

Shape entropy's response to molecular ionization

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Abstract In this work we define a shape entropy by calculating the Shannon's entropy of the shape function. This shape entropy and its linear response to the change in the total number of electrons of the molecule are explored as descriptors of bonding properties. Calculations on selected molecular systems were performed. According to these, shape entropy properly describes electron delocalization while its linear response to ionization predicts changes in bonding patterns. The derivative of the shape entropy proposed turned out to be fully determined by the shape function and the Fukui function.

Keywords Electron delocalization · Fukui function · Shannon's entropy · Shape function

Introduction

Ionization phenomena is of paramount importance in areas ranging from chemistry and physics to applied fields such as

health sciences and industry. Molecular ionization in gas phase draws interest for applications in combustion theory, electric arc generation and other charge transfer reaction mechanisms.

Any tool that could provide insight on changes on molecular bonding derived from electron ionization processes is very valuable. Bonding analysis methodologies are nowadays popular tools for molecular modeling applications [1, 2]. Critical points of electronic density are also used frequently as indicators of chemical bonds [3, 4]. Despite all of these laudable and successful efforts, there is still no streamlined method to explore changes in bonding due to ionization.

In recent years Shannon's entropy has received considerable attention in molecular research [5–10]. This entropy is a measure of uncertainty in terms of a probability distribution [11–14]. Shannon's entropy has been employed in density functional theory (DFT) studies for more than 20 years now [15–23] on molecular and reaction analysis. In recent years there has been a renewed interest in the formal foundations and further applications of this sound concept [24–29]. When applied to the molecular electronic distribution it provides a measure of electron delocalization or lack thereof.

In this contribution we define a shape entropy by calculating the Shannon's entropy of the shape function and propose its linear response to molecular ionization as a descriptor of changes in bonding patterns. We show how this response can be easily calculated provided that analytic Fukui functions are available.

The paper is organized as follows. In the **Theory** section the shape entropy and its linear response to electronic ionization (RSI) is formulated. In the **Computational details** section the computational details are given. In the **Applications** section the discussion of RSI graphics for a selected set of molecules is presented. Concluding remarks and suggestions for further applications are provided in **Conclusions** section.

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Theory

In order to present the formulation of the shape entropy and its linear response to ionization, the concepts pertinent to the subject are defined.

Shannon's entropy

The concept of entropy from information theory, also known as Shannon's entropy [11] has been applied multiple times on signal processing, communications, machine learning, physics and chemistry [5, 11–14].

Shannon's entropy measures uncertainty in terms of a probability distribution. Its definition restricts it to random variables that take discrete values. In order to extend this discrete entropy to continuous variables one must resort to a continuous or differential entropy (referred to as Shannon's entropy for simplicity purposes),

$$S = - \int g(\mathbf{x}) \ln g(\mathbf{x}) d\mathbf{x} = \int \mathbf{s}_g(\mathbf{x}) d\mathbf{x}, \quad (1)$$

where $g(\mathbf{x})$ is a probability density function and $\mathbf{s}_g(\mathbf{x})$ represents the local contribution to Shannon's entropy.

The shape function as an electron probability distribution

The molecular electron density, $\rho(\mathbf{r})$, is the probability of finding any electron at a given point of the space. The electronic density integrates to the total number of electrons of the molecule, N . In its normalized form it is known as the shape function [30–32].

$$\sigma(\mathbf{r}) \equiv \frac{\rho(\mathbf{r})}{N}. \quad (2)$$

This molecular function possess a number of interesting properties which have been discussed by Cedillo, Ayers and co-workers [31–37].

Fukui function

The Fukui function [38–42] measures the tendency of a point or region in the molecule to release or accept electrons. Formally, it is obtained by taking a derivative of the density with respect to the number of electrons, N , at fixed external potential, $v(r)$,

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}. \quad (3)$$

Derivative discontinuity ill-defines the Fukui function. As a result, left and right-hand derivatives have been defined [42–45].

$$f^\pm(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})}^\pm \quad (4)$$

In the context of the Kohn and Sham (KS) [46] implementation of DFT [47, 48] the Fukui functions can be derived as [49]

$$f^-(\mathbf{r}) = |\phi_{\text{HOMO}}(\mathbf{r})|^2 + \sum_{i=1}^{\text{occ}} \mathbf{n}_i \frac{\partial |\phi_i(\mathbf{r})|^2}{\partial N} \quad (5)$$

$$f^+(\mathbf{r}) = |\phi_{\text{LUMO}}(\mathbf{r})|^2 + \sum_{i=1}^{\text{occ}} \mathbf{n}_i \frac{\partial |\phi_i(\mathbf{r})|^2}{\partial N}, \quad (6)$$

where $\{\phi_i\}$ are exact KS orbitals and HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals respectively. The second term of these equations is a correction that takes into account the relaxation of the inner orbitals when an electron is either added or removed. These relaxation terms can be calculated analytically employing linear response theory [50–55].

