



New advances in conceptual-DFT: an alternative way to calculate the Fukui function and dual descriptor

Jesús Sánchez-Márquez¹

Received: 11 September 2018 / Accepted: 21 March 2019 / Published online: 24 April 2019
© Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

An alternative way of calculating the Fukui function and the partial derivative of second order of the electronic density with respect to the number of electrons N is presented, the new formulas agree with the usual ones but only in cases without degeneracy. The new operative formulas are more general than the previous ones and are the right ones for those problematic cases where one or both of the frontier molecular orbitals are degenerate. Finally, we present a new way of applying the finite difference approximation that leads to more realistic results than the usual formulas.

Keywords Reactivity descriptors · Fukui function · Dual descriptor · Finite difference approximation · UCA-FUKUI software · Conceptual DFT

Introduction

Local reactivity parameters are necessary to differentiate the reagent behavior of atoms forming a molecule. The Fukui function [1–4] [$f(\mathbf{r})$] and local softness [5, 6] [$s(\mathbf{r})$] are two of the most commonly used local reactivity parameters (Eq. 1).

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v \quad (1)$$
$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_v = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v \cdot \left(\frac{\partial N}{\partial \mu} \right)_v = f(\mathbf{r}) \cdot S$$

The Fukui function is associated primarily with the response of the density function of a system to a change in the number of electrons (N) under the constraint of a constant external potential [$v(\mathbf{r})$]. The mathematical definitions of the Fukui function and local softness (Eq. 1) come from the so-called ensembles of the conceptual density functional theory

(C-DFT) [7] where all global, local and non local reactivity descriptors are hierarchically organized. The Fukui function arises from the canonical ensemble where the number of electrons and the external potential are the essential variables. Meanwhile, the number of electrons and the electronic chemical potential are the essential variables for the local softness.

Due to the discontinuity of the electron density with regard to N , finite difference approximation leads to three types of Fukui function: $f^+(\mathbf{r})$, $f^-(\mathbf{r})$ and $f^0(\mathbf{r})$. They are defined as follows:

$$f^+(\mathbf{r}) = \rho_{N_0+1}(\mathbf{r}) - \rho_{N_0}(\mathbf{r}), \text{ for nucleophilic attack,} \quad (2)$$

$$f^-(\mathbf{r}) = \rho_{N_0}(\mathbf{r}) - \rho_{N_0-1}(\mathbf{r}), \text{ for electrophilic attack,} \quad (3)$$

$$f^0(\mathbf{r}) = \frac{1}{2} (f^+(\mathbf{r}) + f^-(\mathbf{r})), \text{ for neutral (or radical) attack} \quad (4)$$

Theoretical development

The energy change [8] (ΔE) due to the electron transfer (ΔN) satisfies the parabolic approximation:

$$\Delta E \approx \left(\frac{\partial E}{\partial N} \right)_v \Delta N + \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v \Delta N^2 \approx \mu \Delta N + \frac{1}{2} \eta \Delta N^2 \quad (5)$$

where μ and η are the electronic chemical potential and global hardness. Perdew et al. [9] show how the Hohenberg-Kohn

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00894-019-4000-0>) contains supplementary material, which is available to authorized users.

✉ Jesús Sánchez-Márquez
jesus.sanchezmarquez@uca.es

¹ Departamento de Química-Física, Facultad de Ciencias, Campus Universitario Río San Pedro, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

theorem is extended to a fractional electron number (N), and the implications of derivative discontinuity for conceptual DFT are explored by Ayers and colleagues [10, 11]. Taking into account Eq. (5), and that the total energy is a functional of the density, it is reasonable to think that the second order expansion Eq. (6) can be an appropriate approximation.

$$\Delta\rho_N(\mathbf{r}) \approx \left(\frac{\partial\rho_N(\mathbf{r})}{\partial N}\right)_v \Delta N + \frac{1}{2} \left(\frac{\partial^2\rho_N(\mathbf{r})}{\partial N^2}\right)_v \Delta N^2 \quad (6)$$

if we substitute the values $\Delta N=1$ and $\Delta N=-1$ in Eq. (6), and also calculate $\Delta\rho_N^-(\mathbf{r})$ (corresponding to $\Delta N=-1$) and $\Delta\rho_N^+(\mathbf{r})$ (corresponding to $\Delta N=1$). And finally, substituting in Eq. (6), we obtain:

$$\begin{aligned} \Delta\rho_N^-(\mathbf{r}) &= \rho_{N-1}(\mathbf{r}) - \rho_N(\mathbf{r}) \approx -\left(\frac{\partial\rho_N(\mathbf{r})}{\partial N}\right)_v + \frac{1}{2} \left(\frac{\partial^2\rho_N(\mathbf{r})}{\partial N^2}\right)_v \\ \Delta\rho_N^+(\mathbf{r}) &= \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \approx \left(\frac{\partial\rho_N(\mathbf{r})}{\partial N}\right)_v + \frac{1}{2} \left(\frac{\partial^2\rho_N(\mathbf{r})}{\partial N^2}\right)_v \end{aligned} \quad (7)$$

and we find a very simple system of equations with two unknowns; by solving them, we obtain Eq. (8). Expressions of this type (Eq. 6) have been used in previous works [12–14]. Also, implicit in the two articles the introduction of the concept of the dual descriptor [15, 16] because the expression used for the second derivative of the density with respect to the number of electrons corresponds to this kind of quadratic interpolation. Figure 1 graphically represents the physical meaning of the main parameters of Eqs. (6–8). It can be seen that the new formula of $f(\mathbf{r})$ (see Eq. 8) is the same as that of $f^0(\mathbf{r})$ [see Eq. (4), neutral attack], this is logical since the quadratic expansion does not imply an electrophilic or nucleophilic attack.

$$\begin{aligned} \left(\frac{\partial\rho_N(\mathbf{r})}{\partial N}\right)_v &= f(\mathbf{r}) \approx \frac{1}{2} \cdot (\rho_{N+1}(\mathbf{r}) - \rho_{N-1}(\mathbf{r})) \\ \left(\frac{\partial^2\rho_N(\mathbf{r})}{\partial N^2}\right)_v &= f^{(2)}(\mathbf{r}) \approx \rho_{N+1}(\mathbf{r}) - 2 \cdot \rho_N(\mathbf{r}) + \rho_{N-1}(\mathbf{r}) \end{aligned} \quad (8)$$

On the other hand, the original operational formula proposed by Morell et al. [16] for the dual descriptor [15, 17, 18] is:

$$\left(\frac{\partial^2\rho(\mathbf{r})}{\partial N^2}\right)_{v(\mathbf{r})} = f^{(2)}(\mathbf{r}) = \rho(\mathbf{r})_{N+1} - 2 \cdot \rho(\mathbf{r})_N + \rho(\mathbf{r})_{N-1} \quad (9)$$

As can be seen, the formula obtained by Morell et al. in Eq. (9) is the same as the formula of Eq. (8).

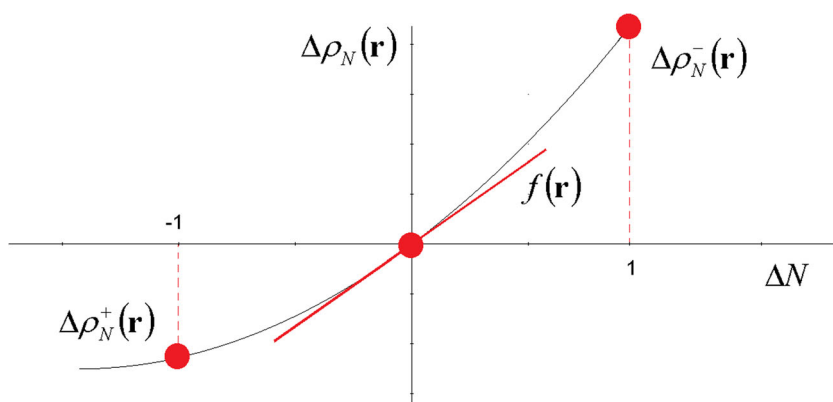
What changes when there is degeneracy of frontier molecular orbitals?

The use of these operational formulae, Eq. (9), can result in failure when applying them to molecular systems that present degeneracy in their frontier molecular orbitals [19]. The issue of degeneracy in conceptual DFT is not restricted to degenerate frontier orbitals because (in rare cases) you can have degenerate ground states in DFT without degenerate frontier orbitals [19–22].

To overcome this limitation of the dual descriptor (and Fukui functions), a more general operational formula was proposed by Martínez-Araya [23, 24]:

$$f^{(2)}(\mathbf{r})_{\text{Martínez-Araya}} \approx \frac{q \cdot \rho(\mathbf{r})_{N+p} - (p+q) \cdot \rho(\mathbf{r})_N + p \cdot \rho(\mathbf{r})_{N-q}}{p \cdot q} \quad (10)$$

Fig. 1 Graphic representation of the main parameters of Eqs. (6–8)



where p and q stand for the degree of degeneracy of LUMO and HOMO, respectively.

