities shows that the energy profile of the identity S_N2 exchange reaction bears no simple behavior with respect to the LMC and FS measures. Most of the chemical features of interest (BCER, B–B/F and CT) are only revealed when particular information-theoretic aspects of localizability (L or J), uniformity (D) and disorder (I) are considered.

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1 Introduction

The application of complexity concepts in physical sciences has acquired increasing interest over the last years. Since the definition of complexity is not unique, its quantitative characterization has been an important subject of research and it has received considerable attention [1–9]. For instance, Anteneodo and Plastino [10] have discussed several notions of complexity and noted that there is not yet a consensus on a precise definition. Thus, the term *complexity* has been referred to different meanings established prior to the recent attempts to use it as indicative for structure in natural systems. For example, Kolmogorov [1,2] complexity or *algorithmic information theory* [11] are understood from the point of view of the information content of a string, which is equivalent to the length of the shortest possible self-contained representation of that string which is essentially a program. Further, *computational complexity theory* has been focused on classifying computational problems according to their inherent difficulty, measuring the amounts of resources required for the execution of algorithms [12]. In contrast, *statistical complexity theory* [8] refers to the measure of the randomness and unpredictability of a system which adequately captures the correlation of the system's components in its behavior. Roughly speaking, the larger and more intricate the "correlations" between the system's constituents, the more structured its underlying probability distribution. A comprehensive study of the application of complexity measures on atoms and molecules has been recently published [13].

Fundamental concepts such as *uncertainty* or *randomness* are frequently employed in the definitions of complexity, although some other concepts like *clustering*, *order*, *localization* or *organization* might be also important for characterizing the complexity of systems and processes as general indicators of pattern, structure and correlation. It is not clear how the aforementioned concepts might intervene in the definitions so as to quantitatively assess the complexity of the system. However, recent proposals have formulated this quantity as a product of two factors, taking into account *order/disequilibrium* and *delocalization/uncertainty*. This is the case of the definition of López-Mancini-Calbet (LMC) shape complexity [8–10] that, like others, satisfies the boundary conditions by reaching its minimal value in the extreme *ordered* and *disordered* limits.

The LMC complexity measure has been criticized [10,18,19], modified and generalized [21] leading to a useful estimator which satisfies several desirable properties of invariance under scaling transformations, translation, and replication [22,24]. The utility of this improved complexity has been verified in many fields [15–17] and allows reliable detection of periodic, quasiperiodic, linear stochastic, and chaotic dynamics [22–24]. The LMC measure is constructed as the product of two important information-theoretic quantities (see below): the so-called disequilibrium D (also known as self-similarity [25] or information energy [26]), which quantifies *the departure of the probability density from uniformity* [18,19,23] (equiprobability) and the Shannon entropy S, which is a general measure of randomness/uncertainty of the probability

density [3], and *quantifies the departure of the probability density from localizability*. Both global quantities are closely related to the measure of spread of a probability distribution. On the other hand the Fisher-Shannon product FS has been employed as a measure of atomic correlation [27] and also defined as a statistical complexity measure [28–31]. The product of the power entropy J -explicitly defined in terms of the Shannon entropy - and the Fisher information measure, I, combine both the global character (depending on the distribution as a whole) and the local one (in terms of the gradient of the distribution), to preserve the general complexity properties. As compared to the LMC complexity, aside of the explicit dependence on the Shannon entropy which serves to measure the uncertainty (localizability) of the distribution, the Fisher-Shannon complexity replaces the disequilibrium global factor D by the Fisher local one to *quantify the departure of the probability density from disorder* [4,5] of a given system through the gradient of the distribution.

From a different perspective, the energetics of chemical reactions [32] has been the focus of quantum chemistry studies over the last decades. For instance, a variety of calculations of potential energy surfaces have been performed at various levels of sophistication [33]. Within the broad scope of these investigations, particular interest has been focused on extracting information about the stationary points of the energy surface. Despite the fact that minima, maxima, and saddle points are useful mathematical features of the energy surface to reaction-path following [34], it has been difficult to attribute too much chemical or physical meaning to these critical points [35]. Whereas the reaction rate and the reaction barrier are chemical concepts, which have been rigorously defined and experimentally studied since the early days of the transition state (TS) theory [36,37] the structure of the TS remains as a quest of physical organic chemistry. Understanding the TS is a fundamental goal of chemical reactivity theories, which implies the knowledge of the chemical events that take place to better understand the kinetics and the dynamics of a reaction. On the other hand, a variety of density descriptors have been employed to study chemical reactions [36–39]; among them, it is worthy to mention the reaction force studies on the potential energy of reactions, which characterize changes in the structural and/or electronic properties in chemical reactions [40–46]. In past years, there has been an increasing interest to analyze the electronic structure of atoms and molecules by applying information theory (IT) [47–67]. In more recent studies we have shown that information-theoretic measures are capable of providing simple pictorial chemical descriptions of atoms and molecules. For instance, theoretic-information analyses have shown useful to describe phenomenologically the course of elementary chemical reactions through the localized/delocalized behavior of the electron densities in position and momentum spaces by revealing important chemical regions that are not present in the energy profile such as the ones in which bond forming and bond breaking occur and also the bond cleavage energy regions (BCER) [68]. Furthermore, the synchronous reaction mechanism of a S_N2 type chemical reaction and the non-synchronous behavior of the simplest hydrogen abstraction reaction were predicted by use of Shannon entropies analysis [69]. Also, the chemical phenomena of B-B/F was recently studied by the Fisher information measure for both reactions showing that this local measure in momentum space is highly sensitive in detecting these chemical events, whereas the one in position space is able to detect differences in their mechanisms [70]. In a very

recent study on the complexity of the hydrogenic abstraction reaction [71], we have employed the information-theoretic functionals *D*, *L*, *I*, *J* and joint information-theoretic measures, i.e., the *I-D*, *D-L* and *I-J* planes and the Fisher-Shannon and LMC shape complexities. These measures were found to reveal all the chemically significant aspects of the course of the reaction, i.e., the reactant/product regions, the bond cleavage energy region, the bond breaking/forming region and the transition state. Besides, the information-theoretic concepts of uniformity, disorder, localizability were useful to reveal the chemical phenomena of energy accumulation/releasing and to identify the mechanisms for bond forming and spin coupling.

Throughout the present study we intend to enrich the theory of chemical reactions within the framework of Information Theory by use of complexity measures (*LMC* and *FS*) and information planes for the hydrogenic identity $S_N 2$ exchange reaction. The study is organized as follows, in Sect. 2 we define the complexity measures along with their information-theoretic components. In Sect. 3 we calculate the information components as well as the *Fisher-Shannon* and *LMC complexities*. These information-theoretic functionals of the one-particle density are computed in position (*r*), momentum (*p*) as well as in the joint product space (*rp*) that contains more complete information about the system. Besides, the Fisher-Shannon (*I–J*), the disequilibrium-Shannon (*D–L*) and Fisher-disequilibrium (*I–D*) planes are studied. Finally, in Sect. 4, some conclusions are given.