Shape entropy

The shape function is a normalized probability function that describes the distribution of electrons. Therefore, it is an appropriate probability function for the definition of a Shannon's entropy that could measure electron delocalization,

$$S_\sigma = - \int \sigma(\mathbf{r}) \ln \sigma(\mathbf{r}) d\mathbf{r} = \int \mathbf{s}_\sigma(\mathbf{r}) d\mathbf{r}, \quad (7)$$

from here on referred to as shape entropy.

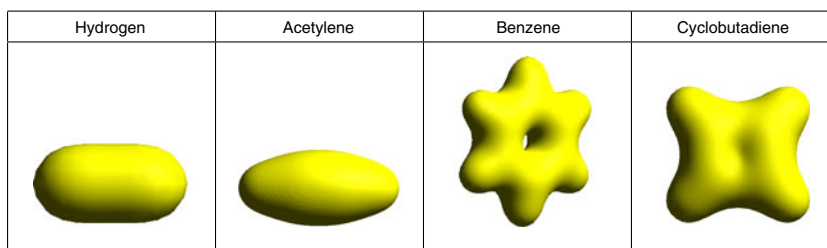
In order to have an appreciable delocalization the shape function cannot be too small because there would not be electrons to delocalize at all. In the opposite case, large values of the shape function would result in a very restricted condition with too many electrons in a small region. Regions with a value of $e^{-1} \approx 0.36$ for the shape function will result in the largest delocalization. Thus, delocalization here means to have an appreciable number of electrons in a condition where different configurations can be adopted while producing the same density.

Shape entropy's linear response to ionization

The linear response to ionization of the shape entropy can be calculated by direct differentiation with respect to the total number of electrons,

$$t_\sigma(\mathbf{r}) \equiv \frac{\partial \mathbf{s}_\sigma}{\partial N} = - \frac{\partial \sigma}{\partial N} (\ln \sigma(\mathbf{r}) + 1). \quad (8)$$

Similar results related to the linear response of the shape function can be found in works of Cedillo and co-authors

Fig. 1 Isosurfaces for shape functions

[31, 32, 34, 37], the derivative of the shape function is obtained by differentiating Eq. (2),

$$\frac{\partial \sigma}{\partial N} = \frac{1}{N} \frac{\partial \rho(\mathbf{r})}{\partial N} - \frac{\rho(\mathbf{r})}{N^2}. \quad (9)$$

Assuming a vertical ionization process, the derivative of the density with respect to the total number of electrons can be interpreted as the Fukui function. In our formulation there will be no restriction on the orbital targeted by the ionization. The RSI will depend on the orbital from which electrons are removed from or added to. Introducing a generalized Fukui function, $f^p(\mathbf{r})$, for the ionization associated to p th orbital it follows:

$$t_{\sigma}^p(\mathbf{r}) = \frac{-1}{N} (f^p(\mathbf{r}) - \sigma(\mathbf{r})) (\ln \sigma(\mathbf{r}) + \mathbf{1}), \quad (10)$$

with the following generalized form of the Fukui function:

$$f^p(\mathbf{r}) = |\phi_p(\mathbf{r})|^2 + \sum_{i=1}^{\text{occ}} \mathbf{n}_i \frac{\partial |\phi_i(\mathbf{r})|^2}{\partial N}. \quad (11)$$

Computational details

All calculations were performed at the auxiliary density functional theory level employing the deMon2k program [61]. These calculation employed the local density approximation by combining Dirac's exchange functional [56] and the Vosko, Wilk and Nusair correlation functional [57]. The DZVP basis set [58] was employed in all calculations, while the A2 set [59, 60] was the auxiliary function of choice.

Graphics were generated with a development version of the software Sinapsis [62].

Applications

Shape function and shape entropy

Figure 1 plots the shape function, $\sigma(\mathbf{r})$, for hydrogen molecule, acetylene, benzene and cyclobutadiene.