When we apply these ideas proposed by Martínez-Araya to the system of Eq. (7), we obtain a new operative formula of $f^{(2)}(\mathbf{r})$ for degenerate cases:

$$f^{(2)}(\mathbf{r})_{\text{Quadratic expansion}} \approx \frac{2 \cdot [q \cdot \rho(\mathbf{r})_{N+p} - (p+q) \cdot \rho(\mathbf{r})_N + p \cdot \rho(\mathbf{r})_{N-q}]}{p \cdot q \cdot (p+q)} \tag{11}$$

which is slightly different from the formula obtained by Martínez-Araya Eq. (10), but they are proportional. On the other hand, Eq. (12) is the operative formula for $f^0(\mathbf{r})$ in cases with degeneracy (applying the ideas of Martínez-Araya),

$$f^0(\mathbf{r})_{\text{Martínez-Araya}} = \frac{q \cdot \rho(\mathbf{r})_{N+p} + (p-q) \cdot \rho(\mathbf{r})_N - p^2 \cdot \rho(\mathbf{r})_{N-q}}{2 \cdot p \cdot q} \tag{12}$$

on the other hand, starting from the system of Eq. (7), we obtain:

$$f(\mathbf{r})_{\text{Quadratic expansion}} = \frac{q^2 \cdot \rho(\mathbf{r})_{N+p} + (p^2 - q^2) \cdot \rho(\mathbf{r})_N - p^2 \cdot \rho(\mathbf{r})_{N-q}}{(p^2 \cdot q + q^2 \cdot p)} \tag{13}$$

In this case, it can be seen that $f^0(\mathbf{r})_{\text{Martínez-Araya}}$ and $f(\mathbf{r})_{\text{Quadratic expansion}}$ are not proportional. Appendix I in supplementary material includes a simple example that complements this conclusion and shows that the new operative formulas $f(\mathbf{r})$ and $f^{(2)}(\mathbf{r})$ are different from the old ones. Finally, we propose a parabolic expansion as an alternative methodology to the finite difference approximation, and we rationalize this affirmation with the very simple example shown in Appendix II.

The new operational formulae for Fukui function and dual descriptor taking into account degrees of degeneracy in HOMO and LUMO are different to those ones based on finite difference. That makes sense in the case of a fractional value of ΔN . But when there is a degree of degeneracy greater than 1, meaning $\Delta N > 1$, in such case there is no certainty that the Taylor expansion (Eq. 6) converges. The, from the mathematical point of view, finite difference is a suitable approximation because it does not depend on the means of truncation of the Taylor expansion. That is why Eqs. (10) and (12) can be used as reference expressions, so that:

$$f^{(2)}(\mathbf{r})_{\text{Martínez-Araya}} - f^{(2)}(\mathbf{r})_{\text{Quadratic expansion}} = \left(1 - \frac{2}{p+q}\right) f^{(2)}(\mathbf{r})_{\text{Martínez-Araya}} \tag{14}$$

and for the Fukui function (the expression is not so simple):

$$f^0(\mathbf{r})_{\text{Martínez-Araya}} - f(\mathbf{r})_{\text{Quadratic expansion}} = \frac{q \cdot \rho(\mathbf{r})_{N+p} + (p-q) \cdot \rho(\mathbf{r})_N - p^2 \cdot \rho(\mathbf{r})_{N-q} - [q^2 \cdot \rho(\mathbf{r})_{N+p} + (p^2 - q^2) \cdot \rho(\mathbf{r})_N - p^2 \cdot \rho(\mathbf{r})_{N-q}]}{2 \cdot p \cdot q - (p^2 \cdot q + q^2 \cdot p)} \tag{15}$$

Computational details

All the structures included in this study were optimized at B3LYP/6-31G(d) [25, 26] theory level by using the Gaussian09 package. [27] The densities used in the new methodology were calculated at the same level of calculation for the neutral molecule, the cation and anion, through Gaussian09 software.

The new indices included in this study were calculated with a modified version of UCA-FUKUI v.2.1 software (http://www2.uca.es/dept/quimica_fisica/software/UCA-FUKUI_v2.exe) [28]. Figure 2 includes two screenshots of the main menu showing the calculation modules that have been added to obtain the new indexes. Figures S1–S3 in the supplementary material show some screenshots of the UCA-FUKUI software displaying the correspondence between the program interface and the equations of the text.

