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REGULAR ARTICLE

Local hardness: a critical account

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Abstract This paper gives a critical account on the present status of the local hardness. We analyze the behavior of hardness related global, local, and nonlocal properties, paying particular attention to local hardness. Although this reactivity index has become very useful in predicting the regioselectivity of chemical reactions, the lack of a rigorous definition in the literature has shown that different approximations can yield different and sometimes contradictory conclusions. The present paper tries to provide insights into this controversial issue, starting from an approximate model of the hardness kernel and analyzing the features of the different models to evaluate the local and global hardnesses.

Keywords Density functional theory (DFT) · Conceptual DFT · Hardness · Hardness kernel · Local hardness

1 Introduction

Conceptual density functional theory (CDFT) [1–3] has been quite successful in providing rigorous quantitative definitions for popular qualitative chemical concepts like electronegativity [4], hardness [5,6], and electrophilicity [7,8] as well as theoretical bases for the associated electronic structure principles such as the electronegativity equalization principle [9–11], the hard-soft acid-base principle [6,12–14], the maximum hardness principle [15–18], etc. The central quantities of the CDFT are the response functions and they can be split up into three general groups: global, local, and nonlocal [1–3].

The global reactivity descriptors are response functions defined for the whole system (atom/ion/molecule/solid) like the electronegativity (χ) [19], chemical potential (μ) [19], global hardness (η) [20], global softness (S) [20], and electrophilicity (ω) [8], which are respectively defined as

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

$$\eta = \frac{1}{S} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})}, \text{ and} \tag{2}$$

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}, \tag{3}$$

where E, N, and $v(\vec{r})$ are the electronic energy, number of electrons, and external potential, respectively. The chemical potential has also been written as the Lagrangian multiplier in the Euler equation of the Hohenberg-Kohn equations

$$\mu = \left(\frac{\delta E}{\delta \rho(\vec{r})}\right)_{v(\vec{r})}. \tag{4}$$

In order to know the site selectivity in a molecule through the behavior of individual atomic sites various local quantities have been defined, e.g., electronic density, Fukui function, local hardness, local softness, and local electrophilicity. Of course, the most important of them is the electronic density, $\rho(\vec{r})$ itself, defined as follows:

$$\rho(\vec{r}) = \left(\frac{\delta E}{\delta v(\vec{r})}\right)_N. \tag{5}$$

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The Fukui function, $f(\vec{r})$ [21,22], has been defined to make a connection between the frontier orbital theory and DFT:

$$f(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\delta\mu}{\delta v(\vec{r})}\right)_N. \tag{6}$$

A local version of softness, $s(\vec{r})$ [23], can also be obtained as

$$s(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial\mu}\right)_{v(\vec{r})} = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{v(\vec{r})}\left(\frac{\partial N}{\partial\mu}\right)_{v(\vec{r})} = f(\vec{r})S. \tag{7}$$

Therefore $s(\vec{r})$ integrates to S as $f(\vec{r})$ is normalized to unity. In other words $f(\vec{r})$ redistributes the global softness to various parts of the molecule and the global reactivity stems from the corresponding local behavior, in conformity with the chemical intuition. In the similar spirit a local electrophilicity, $\omega(\vec{r})$, may be defined as [24,25]

$$\omega(\vec{r}) = \omega f(\vec{r}) \tag{8}$$

and applying the condensed-to-atom variant [26] of $f(\vec{r})$ *viz.*, f_k^α (α =+, −, and 0 referring to nucleophilic, electrophilic, and radical attacks, respectively) for the kth atom in a molecule, one can have s_k^α and ω_k^α.

Defining a local version of hardness is, however, not that straightforward and the lack of a rigorous definition has produced a decrease of its popularity. The first definition of local hardness, $\eta(\vec{r})$, has been [27,28]

$$\eta(\vec{r}) = \frac{1}{N}\int \frac{\delta^2 F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}\rho\left(\vec{r}\,'\right)d\vec{r}\,', \tag{9}$$

where $F\left[\rho(\vec{r})\right]$ is the Hohenberg–Kohn universal functional [29]. Also, as was pointed out some time ago [27]

$$d(E - N\mu) = -\iint \frac{\delta^2 F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}\rho\left(\vec{r}\,'\right)\delta\rho(\vec{r})d\vec{r}d\vec{r}\,'. \tag{10}$$

Combining Eqs. (9) and (10), one obtains

$$dE - \mu dN - Nd\mu = -N\int \eta(\vec{r})\delta\rho(\vec{r})d\vec{r}. \tag{11}$$

Considering now the Taylor series function expansion of the E and μ in terms of $v(\vec{r})$ and N

$$\begin{aligned} dE &= \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} dN + \int\left(\frac{\delta E}{\delta v(\vec{r})}\right)_N \delta v(\vec{r})d\vec{r} \\ &= \mu dN + \int \rho(\vec{r})\delta v(\vec{r})d\vec{r} \quad \text{and} \end{aligned} \tag{12}$$

