

# Chemical bonding and reactivity: a local thermodynamic viewpoint

Pratim K. Chattaraj<sup>a,c,1</sup>, E. Chamorro<sup>b</sup>, P. Fuentealba<sup>c,\*</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

<sup>b</sup> Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago de Chile, Chile

<sup>c</sup> Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago de Chile, Chile

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## Abstract

The possibility of gaining insight into chemical bonding and reactivity through various local temperatures and associated entropy densities is explored. Comparisons of these quantities with other local reactivity descriptors like the electron density, the Laplacian of the density, the Fukui function and the electron localization function are made. The water molecule has been chosen as a prototype for analyzing the above-mentioned quantities. The global entropies are also calculated for the atoms He to Ne. Most of the local quantities preserve the molecular symmetry and some are well suited for use as reactivity indices. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Density functional theory (DFT) [1,2] has been found to be highly successful for aiding our understanding of molecular structure, properties, bonding, reactivity and dynamics. DFT also provides [1] quantitative definitions of popular qualitative chemical concepts like electronegativity ( $\chi$ ) and hardness ( $\eta$ ). For an  $N$ -electron system with a total energy  $E$ , these quantities are defined as the following first-order [3] and second-order [4] derivatives

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (1)$$

and

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad (2)$$

where  $v(\mathbf{r})$  and  $\mu$  are, respectively, the external and chemical potentials. Electronegativity was introduced by Pauling [5] as the “power of an atom in a molecule to attract electrons to itself” and was made use of by Sanderson [6] in his electronegativity equalization principle. Hardness was introduced by Pearson through his hard–soft acid–base [7,8] and maximum hardness [9–12] principles. The hardness can be approximated by [9]

$$\eta = (I - A)/2 \quad (3)$$

where  $I$  and  $A$  are the ionization potential and electron affinity of the system, respectively. Using

\* Corresponding author. Fax: +562-2712973; E-mail: pfuentea@abello.dic.uchile.cl

<sup>1</sup> E-mail: pkej@hijli.iitkgp.ernet.in

Koopmans' theorem, Eq. (2) can be further approximated as [9]

$$\eta = (\varepsilon_L - \varepsilon_H)/2 \quad (4)$$

where  $\varepsilon_L$  and  $\varepsilon_H$  are the lowest unoccupied and highest occupied molecular orbital energies, respectively.

Equivalently, hardness can be expressed [13] as follows

$$\eta = \frac{1}{N} \iint \eta(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') \rho(\mathbf{r}) \, d\mathbf{r} \, d\mathbf{r}' \quad (5)$$

where  $\eta(\mathbf{r}, \mathbf{r}')$  is the hardness kernel [13] and  $f(\mathbf{r})$  is the Fukui function [14] defined as follows:

$$f(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_{v(\mathbf{r})}. \quad (6)$$

The electron localization function (ELF) [15–18] has been shown to be a reliable descriptor of chemical bonding. It is defined as follows [15]

$$L(\mathbf{r}) = \left\{ 1 + \left[ \frac{D(\rho(\mathbf{r}))}{t_{\text{TF}}(\rho(\mathbf{r}))} \right]^2 \right\}^{-1}. \quad (7)$$

In Eq. (7),  $D(\rho(\mathbf{r}))$  and  $t_{\text{TF}}(\rho(\mathbf{r}))$  are, respectively, the local excess of kinetic energy due to Pauli repulsion [15] and the kinetic energy density for an homogeneous electron gas, viz.

$$D(\rho(\mathbf{r})) = t_{\text{KS}}(\rho(\mathbf{r})) - t_{\text{W}}(\rho(\mathbf{r})) \quad (8)$$

and

$$t_{\text{TF}}(\rho(\mathbf{r})) = c_K \rho(\mathbf{r})^{5/3}. \quad (9)$$

In Eqs. (8) and (9),  $t_{\text{KS}}$  and  $t_{\text{W}}$  are, respectively, the Kohn–Sham (KS) and von Weizsäcker (W) kinetic energy densities and  $c_K$  is the Thomas–Fermi (TF) constant.

Ghosh et al. [19] have demonstrated that a local thermodynamic description of the many-electron system can be developed within the purview of ground state DFT. A local temperature  $\theta(\mathbf{r})$  is defined in terms of the kinetic energy density

$$t(\rho(\mathbf{r})) = \frac{3}{2} \rho(\mathbf{r}) k_B \theta(\mathbf{r}) \quad (10)$$

$k_B$  being the Boltzman constant.