Results and discussion

Obtaining atomic indices (condensed-to-atom)

Starting from Eq. (7) and by taking into account the response-of-molecular-fragment approach [29], (which is equivalent to the fragment-of-molecular-response approach for Hirshfeld partitioning [30–32]), the next condensed-to-atom system can be obtained:

$$\Delta q_k^- = q_k^{N-r} - q_k^N \approx - \left(\frac{\partial q_k^N}{\partial N}\right)_v \cdot r + \frac{1}{2} \left(\frac{\partial^2 q_k^N}{\partial N^2}\right)_v \cdot r^2 \tag{16}$$

$$\Delta q_k^+ = q_k^{N+p} - q_k^N \approx \left(\frac{\partial q_k^N}{\partial N}\right)_v \cdot p + \frac{1}{2} \left(\frac{\partial^2 q_k^N}{\partial N^2}\right)_v \cdot p^2$$

where r and p are the global net charges of the ions. Solving the system:

$$\left(\frac{\partial q_k^N}{\partial N}\right)_v = \frac{r^2 \cdot q_k^{N+p} + (p^2 - r^2) \cdot q_k^N - p^2 \cdot q_k^{N-r}}{(p^2 \cdot r + r^2 \cdot p)} \tag{17}$$

$$\left(\frac{\partial^2 q_k^N}{\partial N^2}\right)_v = \frac{2 \cdot [r \cdot q_k^{N+p} - (p+r) \cdot q_k^N + p \cdot q_k^{N-r}]}{p \cdot r \cdot (p+r)}$$

where q_k^N , q_k^{N+p} and q_k^{N-r} are the net atomic charges calculated with some population analysis (Hirshfeld, Mulliken, ...) for the neutral molecule and the corresponding ions. As an example, Table 1 shows the condensed $f_k^{\text{Quadratic expansion}}$ and f_k^0 (finite difference approximation [33]) indices obtained for

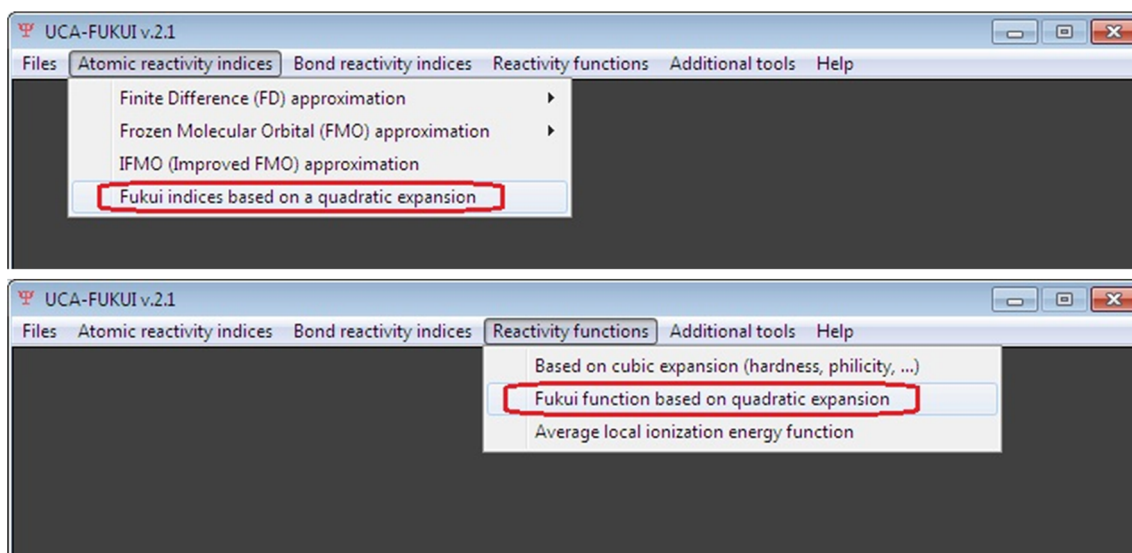


Fig. 2 Upper panel UCA-FUKUI main menu: atomic Fukui indices based on a quadratic expansion. Lower panel UCA-FUKUI main menu: Fukui function based on a quadratic expansion

SF₆, which has triply degenerate HOMO, using the three different population analysis: Hirshfeld [34–36], Mulliken [37] and natural population analysis (NPA) [38–40]. As can be seen in Table 1, the $f_k^{\text{Quadratic expansion}}$ and f_k^0 indices are different.