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} dN + \int\left(\frac{\delta \mu}{\delta v(\vec{r})}\right)_N \delta v(\vec{r})d\vec{r} \\ &= \eta dN + \int f(\vec{r})\delta v(\vec{r})d\vec{r}. \end{aligned} \tag{13}$$

Combining Eqs. (12) and (11), one gets

$$d\mu = \int \eta(\vec{r})\delta\rho(\vec{r})d\vec{r} + \frac{1}{N}\int \rho(\vec{r})\delta v(\vec{r})d\vec{r}. \tag{14}$$

Thus, analyzing Eq. (14) it is possible to deduce another expression for $\eta(\vec{r})$ [27]

$$\eta(\vec{r}) = \left(\frac{\delta\mu}{\delta\rho(\vec{r})}\right)_{v(\vec{r})}. \tag{15}$$

Comparing Eq. (14) with Eq. (13) and using the definition of the Fukui function ($\delta\rho(\vec{r}) = f(\vec{r})dN$), one deduces the relationship between global and local hardness

$$\eta = \int \eta(\vec{r})f(\vec{r})d\vec{r}. \tag{16}$$

Looking at Eqs. (7) and (16), it is easy to deduce the connection between $\eta(\vec{r})$ and $s(\vec{r})$

$$\int \eta(\vec{r})s(\vec{r})d\vec{r} = 1. \tag{17}$$

Contrary to $s(\vec{r})$ or $\omega(\vec{r})$, Eqs. (7) and (8), the simple integration of $\eta(\vec{r})$ does not yield the corresponding global quantity, η. Therefore $\eta(\vec{r})$ cannot be identified as η distributed over the various parts of the molecule. Actually $s(\vec{r})$ should be considered to be an electronic reactivity index (a measure of electron fluctuations [23]), whereas $\eta(\vec{r})$ should be considered as a nuclear reactivity index [30]. Both $\eta(\vec{r})$ and $s(\vec{r})$ cannot be represented in an unambiguous way within the same representation. While the former is better explained in the isomorphic ensemble $\left(F\left[N, \rho(\vec{r})\right]\right)$, the grand canonical ensemble $\left(\Omega\left[\mu, v(\vec{r})\right]\right)$ is a better option for the latter [31].

Finally, the nonlocal reactivity indices are descriptors that depend on more than one position of the space, e.g., softness kernel, hardness kernel, and linear response function. The softness kernel, $s\left(\vec{r}, \vec{r}\,'\right)$, provides the following response [32]

$$s\left(\vec{r}, \vec{r}\,'\right) = -\frac{\delta\rho(\vec{r})}{\delta u(\vec{r}\,')}; \quad u\left(\vec{r}\,'\right) = v\left(\vec{r}\,'\right) - \mu \tag{18}$$

and it is connected with the linear response function, $\chi\left(\vec{r}, \vec{r}\,'\right)$, with the following relationship [32]

$$\chi\left(\vec{r}, \vec{r}\,'\right) = \left(\frac{\delta\rho(\vec{r})}{\delta v(\vec{r}\,')}\right)_N = -s\left(\vec{r}, \vec{r}\,'\right) + \frac{s(\vec{r})s\left(\vec{r}\,'\right)}{S}. \tag{19}$$

The "inverse" of the softness kernel is the hardness kernel, $\eta\left(\vec{r}, \vec{r}\,'\right)$, defined as

$$\eta\left(\vec{r}, \vec{r}\,'\right) = -\frac{\delta\mu(\vec{r})}{\delta\rho(\vec{r}\,')} = \frac{\delta^2 F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')}, \tag{20}$$

and the link connecting both nonlocal properties is

$$\int s\left(\vec{r}, \vec{r}\,'\right)\eta\left(\vec{r}\,', \vec{r}\,''\right)d\vec{r}\,' = \delta\left(\vec{r} - \vec{r}\,''\right). \tag{21}$$

In the present article we will analyze the behaviour of the hardness related global, local, and nonlocal properties, paying particular attention to $\eta(\vec{r})$, due to its controversial character in the literature [33–36]. Although this reactivity index has become very useful predicting the regioselectivity of chemical reactions [37–51], the lack of a rigorous definition has the consequence that different approximations can yield different and sometimes contradictory conclusions [33–36,52–60]. The present article will try to give insight into this controversial issue, starting from an approximate model of the hardness kernel and analyzing the features of the different models to evaluate the local and global hardnesses.