Figure 2 shows plots of the local shape entropy, $s_{\sigma}(\mathbf{r})$, for the same set of molecules. We decided to map $s_{\sigma}(\mathbf{r})$ on top of the shape function, $\sigma(\mathbf{r})$ in order to contrast the two fields. In addition, a plot of shape entropy on the plane containing all the atoms is presented. Here, a color ramp from red to blue corresponds to high to low local shape entropy values.

To gain better insight on the information pertained to shape entropy, we first analyzed the hydrogen molecule in which there is only a single sigma bond. We observe that the local shape entropy correctly defines regions of space which are likely to contain delocalized electrons. The region with higher shape entropy is along the line containing the two hydrogen atoms. One can see that while an appreciable density of electrons is confined to the interatomic region, these electrons are not localized. This delocalization contributes to the binding of atoms by providing different configurations to reach the same bonding density. That is to say, we have an entropic stabilization.

Acetylene molecule presents a higher shape entropy in the C-C bonding region, including sigma- and pi-bonding. C-H bonds are also high entropy regions but not as high as C-C region as seen in Fig. 2.

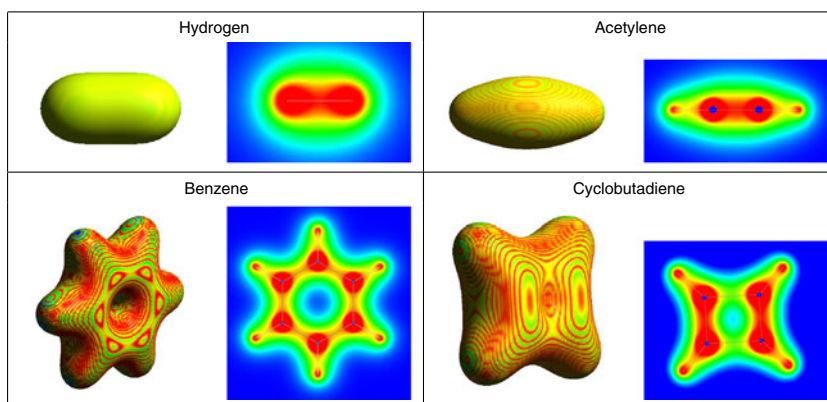
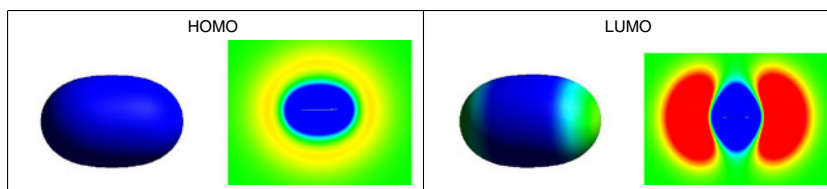
Fig. 2 Local shape entropy

Fig. 3 Hydrogen plots for linear response to ionization for local Shannon's entropy of shape function



Continuous red lines are found parallel to the molecular plane suggesting the ring delocalization usually attributed to benzene aromaticity. This ring maxima is present close to the molecular plane, as one goes away from the molecule the red rings tend to disappear. On the sigma plane we observed lower entropy over the C-H bonds than over the C-C bonds.

Cyclobutadiene presents two stronger bonds according to the red color in Shannon's entropy. This is in agreement with the widely accepted idea of cyclobutadiene being an anti-aromatic compound.

Shape entropy's linear response to ionization

As the local shape entropy seems to properly describe the bonding regions in molecules, we decided to plot the shape entropy's linear response to ionization. These plots present the variation of shape entropy of a system after an ionization. Here, the red coloring shows a raise in shape entropy, which we associate with bond strengthening, the blue coloring on the opposite end of the color ramp is associated with bond weakening and the green zones are where the shape entropy was unaffected by the ionization. In larger molecules, ionization from representative internal orbitals is analyzed along with the frontier orbitals.

Hydrogen molecule

Both the addition and removal of an electron from the H_2 system leads to a weakened H-H bond as expected. For the electron removal the plot shows a halo of mild entropy growth around the system. For the electron addition we observe a sharp growth in entropy next to the hydrogens which displays the symmetric probability of any hydrogen

holding the added electron while dissociating the H-H bond. Plots are shown in Fig. 3.

Acetylene

The addition of an electron to acetylene shows a decrease of entropy over all the molecule bonds on the molecular plane while a raise in entropy is observed around the C-H bond. Looking at the molecular plane plot it is clear that the growth in shape entropy is closer to the carbon nuclei than to the hydrogens and it could indicate a structure bending to the cis or trans structure of the $C_2H_2^-$ anion.