Advantages of this method: Generalization of the finite difference approximation

The quadratic expansion Eq. (6) provides an important advantage, allowing interpolation $\Delta\rho(\mathbf{r})$ for *fractional* values of ΔN ($-1 < \Delta N < 1$). Thanks to this, we can use the finite difference approximation more generally. Suppose that ΔN is the fractional value ΔN^* , and, that, by substituting this value in Eq. (6), we are led to $\Delta\rho^*(\mathbf{r})$:

$$\Delta\rho(\mathbf{r}) \approx \left(\frac{\partial\rho(\mathbf{r})}{\partial N} \right)_v \Delta N^* + \frac{1}{2} \left(\frac{\partial^2\rho(\mathbf{r})}{\partial N^2} \right)_v (\Delta N^*)^2 \quad (18)$$

Now, the function $\Delta\rho(\mathbf{r})^*$ allows the finite difference approximation to be applied to calculate the Fukui indices in a more general way:

$$f(\mathbf{r})^* = \frac{\Delta\rho(\mathbf{r})^*}{\Delta N^*} \quad (19)$$

Note that Fukui functions $f(\mathbf{r})^+$ and $f(\mathbf{r})^-$ are particular cases of Eq. (19), where ΔN^* takes the non-fractional values +1 and -1. The recent work from the Gazquez group [41, 42] is the closest approach that we have been able to find in relation to this idea.

On the other hand, the amount of charge transfer $\Delta N^{A:B}$ associated to the formation of $A:B$ complex from acid A and base B , may be written as [43]:

$$\Delta N^{A:B} = \frac{\mu_B - \mu_A}{\eta_A + \eta_B} \quad (20)$$

then, combining Eqs. (18), (19), and (20), we obtain the formula:

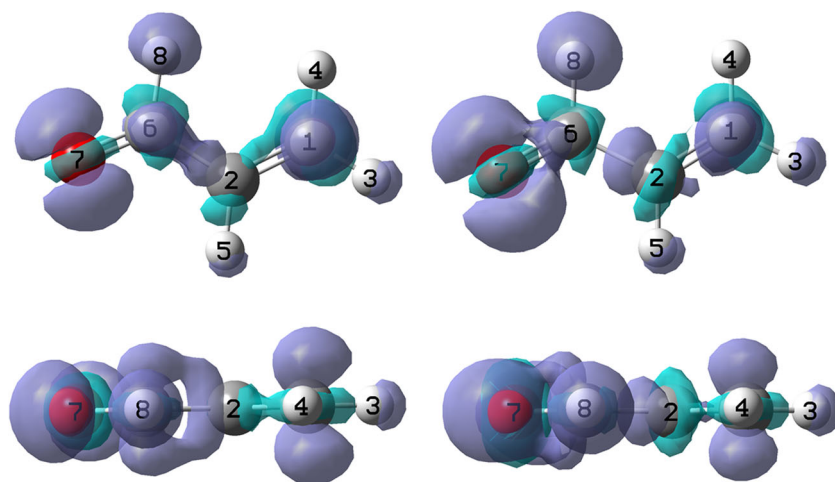
$$f(\mathbf{r})^{A:B} = \frac{\Delta\rho(\mathbf{r})^{A:B}}{\Delta N^{A:B}} \quad (21)$$

that allows to estimate an approximate Fukui function corresponding to a molecule (for example an acid A) when it is attacked by another *concrete* molecule (for example a base B). It is important to note that $f(\mathbf{r})^{A:B}$ (Eq. 21) is being calculated with a charge variation $\Delta N^{A:B}$ with *physical meaning*, and the same can be said for variations $\Delta\rho(\mathbf{r})^{A:B}$. The idea of using a model based on chemical potentials μ_A and μ_B , instead of a finite-difference approximation, can be traced back to Parr

Table 1 Comparison of the $f_k^{\text{Quadratic expansion}}$ indices with the corresponding f_k^0

	Hirshfeld population		Mulliken population		NPA	
	f_k^0	$f_k^{\text{Quadratic expansion}}$	f_k^0	$f_k^{\text{Quad.exp.}}$	f_k^0	$f_k^{\text{Quad.exp.}}$
S	0.1189	0.1452	0.1705	0.2215	0.1190	0.1989
F	0.1469	0.1424	0.1383	0.1298	0.1469	0.1335

Fig. 3 *Left* Function $f(\mathbf{r})^{A:B}$ of the CH_2CHCHO when it is attacked by a H_2 molecule. *Right* Fukui function $f(\mathbf{r})^-$ of the CH_2CHCHO . The four images were obtained with isovalue: 0.0002



and Bartolotti [44] (the value of such an approach and also its limitations was recently stressed by Heidar-Zadeh et al. [45, 46] and the Gazquez group recently showed that the parabolic model is especially relevant [47]).