2 Discussion

One of the main problems attributed to the expression of the hardness kernel in Eq. (15) is the dependency between the density and the external potential [33,43,58]. Note that the well-known expression [see Eq. (4)] for the chemical potential is formally analogous to Eq. (15). Another problem of Eq. (15) is that it cannot be easily evaluated, stressing the relevance of the definition of the local hardness given in Eq. (9). However this expression also has been a source of controversy, because the $\rho(\vec{r})/N$ of the Eq. (9) can be replaced by any normalized function $\int \lambda(\rho(\vec{r}))d\vec{r} = 1$ [33,52,61], e.g., the Fukui function

$$\eta(\vec{r}) = \int \frac{\delta^2 F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} f\left(\vec{r}'\right)d\vec{r}'. \tag{22}$$

Then, two computable expressions of $\eta(\vec{r})$ are given, Eqs. (9) and (22), and two expressions for η are obtained applying these two definitions of $\eta(\vec{r})$ to Eq. (16). Finally Harbola et al. [33] propose that if the exact $F\left[\rho(\vec{r})\right]$ is used in Eq. (22), $\eta(\vec{r})$ is constant and equal to η

$$\eta = \eta(\vec{r}) = \int \frac{\delta^2 F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} f\left(\vec{r}'\right)d\vec{r}'. \tag{23}$$

In conclusion, following the literature, given a model for the hardness kernel, two [Eqs. (9) and (22)] and three [Eqs. (9) and (22) applied to Eq. (16) and Eq. (23)] definitions of the local and global hardness are obtained, respectively. To analyze the different features of these $\eta(\vec{r})$ and η definitions, a model of $\eta\left(\vec{r}, \vec{r}'\right)$ is required, which will be evaluated using the following approximated Hohenberg–Kohn universal function

$$\begin{aligned} F\left[\rho(\vec{r})\right] = {} & T_0\left[\rho(\vec{r})\right] + T_2\left[\rho(\vec{r})\right] + J\left[\rho(\vec{r})\right] + E_X\left[\rho(\vec{r})\right] \\ & + E_C\left[\rho(\vec{r})\right], \end{aligned} \tag{24}$$

where $T_0\left[\rho(\vec{r})\right]$ is the Thomas–Fermi functional [62,63],

$$T_0\left[\rho(\vec{r})\right] = C_K \int \rho^{5/3}(\vec{r})d\vec{r}; \quad C_K = \frac{3}{10}\left(3\pi^2\right)^{2/3}, \tag{25}$$

$T_2\left[\rho(\vec{r})\right]$ is the 1/9th of the Weizsäcker functional, $T_w\left[\rho(\vec{r})\right]$ [64],

$$T_2\left[\rho(\vec{r})\right] = \frac{1}{72}\int \frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}d\vec{r}, \tag{26}$$

$J[\rho]$ is the classical Coulomb repulsion energy,

$$J\left[\rho(\vec{r})\right] = \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho\left(\vec{r}'\right)}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}', \tag{27}$$

$E_X\left[\rho(\vec{r})\right]$ is the Dirac exchange functional [65],

$$E_X\left[\rho(\vec{r})\right] = -C_X \int \rho^{4/3}(\vec{r})d\vec{r}; \quad C_X = \frac{3}{4\pi}\left(3\pi^2\right)^{1/3}, \tag{28}$$

and $E_C\left[\rho(\vec{r})\right]$ is a Wigner-type local correlation functional [66],

$$E_C\left[\rho(\vec{r})\right] = -\int \frac{0.0466\rho^{4/3}(\vec{r})}{1+0.458\rho^{1/3}(\vec{r})}d\vec{r}. \tag{29}$$

Using this approximate model of $F\left[\rho(\vec{r})\right]$ in Eq. (20), one gets the following $\eta\left(\vec{r}, \vec{r}'\right)$ [for a summary of functional derivatives see Appendix A of the Ref. [1], while a detailed derivation of the Weizsäcker functional term can be found in the Appendix]:

$$\begin{aligned} \eta\left(\vec{r}, \vec{r}'\right) = {} & \frac{2}{9}\rho^{-1/3}\left(\vec{r}'\right)\delta\left(\vec{r}'-\vec{r}\right) \\ & \times\left[5C_K - 2C_X\rho^{-1/3}\left(\vec{r}'\right) \right. \\ & \left. -0.0466\frac{0.458+2\rho^{-1/3}\left(\vec{r}'\right)}{\left(1+0.458\rho^{1/3}\left(\vec{r}'\right)\right)^3}\right] \\ & +\frac{1}{36}\left[\left(-\frac{\left|\nabla_{\vec{r}'}\rho\left(\vec{r}'\right)\right|^2}{\rho^3\left(\vec{r}'\right)} + \frac{\nabla^2_{\vec{r}'}\rho\left(\vec{r}'\right)}{\rho^2\left(\vec{r}'\right)}\right)\delta\left(\vec{r}'-\vec{r}\right)\right. \\ & \left. +\frac{\nabla_{\vec{r}'}\rho\left(\vec{r}'\right)}{\rho^2\left(\vec{r}'\right)}\nabla\delta\left(\vec{r}'-\vec{r}\right) - \frac{\nabla^2_{\vec{r}'}\delta\left(\vec{r}'-\vec{r}\right)}{\rho\left(\vec{r}'\right)}\right] \\ & +\frac{1}{|\vec{r}-\vec{r}'|}, \end{aligned} \tag{30}$$

where the first square bracket contains the hardness kernel contributions from the Thomas-Fermi, Dirac, and Wigner functions, while the second square bracket is the contribution of the 1/9th of the Weizsäcker functional. Finally, the remaining term of Eq. (30) is the Coulomb contribution. Then, two $\eta(\vec{r})$ are obtained employing the previous result in Eqs. (9)