The removal of an electron from the HOMO causes a raise in entropy around the C-C bond and on the outside of the hydrogen nuclei. This could evince the formation of the C-C-H and H cations when the drop in entropy along the C-H bonds is taken into account.

The electron removal from the MO 3 provokes a rise on the entropy along the C-C bond that extends from the sigma to the pi region. While the entropy drops around the C-H bonds, it also grows on the outside of the structure next to the hydrogens.

For the core orbital (MO 2) ionization the entropy decreases sharply all over the proximity of the molecule while an entropy growth is observed close around the carbon nuclei and on the outside of the system, extending slightly over the hydrogens.

Plots are shown in Fig. 4.

Benzene

The electron removal from the core orbitals (MO 6) shows an entropy growth closely around the carbon nuclei while every bond on the molecular plane experiences an entropic decrease.

Fig. 4 Acetylene plots for linear response to ionization for local Shannon's entropy of shape function

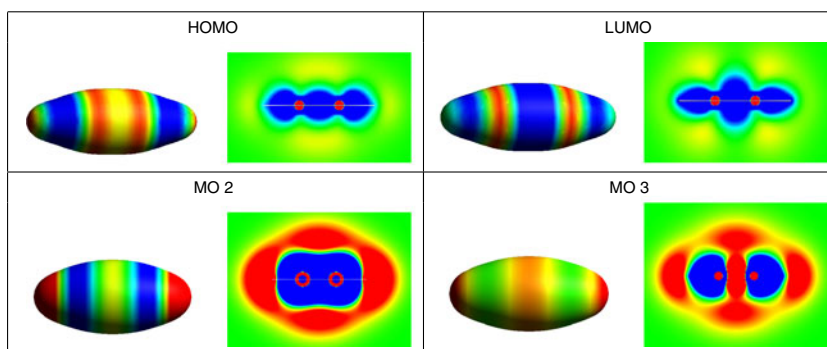
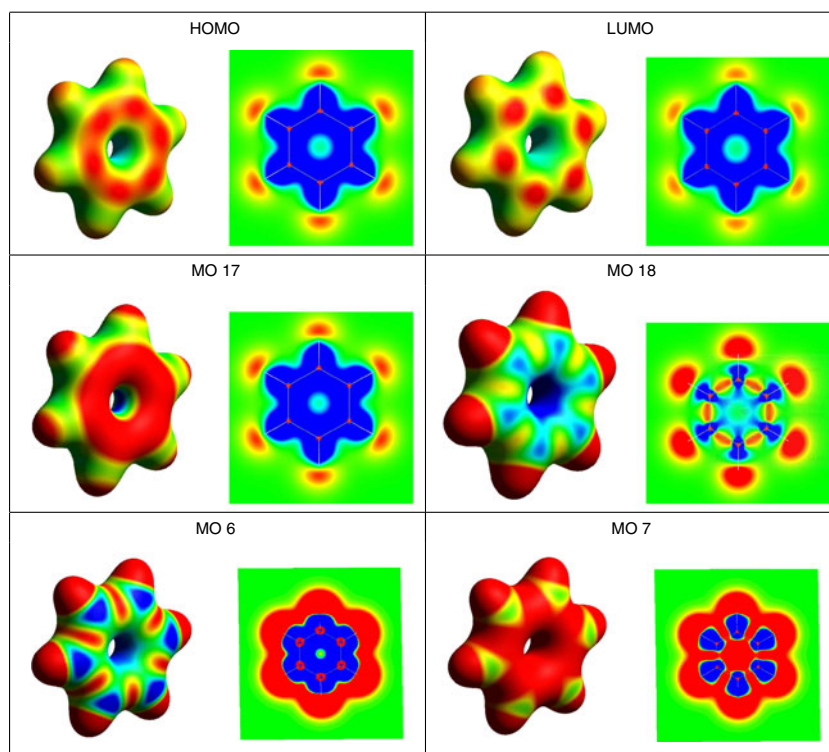


Fig. 5 Benzene plots for linear response to ionization for local Shannon's entropy of shape function