The associated entropy density  $s(\mathbf{r})$  is given by [19,20]

$$s(\mathbf{r}) = \frac{3}{2} k_B \rho(\mathbf{r}) \left\{ \lambda + \ln \left[ \frac{t(\rho(\mathbf{r}))}{t_{\text{TF}}(\rho(\mathbf{r}))} \right] \right\} \quad (11)$$

where the constant  $\lambda$  is

$$\lambda = \frac{5}{3} + \ln \left( \frac{4\pi c_K}{3} \right). \quad (12)$$

The global entropy is given by

$$S = \int s(\mathbf{r}) \, d\mathbf{r} \quad (13)$$

which is equivalent to the Shannon entropy of information theory [21] and becomes a maximum for the most probable distribution [22]. It would be interesting to see whether the maximum entropy principle [22] and the maximum hardness principle [9,10] are somehow related. An extension of the thermodynamic formalism has been also published [23], and the relationship with the electronic entropy introduced by Gadre and Bendale [24] clarified [20].

In the present work, we explore the possibility of gaining insight into the chemical bonding and reactivity through various types of local temperatures and the associated entropy densities. The local temperature has been calculated for atoms [25] and molecules [26]. Here, comparisons of these quantities with other local reactivity descriptors like  $\rho(\mathbf{r})$  and  $f(\mathbf{r})$  and bonding descriptors like  $L(\mathbf{r})$  are made. The water molecule has been chosen as a prototype for investigating the mentioned quantities. A theoretical background of the present work is given in Section 2 and Section 3 contains the computational details. Section 3 also provides the results and discussion and Section 4 presents some concluding remarks.

## 2. Theoretical background

An ideal gas expression (Eq. (10)) for the kinetic energy density defines the local temperature  $\theta(\mathbf{r})$ . In the present Letter, we analyze various temperatures

associated with respective kinetic energy densities, viz.

$$t_x(\rho(\mathbf{r})) = \frac{3}{2}\rho(\mathbf{r})k_B\theta_x(\mathbf{r}); \quad x = \text{TF, W, KS}, \quad (14)$$

where

$$t_{\text{KS}}(\rho(\mathbf{r})) = \frac{1}{2} \sum n_i |\nabla \phi_i(\mathbf{r})|^2 \quad (15)$$

$$\rho(\mathbf{r}) = \sum n_i |\phi_i(\mathbf{r})|^2$$

and

$$t_{\text{W}}(\rho(\mathbf{r})) = \frac{1}{8} \frac{\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r})}{\rho(\mathbf{r})} \quad (16)$$

In Eq. (Eq. (16)), the sums run over the first  $N$  occupied KS orbitals  $\{\phi_i\}$  with occupation numbers  $\{n_i\}$ . Note that the kinetic energy density is not uniquely defined. It is always possible to add the Laplacian of the density times an arbitrary factor.

Now, the corresponding entropy densities can be written as

$$s_x(\mathbf{r}) = \frac{3}{2}k_B\rho(\mathbf{r}) \left\{ \lambda + \ln \left[ \frac{t_x(\rho(\mathbf{r}))}{t_{\text{TF}}(\rho(\mathbf{r}))} \right] \right\} \quad (17)$$

and the global entropies turn out to be

$$S_x = \int s_x(\mathbf{r}) \, d\mathbf{r}. \quad (18)$$

It is easy to provide a thermodynamic interpretation for the ELF in terms of the local temperatures, viz.

$$L(\mathbf{r}) = \left\{ 1 + \left[ \frac{\theta_{\text{KS}}(\mathbf{r}) - \theta_{\text{W}}(\mathbf{r})}{\theta_{\text{TF}}(\mathbf{r})} \right]^2 \right\}^{-1} \quad (19)$$

In order to obtain more insight into the local reactivity, we have generated the local temperatures