$$\begin{aligned} \eta(\vec{r}) = {} & \frac{2}{9N}\rho^{1/3}(\vec{r}) \\ & \times\left[5C_K\rho^{1/3}(\vec{r}) - 2C_X - 0.0466\frac{0.458\rho^{1/3}(\vec{r})+2}{\left(1+0.458\rho^{1/3}(\vec{r})\right)^3}\right] \\ & +\frac{1}{N}\int \frac{\rho\left(\vec{r}'\right)}{|\vec{r}-\vec{r}'|}d\vec{r}' \end{aligned} \tag{31}$$

and (22) [52]

$$\begin{aligned}\eta(\vec{r}) = {}& \frac{2}{9} f(\vec{r})\rho^{-1/3}(\vec{r})\\ &\times\left[5C_K - 2C_X\rho^{-1/3}(\vec{r}) - 0.0466\frac{0.458+2\rho^{-1/3}(\vec{r})}{\left(1+0.458\rho^{1/3}(\vec{r})\right)^3}\right]\\ &-\frac{1}{36\rho(\vec{r})}\nabla\left[\rho(\vec{r})\nabla\left(\frac{f(\vec{r})}{\rho(\vec{r})}\right)\right] + \int \frac{f(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|}d\vec{r}'.\end{aligned} \tag{32}$$

The Eqs. (31) and (32) can be written in a more compact way as

$$\begin{aligned}\eta(\vec{r})\left[\rho(\vec{r}')/N\right] \cong {}& \eta_{T0}(\vec{r})\left[\rho(\vec{r}')/N\right]\\ &+\eta_{Ex}(\vec{r})\left[\rho(\vec{r}')/N\right]\\ &+\eta_{Ec}(\vec{r})\left[\rho(\vec{r}')/N\right] + \eta_J(\vec{r})\left[\rho(\vec{r}')/N\right] \quad \text{and}\end{aligned} \tag{33}$$

$$\begin{aligned}\eta(\vec{r})\left[f(\vec{r}')\right] \cong {}& \eta_{T0}(\vec{r})\left[f(\vec{r}')\right] + \eta_{T2}(\vec{r})\left[f(\vec{r}')\right]\\ &+\eta_{Ex}(\vec{r})\left[f(\vec{r}')\right]+\eta_{Ec}(\vec{r})\left[f(\vec{r}')\right]+\eta_J(\vec{r})\left[f(\vec{r}')\right],\end{aligned} \tag{34}$$

where the expression between brackets is the normalized function used to evaluate the local hardness. It is interesting to note that the right hand sides of Eqs. (31) and (32) are local and according to Harbola et al. [33] when the exact functional $F\left[\rho(\vec{r})\right]$ is used in Eq. (22), the equivalent of the local hardness of Eq. (32) becomes constant in all the positions of the space and equal to the global hardness. This equality of η and $\eta(\vec{r})$ indicates a hardness equalization [33,67] a la Sanderson [9–11,19] (electronegativity equalization) and it implies a geometric mean principle for hardness [67,68], a companion to the principles of geometric mean of electronegativities [9–11,19] and arithmetic mean of softnesses of the isolated atoms [69]. As far as we know, the few calculations of local and global hardnesses using these methodologies reported in the literature [27,32,36,61,70–72] have shown that the major contribution is provided by the classical Coulomb repulsion term, although the kinetic term for some species can become as important as the Coulombic [70,71]. Since the exact functional form for $F\left[\rho(\vec{r})\right]$ is unknown till date, a stringent test for the goodness of an approximate $F\left[\rho(\vec{r})\right]$ may be envisaged through the constancy of $\eta(\vec{r})$ especially when applied to the ground states [33].

On the other hand, another important difference between these two $\eta(\vec{r})$ is that the contribution of the 1/9th of the Weizsäcker functional in Eq. (31) becomes [for a detailed derivation of Eqs. (35) and (36) see the Appendix]

$$\int \frac{\delta^2 T_2\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\rho(\vec{r}')d\vec{r}' = 0, \tag{35}$$

while in Eq. (32) it is

$$\int \frac{\delta^2 T_2\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} f(\vec{r}')d\vec{r}' = -\frac{1}{36}\frac{1}{\rho(\vec{r})}\nabla\left[\rho(\vec{r})\nabla\left(\frac{f(\vec{r})}{\rho(\vec{r})}\right)\right]. \tag{36}$$