2 Theoretical details

2.1 Information-theoretic measures and complexities

In the independent-particle approximation, the total density distribution in a molecule is a sum of the contributions from the electrons in each of the occupied orbitals. This is the case in both *r*- and *p*-spaces, position and momentum respectively. In momentum space, the total electron density, $\gamma(\mathbf{p})$, is obtained through the molecular momentals (momentum-space orbitals) $\varphi(\mathbf{p})$, and similarly for the position density, $\rho(\mathbf{r})$, through the molecular position-space orbitals $\phi(\mathbf{r})$. The momentals (atomic units are employed throughout) can be obtained by three-dimensional Fourier transformation of the corresponding orbitals (and conversely)

$$\varphi_i(\mathbf{p}) = (2\pi)^{-3/2} \int d\mathbf{r} \exp(-i\mathbf{p} \cdot \mathbf{r})\phi_i(\mathbf{r}) \tag{1}$$

Standard procedures for the Fourier transformation of position space orbitals generated by ab-initio methods have been described [72]. The orbitals employed in ab-initio methods are linear combinations of atomic basis functions and since analytic expressions are known for the Fourier transforms of such basis functions [73], the transformation of the total molecular electronic wavefunction from position to momentum space is computationally straightforward [74].

As we mentioned in the introduction, the LMC complexity is defined through the product of two relevant information-theoretic measures. So that, for a given

probability density in position space, $\rho(\mathbf{r})$, the $C(LMC)$ complexity is given by [8,19]:

$$C_r(LMC) = D_r e^{S_r} = D_r L_r \tag{2}$$

where D_r is the disequilibrium [25,26]

$$D_r = \int \rho^2(\mathbf{r}) d\mathbf{r} \tag{3}$$

and S is the Shannon entropy [3]

$$S_r = -\int \rho(\mathbf{r}) ln \rho(\mathbf{r}) d\mathbf{r} \tag{4}$$

from wich the exponential entropy $L_r = e^{S_r}$ is defined. Similar expressions for the LMC complexity measure in the conjugated momentum space might be defined for a distribution $\gamma(\mathbf{p})$

$$C_p(LMC) = D_p e^{S_p} = D_p L_p \tag{5}$$

It is important to mention that the *LMC* complexity of a system must comply with the following lower bound [75]:

$$C(LMC) \geq 1 \tag{6}$$

The FS complexity in position space, $C_r(FS)$, is defined in terms of the product of the Fisher information [4,5]

$$I_r = \int \rho(\mathbf{r}) |\overrightarrow{\nabla} ln \rho(\mathbf{r})|^2 d\mathbf{r} \tag{7}$$

and the power entropy [28–31] in position space, J_r

$$J_r = \frac{1}{2\pi e} e^{\frac{2}{n} S_r} \tag{8}$$

which depends on the Shannon entropy defined above. So that, the *FS* complexity in position space is given by

$$C_r(FS) = I_r \cdot J_r \tag{9}$$

and similarly

$$C_p(FS) = I_p \cdot J_p \tag{10}$$

in momentum space.

Let us remark that the factors in the power Shannon entropy J are chosen to preserve the invariance under scaling transformations, as well as the rigorous relationship [76].

$$C(FS) \geq n \tag{11}$$

with n being the space dimensionality, thus providing a universal lower bound to *FS* complexity. The definition in Eq. (8) corresponds to the particular case $n=3$ (atoms and molecules), the exponent containing a factor $2/n$ for arbitrary dimensionality. See [77] for further rigorous bounds on complexity measures and uncertainty products.

It is worthwhile noting that the aforementioned inequalities remain valid for distributions normalized to unity, which is the choice that it is employed throughout this work for the 3-dimensional molecular case.

Aside of the analysis of the position and momentum information measures, we have considered it useful to study these quantities in the product *rp*-space, characterized by the probability density $f(\mathbf{r}, \mathbf{p}) = \rho(\mathbf{r})\gamma(\mathbf{p})$, where the complexity measures are defined as

$$C_{rp}(LMC) = D_{rp}L_{rp} = C_r(LMC)C_p(LMC) \tag{12}$$

and

$$C_{rp}(FS) = 2\pi e I_{rp} J_{rp} = 2\pi e C_r(FS)C_p(FS) \tag{13}$$

From the above two equations, it is clear that the features and patterns of both LMC and FS complexity measures in the product space will be determined by those of each conjugated space.

3 Complexity analysis for the hydrogenic identity $S_N 2$ exchange reaction

For our complexity study we choose a typical nucleophilic substitution ($S_N 2$) reaction: $H_a + CH_4 \rightarrow CH_4 + H_b$. This chemical process involves only one step in contrast with the two-step $S_N 1$ reaction [68]. In the anionic form, the $S_N 2$ mechanism can be depicted as $Y^- + RX \rightarrow RY + X^-$, which is characterized by being kinetically of second order. For identity $S_N 2$ reactions it has been postulated that the observed second order kinetics is the result of passage through the well-known Walden inversion transition state where the nucleophile displaces the nucleofuge (leaving group) from the backside in a single concerted reaction step. Evidence has been presented [69] which shows that the one step mechanism observed for this type of reaction is indeed characterized by its synchronous and concerted behaviour.

In a previous study for this reaction [68], we have shown that Shannon entropy in momentum space holds two maxima at the TS vicinity and we associated these regions to a bond cleavage energy process (BCER) where the necessary energy for bond breaking is supposed to occur. It was interesting to note that for both entropies (position and momentum) the BCER are located at the same IRC coordinate, in contrast with the two-stages mechanism of the hydrogenic abstraction reaction [71], which is indicative of the single step mechanism that characterizes the $S_N 2$ process, which highlights the *localized/delocalized* combination of the position/momentum densities at this particular position of the IRC. At this point, it is interesting to associate the one step mechanism of this reaction to the chemical events that take place. While the nucleophile approaches the molecule the nucleofuge leaves it at unison, i.e., bond forming and bond breaking must occur in a concerted and synchronous manner. Both of these actions increase the energy of the combination: bond breaking requires

energy (momentum density becomes delocalized, see Ref. [68]) to surmount the repulsion between the incoming ionic-complex (nucleophile) into close contact with the carbon's bonding shell. As the reaction process goes forward, the energy increases until a significant bonding begins to occur between the nucleophile and the molecule through a charge transfer (CT) process by releasing the necessary energy to break the carbon-nucleofuge bond which stabilizes the molecule at the transition state.