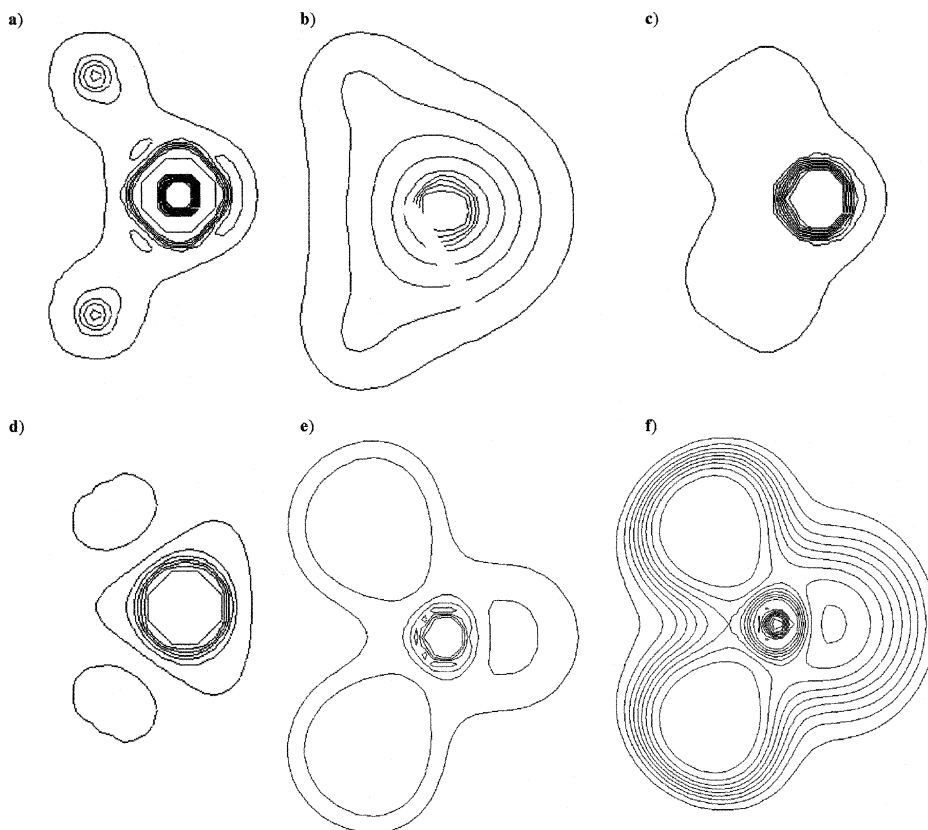


Fig. 1. For the water molecule the calculated plots of (a)  $-\nabla^2\rho$ ; (b)  $\theta_{\text{TF}}(\mathbf{r})$ ; (c)  $\theta_{\text{W}}(\mathbf{r})$ ; (d)  $\theta_{\text{KS}}(\mathbf{r})$ ; (e)  $[\theta_{\text{KS}}(\mathbf{r}) - \theta_{\text{W}}(\mathbf{r})]/\theta_{\text{TF}}(\mathbf{r})$ ; (f) ELF, in au

and entropy densities for the following kinetic energy densities [31,32] which reproduce the global kinetic energy, provide satisfactory local behaviour and acceptable functional derivatives:

$$t_1 = t_{\text{TF}} + \frac{1}{9}t_{\text{W}}, \quad (20)$$

$$t_2 = t_1 - \frac{1}{4}\nabla^2\rho(\mathbf{r}), \quad (21)$$

and

$$t_3 = t_1 - \frac{1}{8}\nabla^2\rho(\mathbf{r}). \quad (22)$$

The Laplacian of the electron density appearing in the two last equations by itself plays an important role in the understanding of chemical reactivity [27].

### 3. Results and discussion

The density and KS orbitals for the water molecule have been generated from a B3LYP calculation with a 6-311G\*\* basis set. The B3LYP method consists

of a hybrid exchange-correlation functional which is characterized by the inclusion of part of the Hartree–Fock exchange calculated with the KS orbitals [28,29]. All the calculations were done using the GAUSSIAN 94 program [30].