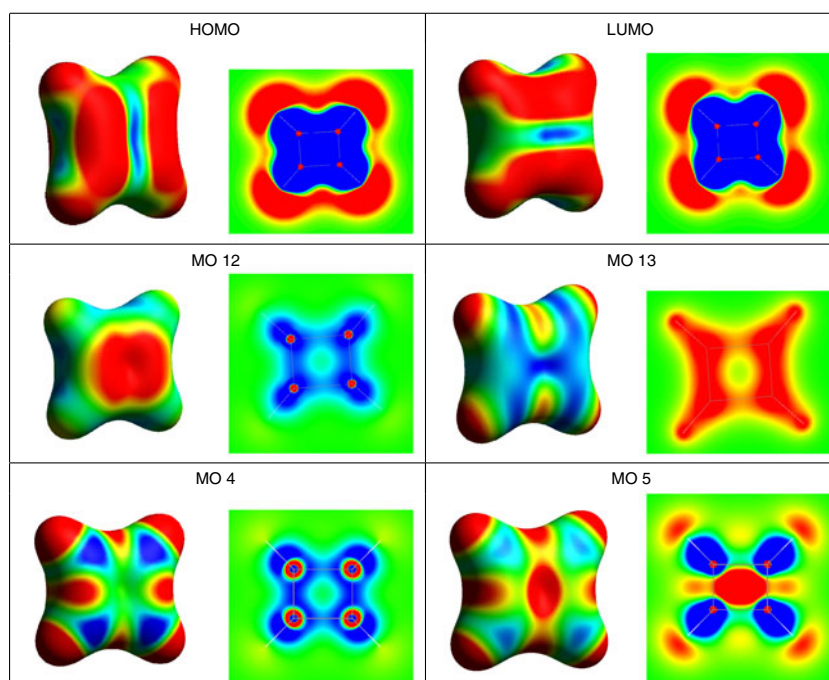
This behavior is reversed on the pi region, as a drop in entropy is observed over the carbon nuclei and the space above the C-C bonds, as well as the hydrogens, has an entropic growth. One thing to note is the high entropy halo around the molecule, right over the hydrogens as if their electrons were able to move freely on the system's periphery.

On the next energy level explored (MO 7), the high entropy ring around the molecule persists. However, in this

case it also extends to the center of the system. This could be interpreted as two high entropy zones connected over the C-C bonds, effectively isolating low entropy zones around the C-H fragments. This entropic response is consistent on both the pi region and the molecule plane.

For the MO 17 electron removal, an entropy decrease is observed on the sigma plane over the general molecule structure while a sharp raise in entropy is experienced all

Fig. 6 Cyclobutadiene plots for linear response to ionization for local Shannon's entropy of shape function



over the pi region above the carbon ring. This response is also observed on both frontier molecular orbitals, with varying degrees of polarization on the trend.

The MO 18 has a peculiar response on the sigma C-C bonds, which present a raise on delocalization while the carbons and the C-H bonds show a sharp growth in electron localization. This response is evenly expanded over the pi region.

Plots are shown in Fig. 5.

Cyclobutadiene

For this system the extraction of an electron from a core orbital (MO 4) leads to an entropy decrease on the C-H bonds and the C-C double bonds. C-C single bonds are affected as well but to a smaller degree. As on benzene, a zone closely around the carbon nuclei suffers an augment in entropy.

For the MO 5 entropy grows in the center of the ring. This growth extends across the C-C double bonds while each C-H fragment experiences an entropy decrease along and around the bond.

On a higher energy level (MO 12) a response similar to the core electron's removal is observed, yet the entropy drop along C-C bonds is more even between single and double bonds. On the pi region the center of the ring experiences a surge in entropy.

MO 13 response projects an entropy growth along the double bonds on the sigma plane while the pi region shows a decrease in entropy over the C-C double bonds and the center of the ring.

The frontier orbitals continue to reflect the trending differentiation between double and single bonds. An entropy growth over the double bonds is revealed after the removal of a HOMO electron. The addition of an electron to the LUMO would see the entropy growth over the single bonds.

Plots are shown in Fig. 6.

Conclusions

The concept of Shannon's entropy has been combined with the local reactivity descriptors shape function and Fukui function. The resulting shape entropy and its linear response to ionization were explored by running calculations on simple molecular systems. These calculations exhibited the shape entropy's ability to describe bonding properties as evidenced by the images in this paper. Calculations on the RSI revealed changes in bond strength and structure altering associated to molecule ionization.

RSIs was expressed with high symmetry due to the fact that calculations were formulated with molecular orbitals. This effectively spreads the response to all atoms forming

the affected molecular orbital. This is evident on the ionization of core orbitals where a keen decrease on entropy is observed on the very center of every carbon nuclei.

An entropy could be formulated employing atomic orbitals rather than molecular ones in order to explore the response to ionization of a single nucleus. This could set a platform for a predictive fragmentation tool useful in the resolution of mass spectrograms.

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