The electronic structure calculations performed in the present study were carried out with the Gaussian 03 suite of programs [78]. Reported TS geometrical parameters for the $S_N 2$ exchange reactions were employed [79]. Calculations for the IRC were performed at the MP2/6-311++G** level of theory, which generated 93 points evenly distributed between the forward and reverse directions of the IRC. Next, a high level of theory and a well-balanced basis set (diffuse and polarized orbitals) were chosen for determining all of the properties for the chemical structures corresponding to the IRC. Thus, the QCISD(T) method was employed in addition to the 6-311++G** basis set. All information-theoretic quantities are calculated in position and momentum spaces for the IRC path of the hydrogenic identity $S_N 2$ exchange reaction and obtained by employing software developed in our laboratory along with 3D numerical integration routines [81], and the DGRID suite of programs [74]. A relative tolerance of 1×10^{-5} was set for the numerical integrations unless otherwise be stated [81].

In order to perform an information-theoretic characterization of the chemical process we have undertaken a complexity analysis since this type of studies provide with complementary sources of information, i.e., D (*departure from uniformity*) with L (*departure from localizability*) through the *C(LMC)* and also with I (*departure from disorder*) and J (*departure from localizability*) through the *C(FS)* measure (Eqs. 2, 5, 9 and 10). In the following sections we will employ global and local quantities so as to provide with a complete description of the identity $S_N 2$ reaction.

3.1 Information measures

In previous works [68–70], we employed Shannon and Fisher Information measures as chemical phenomenological descriptors for elementary reaction processes. In particular for the identity $S_N 2$ reaction, we described regions of chemical interest, the bond cleavage energy region (BCER) and the bond breaking/forming one (B-B/F). To the end of complementing the information above we will show throughout this section some additional features of the chemical reaction from the perspective of the disequilibrium measure (D). This quantity (D_r) has been depicted in Fig. 1, along with the Fisher information in position space, for comparison purposes. As a general observation we may note that D_r closely resemblances the global measure of Shannon in the product space [68] and hence predicts a full description of the chemical phenomena, i.e., the BCER, the B-B/F and the CT processes. On the other hand, I_r indicates that beyond the BCER region there is a significant structural change at $R_x \approx -1.7$ where the inversion of configuration initiates in such a manner that the most disordered structure (minimum value of I_r) corresponds to the ionic complex structure that has gained sufficient energy (BCER) for bond breaking ($R_x \approx -1.0$) and charge transferring ($R_x \approx -0.5$). Afterwards, the chemical structure becomes the most ordered at the
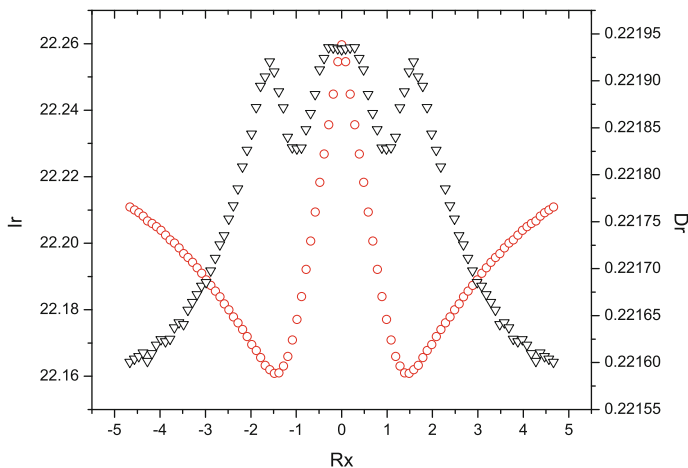
Fig. 1 Disequilibrium (*black open triangles*) and Fisher Information (*red open circles*) in position space

TS where the I_r is maximum. Next, a closer look to the disequilibrium measure in position space describes the chemical route through the concurrent processes occurring in the transient zone [68]. This is located at the onset of the BCER region where the molecule inverts its geometrical configuration (at around $R_x \approx -1.7$) which is characterized by a less uniform electron distribution described by local maxima of D_r. In contrast, note that neither I nor S [68–70], describe the bond breaking nor the CT regions. It is worth observing that D_r holds global maxima at the CT/TS regions which indicates non uniform probability distributions, as compared with the rest of the chemical process, with a slight minimum at the TS, indicating the expected equiprobable distribution at this point. Therefore, the chemical picture describes a process where the bond breaking drives the electronic distribution to a minimum D_r, tending to equiprobability and uniformity; however, according to Fig. 1, the charge transfer phenomenon softens the inertia to equiprobability by augmenting disequilibrium due to the increasing electrostatic repulsion between the nucleophile and the nucleofuge at the vicinity of the TS as the reaction develops, and hence the observed non uniform region with a faint equiprobable structure at the TS (minimum).

In Fig. 2, we have depicted the disequilibrium and the Fisher measures in momentum space. In contrast with the quantities in position space we note that both, D_p and I_p, only describe the BCER and the TS regions in that, at the former, the momentum space density shows the least ordered distribution and the most equiprobable according to the Fisher and the disequilibrium measures, respectively. At the TS, both quantities display maxima, revealing a chemical distribution which is highly ordered and the least uniform among the rest at the vicinity, which corresponds to a highly localized density in momentum space thus characterizing the TS [68]. Also note that D_p shows a complex behavior in the regions associated to the B-B/F and the CT (see discussion above) in that the slope of the disequilibrium measure in between the B-B/F ($R_x \approx -1.0$) and the CT ($R_x \approx -0.5$) diminishes, which is linked to the discussion above in that the charge transfer phenomenon lessens the inertia to non equiprobability due to the
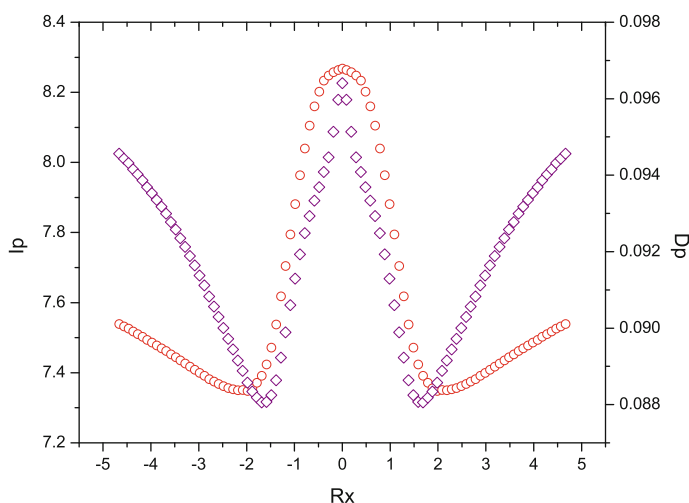
Fig. 2 Disequilibrium (*purple open diamonds*) and Fisher Information (*red open circles*) in momentum space

increasing electrostatic repulsion between the nucleophile and the nucleofuge at the vicinity of the TS as the reaction develops.