Fig. 1 presents the spatial profiles (contour plots) of the negative of the Laplacian of the density, TF, W and KS temperatures,  $(\theta_{\text{KS}} - \theta_{\text{W}})/\theta_{\text{TF}}$  and the ELF. In all these plots, molecular symmetry is well preserved. Two islands characterizing the positions of the hydrogen nuclei are reproduced in the Laplacian of the density  $\theta_{\text{KS}}$ ,  $(\theta_{\text{KS}} - \theta_{\text{W}})/\theta_{\text{TF}}$  and ELF plots. The magnitude of the local temperature is generally high near the nuclear sites, as is expected from the stability of the molecule. Electrons near the nuclear sites have a very high kinetic energy. Note that the Laplacian of the density goes to much higher values near the nuclear sites. The strikingly similar topography of  $(\theta_{\text{KS}} - \theta_{\text{W}})/\theta_{\text{TF}}$  and ELF suggests that this thermodynamic quantity can be used in analyzing chemical bonding in the same way as has

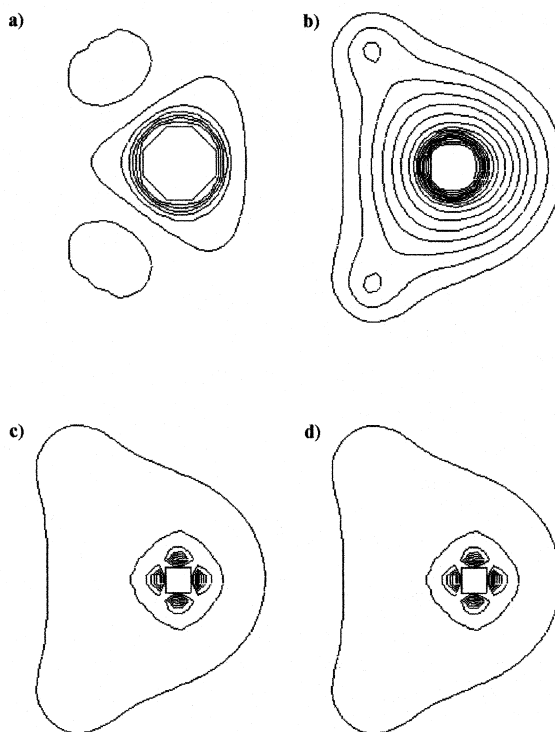


Fig. 2. For the water molecule the plots of (a)  $\theta_{\text{KS}}(\mathbf{r})$ ; (b)  $\theta_1(\mathbf{r})$ ; (c)  $\theta_2(\mathbf{r})$ ; (d)  $\theta_3(\mathbf{r})$ .

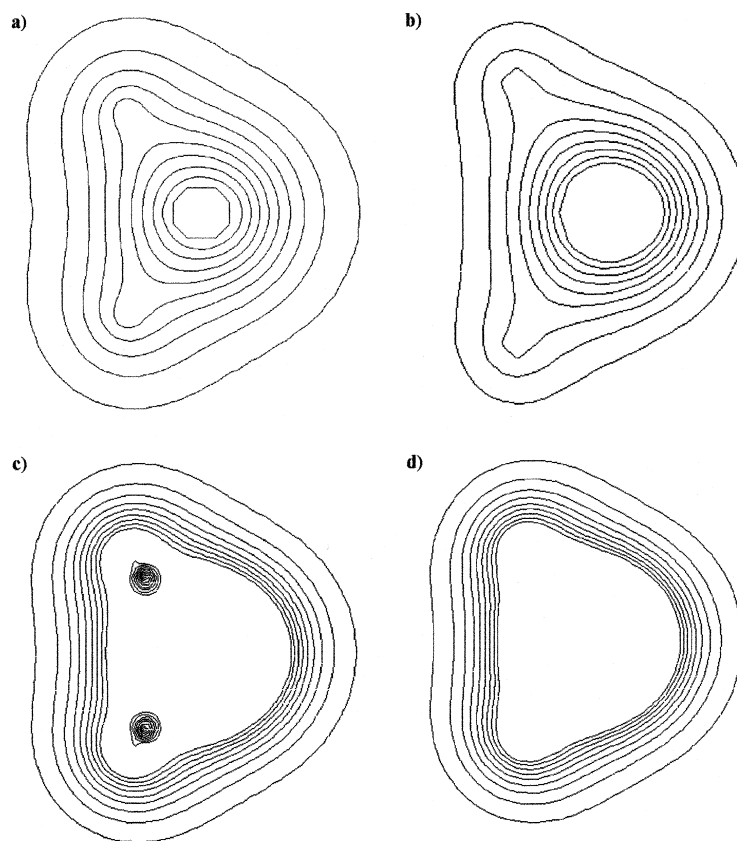


Fig. 3. For the water molecule the plots of (a)  $f(r)$ ; (b)  $\rho(r)$ ; (c)  $s_W(r)/k_B$ ; (d)  $s_{KS}(r)/k_B$ .