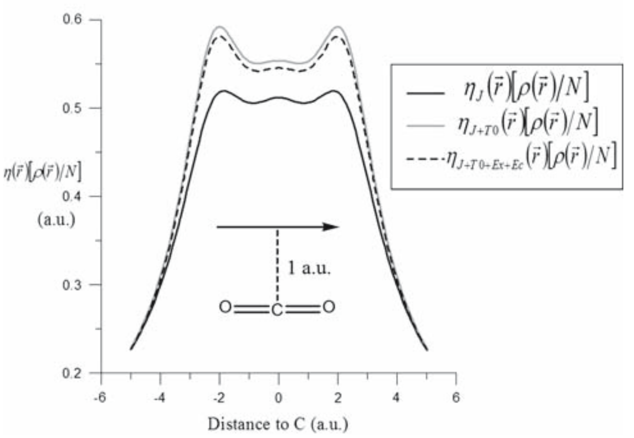

Fig. 1 Local hardness profile parallel to the internuclear axis at a distance of 1 a.u. of the CO_2 molecule with $\eta(\vec{r})$ evaluated using Eq. (31) at B3LYP/6-311++G(2d,2p) level

which will be in general not zero. However, the above quantity is expected to be small as the homogeneous term [52] $(\rho(\vec{r})/N)$ in $f(\vec{r})$ is the dominating term. Other inhomogeneity (gradient) terms are often small [52]. This difference between Eqs. (33) and (34) stresses the relevance of using different normalized functions in the local hardness. In addition, it is worth noting that other authors have noticed that the contribution arising from the independent-fermion kinetic-energy functional to the local hardness is null [36,73,74].

To illustrate some of these points the Figs. 1 and 2 display the $\eta(\vec{r})$ profiles using the Eqs. (31) and (32), respectively, parallel to and at a distance of 1 a.u. from the internuclear axis of the CO_2 molecule. In these profiles the density of the highest occupied molecular orbital (HOMO), $\rho_{\mathrm{HOMO}}(\vec{r})$, has been used as an approximation of the Fukui function. Firstly, it is important to remark that both profiles show the Coulombic contribution as the dominant term and that the Thomas–Fermi contribution is relevant and the remaining terms are

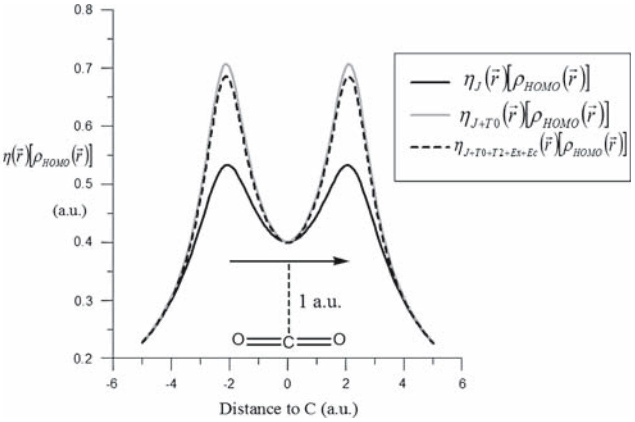

Fig. 2 Local hardness profile parallel to the internuclear axis at a distance of 1 a.u. of the CO_2 molecule with $\eta(\vec{r})$ evaluated using Eq. (32) at B3LYP/6-311++G(2d,2p) level and with $\rho_{\mathrm{HOMO}}(\vec{r})$ as approximation of $f(\vec{r})$

smaller and can be neglected. In addition, both profiles show that the oxygen regions are harder than the carbon region, but only $\eta(\vec{r})$ of Eq. (32) presents a minimum of local hardness on the carbon. On the other hand, one can see in Fig. 1 that the difference of $\eta(\vec{r})$ between the oxygen and the carbon region is small, where chemical intuition would suggest that the change in hardness must be larger (η values of the carbon and oxygen are 10.0 and 12.2 eV, [6] respectively). In contrast, the $\eta(\vec{r})$ profile of Eq. (32) displays a clear difference between the oxygen regions and the carbon one. These two figures clearly pinpoint the importance of the normalized function in order to obtain reliable local hardness profiles, indicating that the inhomogeneity (gradient) terms can be as essential as the homogeneous term, so that $\rho(\vec{r})/N$ is not a good approximation to $f(\vec{r})$. Finally, it is worth noting that $\eta(\vec{r})$ of Fig. 2 is quite far from being a constant in all positions of space, although the exact and unknown functional $F[\rho(\vec{r})]$ has not been used in the Eq. (22).

Furthermore, combining Eqs. (31) and (32) with Eq. (16), one obtains two global hardness expressions

$$\eta = \frac{2}{9N}\int f(\vec{r})\rho^{1/3}(\vec{r})\left[5C_K\rho^{1/3}(\vec{r}) - 2C_X - 0.0466\frac{0.458\rho^{1/3}(\vec{r})+2}{\left(1+0.458\rho^{1/3}(\vec{r})\right)^3}\right]d\vec{r} + \frac{1}{N}\iint\frac{f(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,' \tag{37}$$

and

$$\eta = \frac{2}{9}\int f^2(\vec{r})\rho^{-1/3}(\vec{r})\left[5C_K - 2C_X\rho^{-1/3}(\vec{r}) - 0.0466\frac{0.458+2\rho^{-1/3}(\vec{r})}{\left(1+0.458\rho^{1/3}(\vec{r})\right)^3}\right]d\vec{r} - \int\frac{f(\vec{r})}{36\rho(\vec{r})}\nabla\left[\rho(\vec{r})\nabla\left(\frac{f(\vec{r})}{\rho(\vec{r})}\right)\right]d\vec{r} + \iint\frac{f(\vec{r})f(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,'. \tag{38}$$