3.2 Information planes

In the search of any joint features of *disorder–uniformity* (*I–D*), *uniformity–localizability* (*D–L*), and *disorder–localizability* (*I–J*) for the chemical course of the reaction we have found useful to plot the contribution of I and D to the $I - D$ plane, D and L to the total LMC complexity, and similarly with I and J to the FS complexity.

Notwithstanding that not all information products are good candidates to form complexity measures, i.e., to preserve the desirable properties of invariance under scaling, translation and replication [18,19,75], we have found interesting to study the plane $I - D$, with the purpose of analyzing patterns of *disorder − uniformity*. In Figs. 3 to 5 we have analyzed the phenomenological description of the reaction through the $I_r - D_r$, $D_r - L_r$, $I_r - J_r$ planes, respectively. Our analysis starts with the $I_r - D_r$ plane, that is depicted in Fig. 3, from which we may note that at the R/P the position density is the most equiprobable with the highest *uniformity*; as the reaction proceeds the *order* decreases at the expense of diminishing the *uniformity*; this behavior is almost linear along the reaction path until the BCER is reached. Up to this point, the molecular structure of the ionic complex solely rearranges in preparation for the concurrent processes (B–B/F and the CT) occurring at the transient region. At the onset of the BCER (commencement of the inversion of configuration) the $I_r - D_r$ plane reverts the quasi-linear tendency observed before, i.e., the *uniformity* of the distribution in position space augments as well as its *order*; this occurs until the bond breaking occurs at $R_x \approx -1.0$. Afterwards, the *uniformity* diminishes and the *order* increases in a non-linear way. At the vicinity of the TS the disequilibrium remains
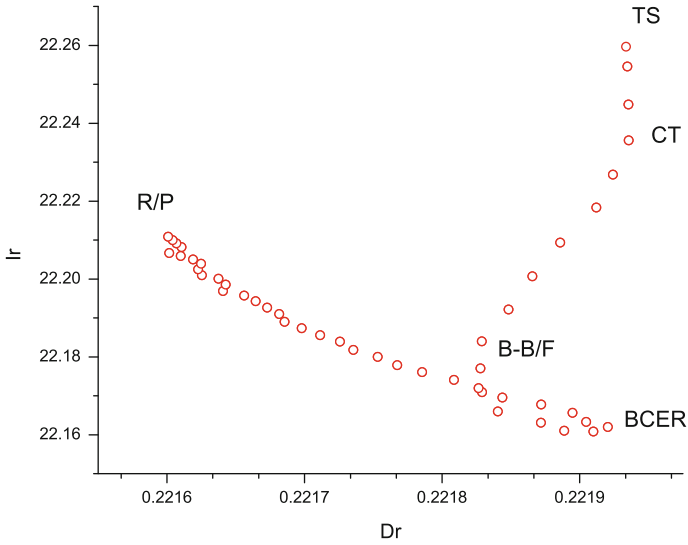
Fig. 3 Fisher-disequilibrium plane in position space along the IRC
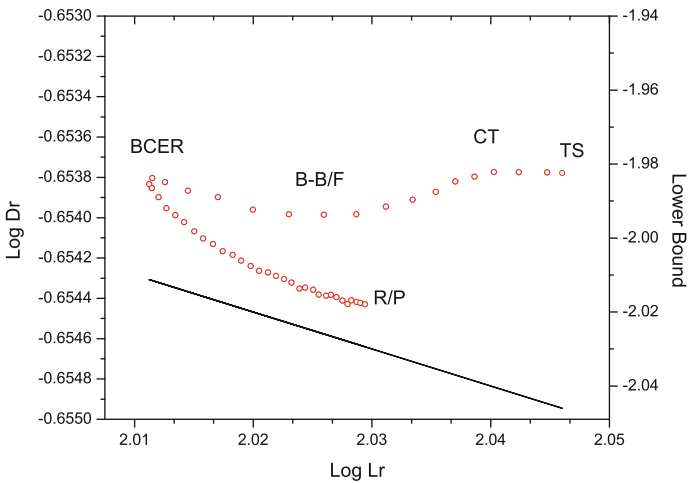
Fig. 4 Disequilibrium-Shannon plane in position space along the IRC

fairly constant at the expense of increasing *order* until the TS is reached. After this point the process gets reverted. Therefore, the $I_r - D_r$ plane shows that the non-linear tendency observed from BCER to TS indicates the presence of chemical phenomena (concurrent processes); i.e. all the electronic arranges that conveys to a chemical reaction proceed in this *transient region*.

Note that in Figs. (4) and (7) we have plotted (in a double-logarithmic scale) the $D_r - L_r$ and $D_p - L_p$ planes for the chemical reaction. At this point it is worth mentioning that there is a rigorous lower bound to the associated $C(LMC)$ complexity, given by Eq. **??**eq6), which is for both spaces. From both Figures we may observe
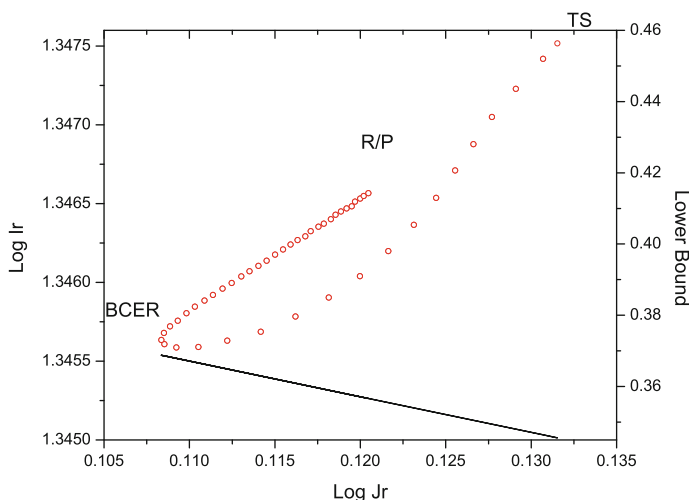
Fig. 5 Fisher-Shannon plane in position space along the IRC

that the *D–L* plane is clearly separated into two regions, according to the inequality (valid for position, momentum as well as product spaces), and the region below the line (equality) corresponds with the forbidden region. Parallel lines to this bound represent isocomplexity regions, showing that an increase (decrease) in uncertainty, *L*, along them is compensated by a proportional decrease (increase) of disequilibrium, and higher deviations from this frontier are associated with greater LMC complexities.