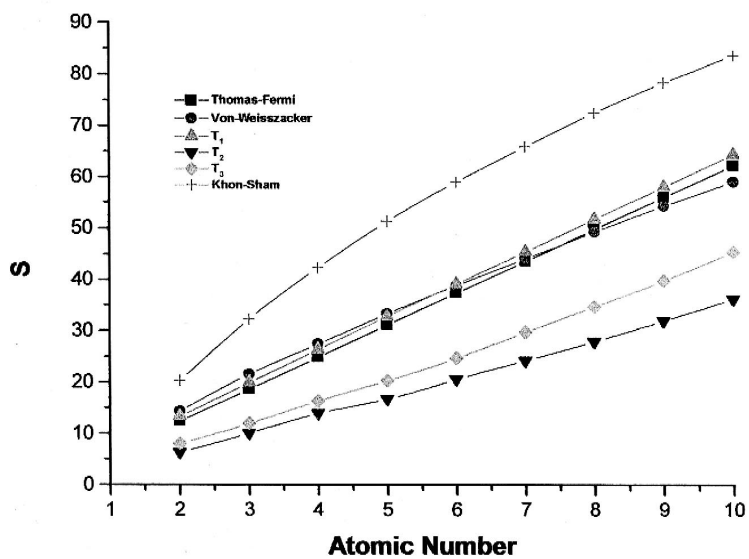


Fig. 4. Global entropies for the atoms He to Ne in units of  $k_B$ .

Table 1

Global entropies for atoms using various kinetic energy density definitions (in units of  $k_B$ ). For the definition of the different kinetic energy densities, see the text

| Atom | $S_{TF}$ | $S_W$ | $S_I$ | $S_2$ | $S_3$ | $S_{KS}$ |
|------|----------|-------|-------|-------|-------|----------|
| He   | 12.46    | 14.41 | 13.32 | 6.34  | 8.09  | 14.38    |
| Li   | 18.69    | 21.51 | 19.87 | 10.11 | 12.02 | 23.16    |
| Be   | 24.92    | 27.42 | 26.35 | 13.95 | 16.40 | 31.36    |
| B    | 31.15    | 33.29 | 32.74 | 16.81 | 20.37 | 39.51    |
| C    | 37.38    | 38.83 | 39.11 | 20.62 | 24.77 | 47.44    |
| N    | 43.61    | 44.12 | 45.45 | 24.32 | 29.76 | 55.34    |
| O    | 49.84    | 49.33 | 51.79 | 27.98 | 34.72 | 63.38    |
| F    | 56.08    | 54.30 | 58.11 | 31.99 | 39.84 | 71.30    |
| Ne   | 62.31    | 59.12 | 64.43 | 36.24 | 45.47 | 79.19    |

been done using ELF [15]. The local temperatures associated with  $t_1$ ,  $t_2$  and  $t_3$  are given in Fig. 2 and are compared with the KS temperature. Only the temperature associated with  $t_1$  shows the presence of

the hydrogen atoms. The values of the temperatures corresponding to  $t_2$  and  $t_3$  are clearly dominated by the Laplacian of the density.

The local behaviour of the Fukui function and different entropy densities in units of  $k_B$  are depicted in Fig. 3. The Fukui function calculated as  $|\phi_{HOMO}|^2$  mimicks the topography of the density which also is the case with all the entropy densities,  $s_x(r)$ ;  $x = TF, W, KS$ . The TF entropy density is not shown because it is almost identical to the KS entropy density. If we compare the contour plots of these entropies with that of ELF it becomes evident that they are grossly similar. Only the W entropy density reproduces the local islands near the nuclear sites which may be considered to be a ramification of the fact that  $t_W(\rho(r))$  reproduces the exact kinetic energy density near the nucleus [31,32].