Finally, the last expression of global hardness will be considered by inserting $\eta(\vec{r})$ of Eq. (9) in Eq. (16), but changing $f(\vec{r})$ of Eq. (16) for the homogenous term, $\rho(\vec{r})/N$. Applying the hardness kernel of Eq. (30), one obtains

$$\eta = \frac{2}{9N^2}\int f(\vec{r})\rho^{4/3}(\vec{r}) \times\left[5C_K\rho^{1/3}(\vec{r}) - 2C_X - 0.0466\frac{0.458\rho^{1/3}(\vec{r})+2}{\left(1+0.458\rho^{1/3}(\vec{r})\right)^3}\right]d\vec{r} + \frac{1}{N^2}\iint\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}d\vec{r}\,' \tag{39}$$

In a similar way for the Eqs. (31) and (32), these equations can be written in a more compact way as

$$\begin{aligned}\eta\left[f(\vec{r}),\rho(\vec{r}\,')/N\right] \cong{}& \eta_{T0}\left[f(\vec{r}),\rho(\vec{r}\,')/N\right] + \eta_{Ex}\left[f(\vec{r}),\rho(\vec{r}\,')/N\right] \\ &+ \eta_{Ec}\left[f(\vec{r}),\rho(\vec{r}\,')/N\right] + \eta_{J}\left[f(\vec{r}),\rho(\vec{r}\,')/N\right],\end{aligned} \tag{40}$$

$$\begin{aligned}\eta(\vec{r})\left[f(\vec{r}),f(\vec{r}\,')\right] \cong{}& \eta_{J}(\vec{r})\left[f(\vec{r}),f(\vec{r}\,')\right] + \eta_{T0}(\vec{r})\left[f(\vec{r}),f(\vec{r}\,')\right] + \eta_{T2}(\vec{r})\left[f(\vec{r}),f(\vec{r}\,')\right] \\ &+ \eta_{Ex}(\vec{r})\left[f(\vec{r}),f(\vec{r}\,')\right] + \eta_{EC}(\vec{r})\left[f(\vec{r}),f(\vec{r}\,')\right],\end{aligned} \tag{41}$$

and

$$\begin{aligned}\eta\left[\rho(\vec{r})/N,\rho(\vec{r}\,')/N\right] \cong{}& \eta_{T0}\left[\rho(\vec{r})/N,\rho(\vec{r}\,')/N\right] + \eta_{Ex}\left[\rho(\vec{r})/N,\rho(\vec{r}\,')/N\right] \\ &+ \eta_{Ec}\left[\rho(\vec{r})/N,\rho(\vec{r}\,')/N\right] + \eta_{J}\left[\rho(\vec{r})/N,\rho(\vec{r}\,')/N\right].\end{aligned} \tag{42}$$

These three expressions of global hardness look quite similar with the exceptions that different normalized functions $[\rho(\vec{r})/N$ and $f(\vec{r})]$ are used and that only the second one contains a contribution of (the 1/9th of) the Weizsäcker functional. In Table 1, Eqs. (37)–(39) are evaluated for six systems [a detailed explanation of the methodology used to calculate the integrals of the Eqs. (37)–(39) can be found in Ref. [72]], where it is worth noting that some of the features displayed in the local hardness profiles are recovered. For instance, the relevance of the Coulombic and Thomas–Fermi contributions and the crucial role of the selection of the normalized function in order to obtain accurate global hardnesses as it has been noticed by some of the present authors in a very recent article [71]. The $\eta\left[\rho(\vec{r})/N,\rho(\vec{r}\,')/N\right]$ approximation predicts that HCl, H_2S, and PH_3 are harder than HF, H_2O, and NH_3, respectively, which is absolutely contrary to the experimental hardness values and the chemical intuition. In contrast, $\eta\left[f(\vec{r}),\rho(\vec{r}\,')/N\right]$ and $\eta\left[f(\vec{r}),f(\vec{r}\,')\right]$ present very similar results and they correctly predict the hardness order for the selected molecules, although we consider the choice $\eta\left[f(\vec{r}),f(\vec{r}\,')\right]$ to be more consistent because it uses in both cases the same normalized function. Another point in favor of Eq. (16) combined with Eq. (22) is that the Eqs. (2) and (16) are connected using twice the chain rule in Eq. (2) and the fact that the electron-nucleus Coulombic attraction

Table 1 Calculated and experimental hardness for some representative molecules illustrating the relevance of the choice of the normalized function to obtain the global hardness. All values are in eV