The behavior of the $D_r - L_r$ plane is shown in Fig. (4) in a log-log scale. From this we might observe two different tendencies for $D - L$ complexity in that one can distinguish a zone delimited by the R/P and BCER regions in which a quasilinear tendency is observed, i.e., this region appears to be more isocomplex than the rest of the chemical route as compared to the $C(LMC)$ bound also shown in Fig. (4), indicating the rearranging of the ionic complex molecule when the reactives approach each other. At this stage, the information-theoretic description shows that the position space distribution augments its *localizability* by lessening its *uniformity* until the BCER is reached. Beyond this point, from BCER to B-B/F, the *informational* behavior departs from quasi-isocomplexity by diminishing *localizability* at the expense of increasing its *uniformity*. Afterwards, the position density tends to the most *delocalized* and *uniform* distribution at the IRC. It is worthy to note that at the vicinity of the TS the disequilibrium measure appears to remain constant until the TS is reached very much alike to the $I_r - D_r$ plane analyzed before.

In Figs. (5) and (8) we have plotted (in a double-logarithmic scale) the $I_r - J_r$ and $I_p - J_p$ planes for the chemical reaction. At this point it is worth mentioning that there is a rigorous lower bound to the associated $C(FS)$ complexity, given in Eq. (11), which is valid for both spaces.

Continuing with the analysis, now for the $I_r - J_r$ plane, we observe similar features (Fig. 5) as compared with the planes above discussed in that two tendencies are clearly shown. From the R/P to the BCER a quasi-linear behavior is observed, i.e., increase of
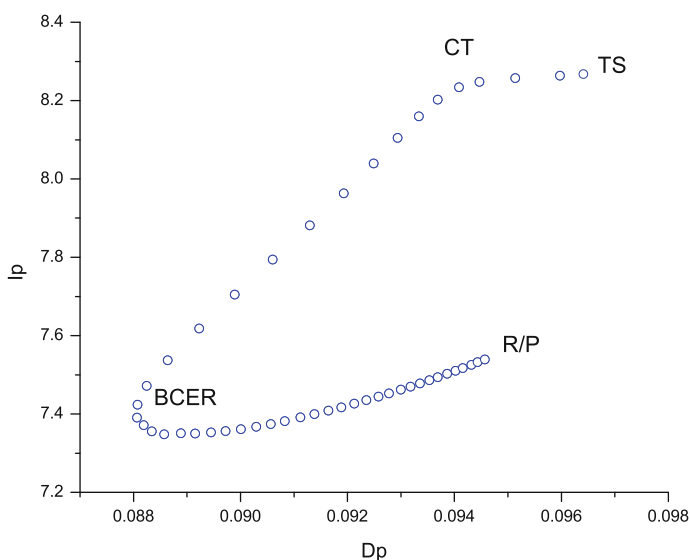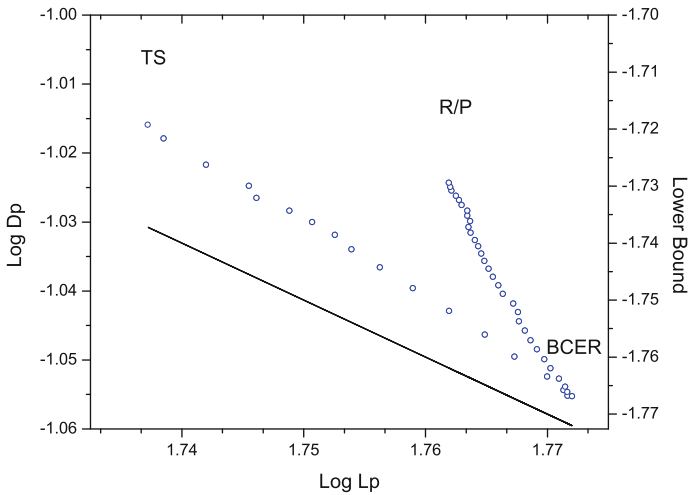
Fig. 6 Fisher-disequilibrium plane in momentum space along the IRC

localizability and *disorder* whereas in the second stage the complexity pattern is much more intricate and is characterized by a simultaneous augment of *delocalizability* and *order* as the reaction proceeds in the forward direction of the reaction.

On the other hand, for the complementary space, we may note some general features from the different planes: $I_p - D_p$, $D_p - L_p$, and $I_p - J_p$. In all of them we might observe two energetic stages: from the R/P to BCER the ionic complex is gaining energy to surmount the barrier at the TS, i.e., at the beginning of the reaction the electronic momentum distributions get delocalized by gaining *uniformity* and diminishing *order* $(I_p - D_p)$, or augmenting uncertainty (either $D_p - L_p$ or $I_p - J_p$). In the second stage, the necessary energy to reach B–B/F and CT, is released from the BCER to the TS, by gaining momentum density *localization*, augmenting *order* or diminishing *uniformity* (see Figs. 6,7,8).

3.3 Complexities

In the search of joint patterns of *uniformity-localizability* through $C(LMC)$ and *disorder-localizability* through $C(FS)$ we have depicted in Figs. 9 and 10 the values for these complexity measures in position and momentum spaces, respectively. The general observation from Fig. 10 is that both complexity measures behave similarly in position space. They reflect a zone where the process is less complex, from R/P to BCER, than the region delimited from BCER to TS; in agreement with the analysis of the information planes for the density in position space. Strictly speaking, for this chemical case, as the reaction proceeds both complexity measures, $C(LMC)$ and $C(FS)$, decrease until the BCER is reached, after this point the reaction evolves in a more complex manner, reflecting the fact that it is in this region where all the chemically meaningful

**Fig. 7** Disequilibrium-Shannon plane in momentum space along the IRC
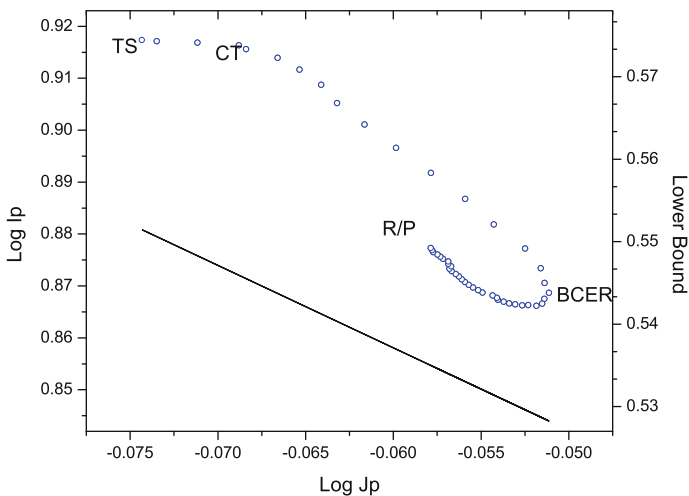
Fig. 8 Fisher-Shannon plane in momentum space along the IRC

phenomena occur through charge depletion/accumulation, yielding concurrent processes such as: BCER, bond breaking/forming and charge transfer, which can only be distinguished through information measures, planes and complexities. It is interesting to note that all of them are necessary to chemically describe the Walden inversion of configuration. In Figs. 9 and 10, we can summarize the observations above in that both complexity measures witness the chemical zone of interest through an augment of complexity entirely at the transient region , i.e., from the BCER to the TS.