In Fig. 4 and Table 1, we present the global entropies in units of  $k_B$  for some atoms. It is clear

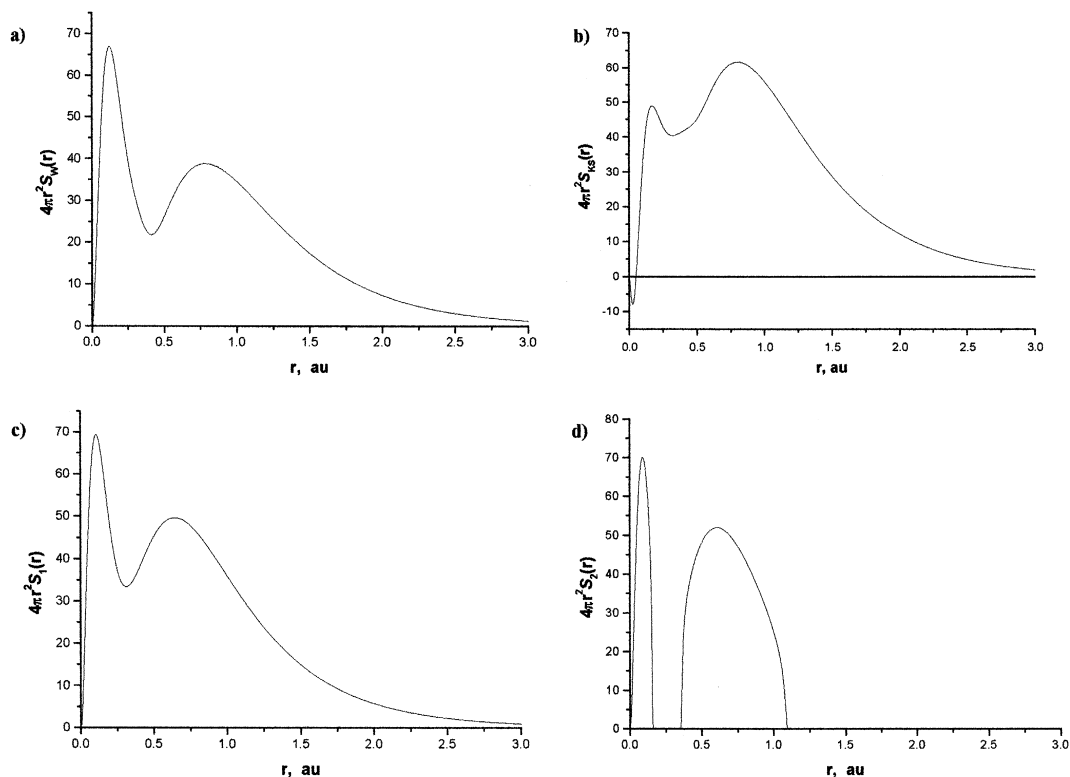


Fig. 5. Radial distributions of the local entropies for the neon atom: (a)  $4\pi r^2 \rho$ ; (b)  $4\pi r^2 s_W/k_B$ ; (c)  $4\pi r^2 s_{KS}/k_B$ ; (d)  $4\pi r^2 s_1/k_B$ ; (e)  $4\pi r^2 s_2/k_B$ , in au

that all of them show a similar trend. They increase with atomic number, and they are very similar to the ones calculated in Ref. [20]. The absolute  $S$  values are much higher than the softness values but it is expected that a proportionality between them exists. In Fig. 5, the radial distributions of the local entropies for the neon atom are shown. The TF local entropy is just the density times a constant. Therefore, it is not plotted. It is interesting to note that the  $W$  as well as the  $t_1$  local entropies very closely follow the density plot. This is a consequence of the similar behaviour of the local TF kinetic energy density and the  $W$  and  $t_1$  kinetic energy densities. On the other hand, the KS local entropy presents a different behaviour becoming negative near the nucleus and decaying more slowly at a larger distance than the others. Since the local entropies using  $t_2$  and  $t_3$  are very similar to each other, only the one generated by  $t_2$  is shown. They are clearly dominated by the Laplacian term. The atomic shell structure is clearly manifested in all these plots. It is interesting to note that Nagy and Parr [20] favored  $t_{KS}$  as determining local temperature and entropy. They also pointed out the relationship of the local temperature with the average local ionization energy introduced by Politzer et al. [33].

#### 4. Conclusions

In this Letter, it has been shown that the most important quantities introduced in the local thermodynamic description of a molecule within density functional theory can be calculated and analyzed. It has been shown that the local temperatures and the associated entropy densities are closely related to the electron localization function, ELF, and some of them can be used as bonding and reactivity indices. The calculated atomic global entropies show similar trends as the atomic number increases.

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