Molecule	$\eta\left[\rho(\vec{r})/N, \rho(\vec{r})/N\right]^{a}$					$\eta\left[\rho_{\mathrm{HOMO}}(\vec{r}), \rho(\vec{r})/N\right]^{b}$					$\eta\left[\rho_{\mathrm{HOMO}}(\vec{r}), \rho_{\mathrm{HOMO}}(\vec{r})\right]^{c}$						
	η_J	η_{To}	η_{Ex}	η_{Ec}	η_{Total}	η_J	η_{To}	η_{Ex}	η_{Ec}	η_{Total}	η_J	η_{To}	η_{T2}	η_{Ex}	η_{Ec}	η_{Total}	η_{exp}^{d}
HF	30.25	27.56	−1.15	−0.02	56.65	24.24	6.96	−0.70	−0.02	30.48	22.60	8.49	0.43	−0.96	−0.03	30.54	22.0
HCl	35.37	39.84	−0.96	−0.01	74.24	16.18	2.49	−0.26	−0.01	18.39	13.42	2.83	0.16	−0.56	−0.02	15.83	16.0
H_2O	25.41	20.90	−0.98	−0.02	45.31	20.24	4.82	−0.58	−0.02	24.46	19.93	9.05	0.81	−1.23	−0.04	28.53	19.0
H_2S	32.07	34.52	−0.88	−0.01	65.70	14.17	1.88	−0.23	−0.01	15.82	12.44	3.31	0.28	−0.76	−0.03	15.23	12.4
NH_3	21.31	15.43	−0.84	−0.02	35.89	16.64	3.30	−0.48	−0.02	19.45	16.83	6.49	0.55	−1.09	−0.04	22.74	16.4
PH_3	28.94	29.62	−0.81	−0.01	57.73	12.44	1.52	−0.20	−0.01	13.75	11.36	2.81	0.23	−0.74	−0.03	13.63	12.0

[a] Hardness values calculated from Eq. (39) at B3LYP/6-311++G(2d,2p) level

[b] Hardness values calculated from Eq. (37) at B3LYP/6-311++G(2d,2p) level, where $\rho_{\mathrm{HOMO}}(\vec{r})$ has been used as approximation of $f(\vec{r})$

[c] Hardness values calculated from Eq. (38) at B3LYP/6-311++G(2d,2p) level, where $\rho_{\mathrm{HOMO}}(\vec{r})$ has been used as approximation of $f(\vec{r})$

[d] The experimental hardness has been evaluated using the approximation $I_{\mathrm{exp}} - A_{\mathrm{exp}}$, where I_{exp} and A_{exp} are the experimental vertical ionization and electron affinities obtained from Ref. [6]

energy depends linearly on $\rho(\vec{r})$ [70]

$$\begin{aligned}\eta &= \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})}\\ &= \iint \frac{\partial \rho(\vec{r})}{\partial N}\frac{\delta^2 E\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\frac{\partial\rho(\vec{r}')}{\partial N}d\vec{r}d\vec{r}'\\ &= \iint f(\vec{r})\frac{\delta^2 F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}f(\vec{r}')d\vec{r}d\vec{r}'\\ &= \int f(\vec{r})\eta(\vec{r})d\vec{r}.\end{aligned}$$

3 Conclusions

Various sources of confusion and misunderstanding concerning the definitions and the working equations of local hardness have been analyzed and put into perspective. Using a model for the hardness kernel including the Thomas–Fermi and 1/9th Weizsäcker kinetic energy functionals, the Dirac Exchange functional and a Wigner type correlation functional together with the classical Coulombic repulsion energy the relative merits of the various expressions for $\eta(\vec{r})$ and η are highlighted. It has been shown that the selection of a good normalized function is essential in order to obtain good local and global hardnesses. Then, taking into account the results of the present article we suggest that the preferred operational equation for $\eta(\vec{r})$ is the Eq. (22), while for η Eq. (16) combined with Eq. (22) is preferred.

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Appendix

Given a functional of the form

$$F\left[\rho(\vec{r})\right] = \int f\left(\vec{r}, \rho(\vec{r}), \nabla\rho(\vec{r}), \nabla^2\rho(\vec{r}), \ldots, \nabla^N\rho(\vec{r})\right)d\vec{r}, \tag{A.1}$$

its functional derivative can be evaluated as

$$\frac{\delta F\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})} = \sum_{i=0}^{N}(-1)^i\nabla^i \times\left(\frac{\partial f\left(\vec{r}, \rho(\vec{r}), \nabla\rho(\vec{r}), \nabla^2\rho(\vec{r}), \ldots, \nabla^N\rho(\vec{r})\right)}{\partial\left(\nabla^i\rho(\vec{r})\right)}\right). \tag{A.2}$$

For instance, in the case of the 1/9th of the Weizsäcker functional the first derivative becomes

$$\begin{aligned}\frac{\delta T_2\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})} &= \frac{1}{72}\left[-\frac{|\nabla\rho(\vec{r})|^2}{\rho^2(\vec{r})} - \nabla\left(2\frac{\nabla\rho(\vec{r})}{\rho(\vec{r})}\right)\right]\\ &= \frac{1}{72}\left[\frac{|\nabla\rho(\vec{r})|^2}{\rho^2(\vec{r})} - 2\frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})}\right].\end{aligned} \tag{A.3}$$