In particular, we can mention the fact that in momentum space the phenomenological description is more intricate than in position space. Complexity measures describe different aspects of the distributions due to their local/global behavior (Fig. 10). For
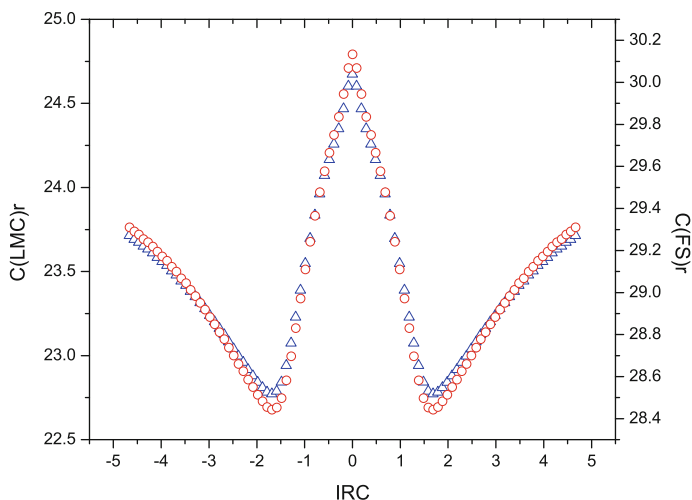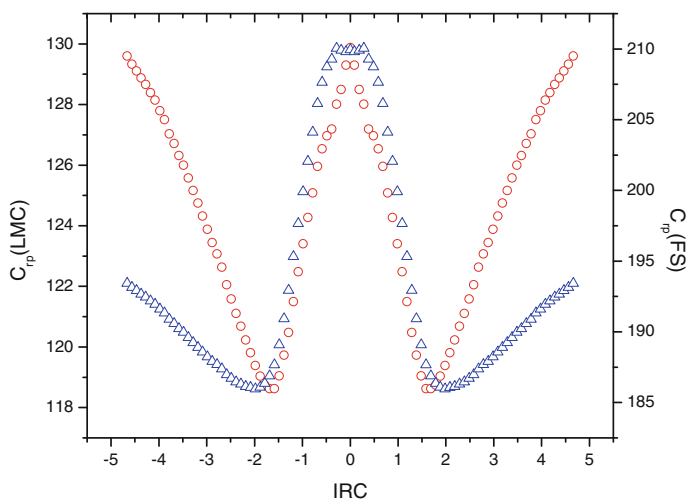
Fig. 9 $C(LMC)$ (*blue open triangles*) and $C(FS)$ (*red open circles*) in position space along the IRC
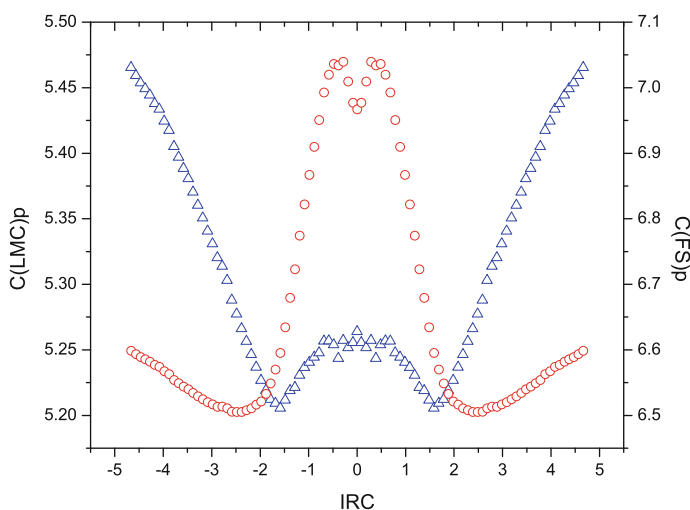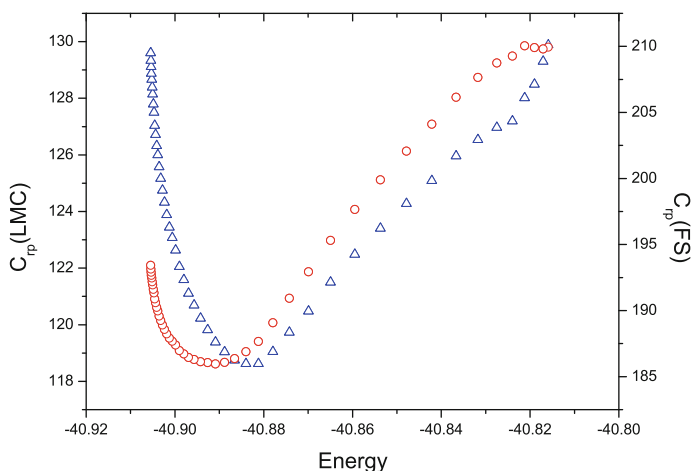

Fig. 10 $C(LMC)$ (*blue open triangles*) and $C(FS)$ (*red open circles*) in momentum space along the IRC

instance, the LMC quantity in momentum space describes a process in which complexity lessens as the reaction evolves (R/P to BCER), once the inversion of configuration is about to occur (at the onset of BCER) the complexity in momentum space increases. At the transient zone, the chemical description passes through the B-B/F which is accurately described by $C(FS)$ whereas the charge transfer is also described by the $C(FS)$.

Continuing with the analysis we account with valuable data to establish a relationship between the information-theoretic features of the reaction to that of the total energy. In contrast with a previous study on the hydrogenic reaction [71], where the

Fig. 11 $C(LMC)$ (*blue open triangles*) and $C(FS)$ (*red open circles*) in the product space (rp) along the IRC

Fig. 12 $C(LMC)$ (*blue open triangles*) and $C(FS)$ (*red open circles*) in the product space (rp) versus the total energy

$C_{rp}(LMC)$ and $C_{rp}(FS)$ complexity values as a function of the energy display a monotonic decreasing behavior for both of them, the situation for the S_N2 reaction of the present study is totally distinct in that there are more concurrent processes in this reaction than in the S_N1 and hence, the relation between the complexity measure in product space and the total energy is not as simple as in the abstraction reaction [71]. Figures 11 and 12 show the behavior of the complexity measures, LMC and FS, in product space versus the IRC and the energy, respectively. In Fig. 11, we observe that all the concurrent processes are present, i.e., BCER, B-B/F, CT and the TS. On the other hand, the values depicted in Fig. 12 might be interpreted as follows: as the reaction evolves

both complexities diminish at the expense of augmenting the energy up to a region of maximum disorder (Fisher in momentum space tends to a minimum, see Fig. 2) for the $C_{rp}(FS)$ measure and to a region of maximum uniformity (disequilibrium in momentum space tend to a minimum, see Fig. 2). Then the energy augments at the expense of increasing both complexities up to the TS is reached. It is worth noting that at the vicinity of the TS, the $C_{rp}(FS)$ complexity possesses a slight maximum which corresponds to the CT region, at this onset the Fisher in momentum space tends to a maximum order where the complex ionic structure initiates the charge transferring. In comparison, for the abstraction reaction in position space, the energy profile bears the joint features of $C(LMC)$ (uniformity-localizability) and $C(FS)$ (disorder-localizability), for the exchange reaction the energy profile can not be associated in a simple manner to any of the complexity measures.

4 Conclusions

In this work, we have investigated the complexity of the S_N2 abstraction reaction by means of information-theoretic functionals D, L, I, J and joint information-theoretic measures, i.e., the $I - D$, $D - L$ and $I - J$ planes and the Fisher-Shannon and LMC shape complexities.

The analysis of the information-theoretic functionals of the one-particle density was performed in position (r) and momentum (p) spaces. These measures were found to reveal all the chemically significant aspects of the course of the reaction, i.e., the reactant/product regions, the bond cleavage energy region, the bond breaking/forming region and the transition state. Besides, the information-theoretic concepts of *uniformity*, *disorder*, *localizability* were useful to reveal the chemical phenomena of energy accumulation/releasing.

The contribution of this study resides in the phenomenological description of the chemical reaction through complexity concepts. Thus, throughout the analysis we related information measures of disequilibrium, Fisher and Shannon to the chemical concurrent processes that undergo the reaction through concepts such as *uniformity, order* and *delocalization*. Hence, we can assign the R/P regions to chemical densities characterized by high uniform and ordered distributions, the BCER to non-uniform and low ordered local densities, the B-B/F to locally uniform distributions, the CT to globally non-uniform distributions and the TS by locally uniform and globally ordered distributions.

On the other hand, the chemical route can be distinguished by two different stages of complexities. In position space, from the R/P to BCER the complexities hold a quasi-linear tendency whereas from the BCER to the TS (throughout the transient zone) the complexity behavior is much more intricate, showing all the concurrent processes of BCER, B-B/F, CT and the TS. On the other side, in momentum space, from the R/P to the BCER, complexities show a zone of energy accumulation, whereas in the transient zone, this energy is released to convey the concurrent processes above mentioned.

The results of this study indicate that further investigations are necessary in order to improve our understanding of the complexity for chemical reactions along the lines

of analyzing different reaction mechanisms, other information-theoretic functionals, and more intrincated aspects of the energy profile, among others. We think that the strategy followed in this study might be useful in more complex cases by describing the phenomenological behavior of the chemical probe regarding their local and global features by use of the three key information measures, i.e., Shannon, Fisher and disequilibrium. Then, the various information planes and complexity measures of the process might be resolved in a feasible manner.

References

1. A.N. Kolmogorov, Probl. Inf. Transm **1**, 3 (1965)
2. G. Chaitin, J. ACM. **13**, 547 (1966)
3. C.E. Shannon, W. Weaver, *The Mathematical Theory of Communication* (University of Illinois Press, Urbana, 1949)
4. R.A. Fisher, Proc. Cambridge Philos. Soc. **22**, 700 (1925)
5. B.R. Frieden, *Science from Fisher Information* (Cambridge University Press, Cambridge, 2004)
6. C.H. Bennet, in *The Universal Turing Machine a Half Century*, ed. by R. Herhen (Oxford University Press, Oxford, 1988), pp. 227–257
7. S. Lloyd, H. Pagels, Ann. Phys. (NY) **188**, 186 (1988)
8. D.P. Feldman, J.P. Crutchfield, Measures of statistical complexity: Why?. Phys Lett A **238**(4–5), 244–252 (1998)
9. P.W. Lamberti, M.T. Martin, A. Plastino, O.A. Rosso, Physica A **334**, 119 (2004)
10. C. Anteonodo, A. Plastino, Phys. Lett. A **223**, 348 (1996)
11. R.J. Solomonoff, *Algorithmic Probability: Theory and Applications, Information Theory and Statistical Learning*, ed. by F. Emmert-Streib, and M. Dehmer (Springer, NY, 2009), ISBN 978-0-387-84815-0.
12. S. Arora, B. Barak, Computational Complexity: A Modern Approach, Cambridge, ISBN 978-0-521-42426-4, http://www.cs.princeton.edu/theory/complexity/ (2009)
13. J.C. Angulo, J. Antolin, R.O. Esquivel, "Atomic and Molecular Complexities: Their Physical and Chemical Interpretations", Chapter in the monograph *Statistical Complexity: Applications in Electronic Structure*, ed. by K.D. Sen, (Springer, UK, 2010) ISBN: 978-90-481-3889-0.
14. M. Sipser (2006) *Introduction to the theory of computation*, 2nd ed., USA: Thomson Course Technology, ISBN 0534950973
15. O.A. Rosso, M.T. Martin, A. Plastino, Physica A **320**, 497 (2003)
16. K.Ch. Chatzisavvas, Ch.C. Moustakidis, C.P. Panos, J. Chem. Phys. **123**, 174111 (2005)
17. A. Borgoo, F. De Proft, P. Geerlings, K.D. Sen, Chem. Phys. Lett. **444**, 186 (2007)
18. R.G. Catalán, J. Garay, R. López-Ruiz, Phys. Rev. E **66**, 011102 (2002)
19. T. Martin, A. Plastino, O.A. Rosso, Phys. Lett. A **311**, 126 (2003)
20. R. López-Ruiz, A. Nagy, E. Romera, J. Sanudo, J. Math. Phys. **50**, 123528 (2009)
21. R. López-Ruiz, R. Biophys. Chem. **115**, 215 (2005)
22. T. Yamano, J. Math. Phys. **45**, 1974 (2004)
23. R. López-Ruiz, H.L. Mancini, X. Calbet, Phys. Lett. A **209**, 321 (1995)
24. T. Yamano, Physica A, 2004, 340,131 (1995)
25. R. Carbó-Dorca, J. Arnau, L. Leyda, Int. J. Quantum Chem **17**, 1185 (1980)
26. O. Onicescu, C.R. Acad. Sci. Paris A **263**, 25 (1966)