To evaluate the contribution of the 1/9th of the Weizsäcker functional in $\eta\left(\vec{r}, \vec{r}'\right)$ it is necessary to remember that any function can be written in terms of a functional using the Dirac delta function

$$\frac{\delta^2 T_2\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} = \frac{1}{72}\frac{\delta}{\delta\rho(\vec{r}')}\int\left[\frac{\left|\nabla_{\vec{r}'}\rho(\vec{r}')\right|^2}{\rho^2(\vec{r}')} - 2\frac{\nabla^2_{\vec{r}'}\rho(\vec{r}')}{\rho(\vec{r}')}\right] \times\delta\left(\vec{r}' - \vec{r}\right)d\vec{r}', \tag{A.4}$$

applying again Eq. (A.2), one finds that

$$\frac{\delta^2 T_2\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')} = \frac{1}{72}\Bigg[-2\frac{\left|\nabla_{\vec{r}\,'}\rho\left(\vec{r}\,'\right)\right|^2}{\rho^3\left(\vec{r}\,'\right)}\delta\left(\vec{r}\,'-\vec{r}\right) -2\nabla_{\vec{r}\,'}\left(\frac{\nabla_{\vec{r}\,'}\rho\left(\vec{r}\,'\right)}{\rho^2\left(\vec{r}\,'\right)}\delta\left(\vec{r}\,'-\vec{r}\right)\right) + 2\frac{\nabla^2_{\vec{r}\,'}\rho\left(\vec{r}\,'\right)}{\rho^2\left(\vec{r}\,'\right)}\delta\left(\vec{r}\,'-\vec{r}\right) - 2\nabla^2_{\vec{r}\,'}\left(\frac{\delta\left(\vec{r}\,'-\vec{r}\right)}{\rho\left(\vec{r}\,'\right)}\right)\Bigg], \tag{A.5}$$

which results finally

$$\frac{\delta^2 T_2\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})\delta\rho(\vec{r}\,')} = \frac{1}{36}\Bigg[\left(-\frac{\left|\nabla_{\vec{r}\,'}\rho\left(\vec{r}\,'\right)\right|^2}{\rho^3\left(\vec{r}\,'\right)} + \frac{\nabla^2_{\vec{r}\,'}\rho\left(\vec{r}\,'\right)}{\rho^2\left(\vec{r}\,'\right)}\right)\delta\left(\vec{r}\,'-\vec{r}\right) + \frac{\nabla_{\vec{r}\,'}\rho\left(\vec{r}\,'\right)}{\rho^2\left(\vec{r}\,'\right)}\nabla\delta\left(\vec{r}\,'-\vec{r}\right) - \frac{\nabla^2_{\vec{r}\,'}\delta\left(\vec{r}\,'-\vec{r}\right)}{\rho\left(\vec{r}\,'\right)}\Bigg]. \tag{A.6}$$

To apply the result of the Eq. (A.6) in Eqs. (9) and (22), it is necessary to remember the property of the derivatives of the Dirac's delta function (See http://mathworld.wolfram.com/DeltaFunction.html)

$$\int\left[x^m f(x)\right]\delta^n(x)dx = (-1)^n\int\frac{\partial^n\left[x^m f(x)\right]}{\partial x^n}\delta(x)dx. \tag{A.7}$$

Then, the contribution of the 1/9th Weizsäcker functional in Eq. (9) becomes

$$\frac{1}{36}\left[-\frac{|\nabla\rho(\vec{r})|^2}{\rho^2(\vec{r})} + \frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})} - \nabla\left(\frac{\nabla\rho(\vec{r})}{\rho(\vec{r})}\right) - 0\right] = 0. \tag{A.8}$$

In contrast, in Eq. (22) one obtains

$$\frac{1}{36}\left[-\frac{|\nabla\rho(\vec{r})|^2 f(\vec{r})}{\rho^3(\vec{r})} + \frac{\nabla^2\rho(\vec{r})f(\vec{r})}{\rho^2(\vec{r})} - \nabla\left(\frac{\nabla\rho(\vec{r})f(\vec{r})}{\rho^2(\vec{r})}\right) - \nabla^2\left(\frac{f(\vec{r})}{\rho(\vec{r})}\right)\right], \tag{A.9}$$

which results finally

$$\frac{1}{36}\left[-\frac{|\nabla\rho(\vec{r})|^2 f(\vec{r})}{\rho^3(\vec{r})} + \frac{\nabla^2\rho(\vec{r})f(\vec{r})}{\rho^2(\vec{r})} - \frac{\nabla^2 f(\vec{r})}{\rho(\vec{r})} + \frac{\nabla\rho(\vec{r})\nabla f(\vec{r})}{\rho^2(\vec{r})}\right] = -\frac{1}{36}\frac{1}{\rho(\vec{r})}\nabla\left[\rho(\vec{r})\nabla\left(\frac{f(\vec{r})}{\rho(\vec{r})}\right)\right], \tag{A.10}$$

which expression will be in general not zero.

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