27. E. Romera, J.S. Dehesa, J. Chem. Phys. **120**, 8906 (2004)
28. J.C. Angulo, J. Antolin, K.D. Sen, Phys. Lett. A **372**, 670 (2008)
29. K.D. Sen, J. Antolín, J.C. Angulo, Phys. Rev. A **76**, 032502 (2007)
30. J.C. Angulo, J. Antolín, J. Chem. Phys. **128**, 164109 (2008)
31. J. Antolín, J.C. Angulo, Int. J. Quantum Chem. **109**, 586 (2009)
32. R. Hoffman, S. Shaik, P.C. Hiberty, Acc. Chem. Res. **36**, 750 (2003)
33. H.B. Schlegel, Adv. Chem. Phys. **67**, 249 (1987)
34. K. Fukui, Acc. Chem. Res. **14**, 363 (1981)
35. S. Shaik, A. Ioffe, A.C. Reddy, A. Pross, J. Am. Chem. Soc. **116**, 262 (1994)
36. H. Eyring, J. Chem. Phys. **3**, 107 (1935)
37. E. Wigner, Trans. Faraday Soc. **34**, 29 (1938)
38. G.S. Hammond, J. Am. Chem. Soc. **77**, 334 (1955)
39. J.E. Leffler, Science **117**, 340 (1953)
40. Z. Shi, R.J. Boyd, J. Am. Chem. Soc. **113**, 1072 (1991)
41. R.F.W. Bader, P.J. MacDougall, J. Am. Chem. Soc. **107**, 6788 (1985)
42. N. Balakrishnan, N. Sathyamurthy, Chem. Phys. Lett. **164**, 267 (1989)
43. M. Ho, H.L. Schmider, D.F. Weaver, J. Chem. Theory Comput. **6**, 153 (2010)
44. V.H. Smith Jr., R.P. Sagar, R.O. Esquivel, Int. J. Quantum Chem. **77**, 376 (2000)
45. E.H. Knoerr, M.E. Eberhart, J. Phys. Chem. A **105**, 880 (2001)
46. A. Tachibana, J. Chem. Phys. **115**, 3497 (2001)
47. S.R. Gadre, in *Reviews of Modern Quantum Chemistry: A Celebration of the Contributions of Robert* ed. by G. Parr, K.D. Sen, Vol 1 (World Scientific: Singapore, 2003), pp 108–147.
48. T. Koga, M. Morita, J. Chem. Phys. **79**, 1933 (1983)
49. S.K. Ghosh, M. Berkowitz, R.G. Parr, Proc. Natl. Acad. Sci. USA **81**, 8028 (1984)
50. J.C. Angulo, J.S. Dehesa, J. Chem. Phys. **97**, 6485 (1992)
51. S.E. Massen, C.P. Panos, Phys. Lett. A **246**, 530 (1998)
52. R.F. Nalewajski, R.G. Parr, J. Phys. Chem. A **105**, 7391 (2001)
53. A. Nagy, J. Chem. Phys. **119**, 9401 (2003)
54. E. Romera, J.S. Dehesa, J. Chem. Phys. **120**, 8906 (2004)
55. P. Karafiloglou, C.P. Panos, Chem. Phys. Lett. **389**, 400 (2004)
56. K.D. Sen, J. Chem. Phys. **123**, 074110 (2005)
57. R.G. Parr, R.F. Nalewajski, P.W. Ayers, J. Phys. Chem. A **109**, 3957 (2005)
58. N.L. Guevara, R.P. Sagar, R.O. Esquivel, J. Chem. Phys. **122**, 084101 (2005)
59. Q. Shi, S. Kais, J. Chem. Phys. **309**, 127 (2005)
60. K.Ch. Chatzisavvas, Ch.C. Moustakidis, C.P. Panos, J. Chem. Phys. **123**, 174111 (2005)
61. K.D. Sen, J. Katriel, J. Chem. Phys. **125**, 074117 (2006)
62. A. Nagy, Chem. Phys. Lett. **425**, 154 (2006)
63. P.W. Ayers, Theor. Chem. Acc. **115**, 253 (2006)
64. L.M. Martyusheva, V.D. Seleznev, Phys. Rep. **426**, 1 (2006)
65. S. Liu, J. Chem. Phys. **126**, 191107 (2007)
66. A. Borgoo, P. Jaque, A. Toro-Labbé, Ch. Van Alsenoy, P. Geerlings, Phys. Chem. Chem. Phys. **11**, 476 (2009)
67. P. Geerlings, A. Borgoo, Phys. Chem. Chem. Phys. **13**, 911–922 (2011)
68. R.O. Esquivel, N. Flores-Gallegos, C. Iuga, E. Carrera, J.C. Angulo, J. Antolin, Theor. Chem. Acc. **124**, 445 (2009)
69. R.O. Esquivel, N. Flores-Gallegos, C. Iuga, E. Carrera, J.C. Angulo, J. Antolin, Phys. Lett. A **374**, 948 (2010)
70. S. López-Rosa, R.O. Esquivel, J.C. Angulo, J. Antolín, J.S. Dehesa, N. Flores-Gallegos, J. Chem. Theory Comput. **6**, 145 (2010)
71. R.O. Esquivel, M. Molina-Espíritu, J.C. Angulo, J. Antolin, N. Flores-Gallegos, J.S. Dehesa, Mol. Phys. **109**, 2353–2365 (2011)
72. D.C. Rawlings, E.R. Davidson, J. Phys. Chem. **89**, 969 (1985)
73. P. Kaijser, V.H. Smith Jr., Adv. Quant. Chem. **10**, 37 (1997)
74. M. Kohout, program DGRID, 2007, version 4.2.
75. S. López-Rosa, J.C. Angulo, J. Antolín, Physica A **388**, 2081 (2009)
76. A. Dembo, T.M. Cover, J.A. Thomas, Information theoretic inequalities. IEEE Trans. Inf. Theory **37**, 1501–1518 (1991)

77. A. Guerrero, P. Sánchez-Moreno, J.S. Dehesa, Phys. Rev. A. **84**(042105) (2011)
78. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Cli®ord, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03, Revision D.01* (Gaussian, Inc., Wallingford, CT, 2004)
79. Z. Shi, R.J. Boyd, J. Am. Chem. Soc. **111**, 1575–1579 (1989)
81. J.M. Pérez-Jordá, E. San-Fabián, Comput. Phys. Commun. **77**, 46 (1993)
81. J.M. Pérez-Jordá, A.D. Becke, E. San-Fabián, J. Chem. Phys. **100**, 6520 (1994)
82. M.N. Glukhovtsev, A. Pross, L. Radom, J. Am. Chem. Soc. **117**, 2024–2032 (1995)