As an example, Fig. 3 (left) shows function $f(\mathbf{r})^{A:B}$ for the dienophile CH_2CHCHO when it is attacked by a H_2 molecule. In Fig. 3 (right) the function of Fukui $f(\mathbf{r})^-$ (Eq. 3) has been included to facilitate comparison. The images are similar because the two functions represent the nucleophile character of the CH_2CHCHO molecule but they show some differences since function $f(\mathbf{r})^{A:B}$ takes into account the characteristics of the attacker (H_2 molecule). All the images of Fig. 3 have been performed with Gaussview [48] and the “.cub” files used as a starting point were obtained from UCA-FUKUI software.

Starting from the previous idea and Eq. (17) the condensed-to-atom value Δq_k^* of Eq. (22) can be obtained:

$$\Delta q_k^* \approx \left(\frac{\partial q_k^N}{\partial N} \right)_v \Delta N^* + \frac{1}{2} \left(\frac{\partial^2 q_k^N}{\partial N^2} \right)_v (\Delta N^*)^2 \quad (22)$$

The values Δq_k^* and ΔN^* lead to the operative formula:

$$f_k^* = \frac{\Delta q_k^*}{\Delta N^*} \quad (23)$$

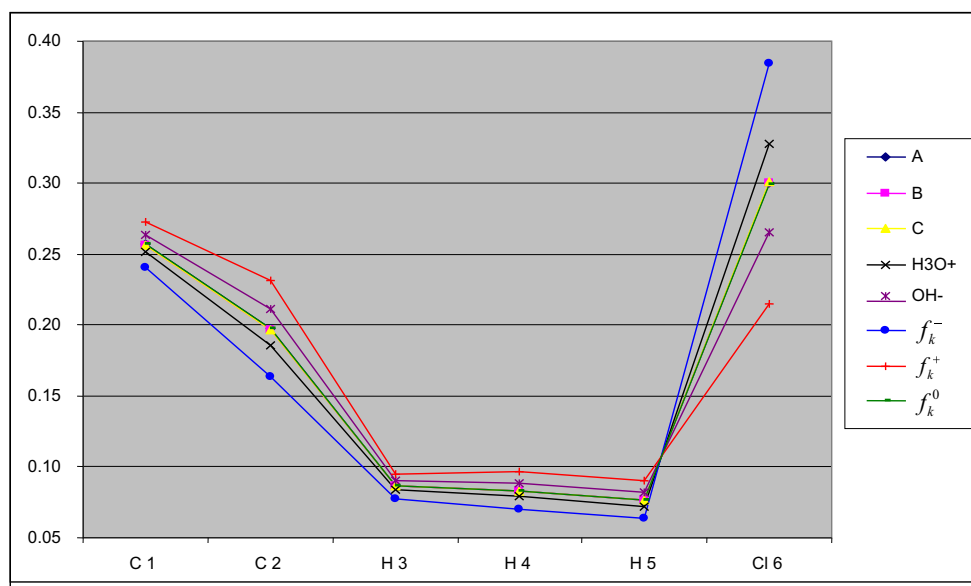
Note that the Fukui indices f_k^+ and f_k^- are particular cases of Eq. (21). Finally, combining Eqs. (22), (23), and (20) we obtain the formula:

$$f_k^{A:B} = \frac{\Delta q_k^{A:B}}{\Delta N^{A:B}} \quad (24)$$

that is the condensed-to-atom version of Eq. (21).

Figure 4 shows the parameters $f_k^{A:B}$ calculated for the dienophile CH_2CHCl when it is attacked by different reagents

Fig. 4 Parameter $f_k^{A:B}$ calculated with Eq. (21) and Hirshfeld population analysis for the CH_2CHCl molecule taking into account different attackers. The parameters f_k^+ , f_k^- and f_k^0 have been added for comparison



(Hirshfeld population analysis was used to obtain atomic populations). The attackers A–C correspond to a set of dienes (see Fig. S4 in the Supplementary material), in addition the attackers H_3O^+ and OH^- have been included. The condensed-to-atom indices f_k^+ , f_k^- and f_k^0 (Eqs. 2–4), nucleophilic, electrophilic and neutral attacks) have also been added for comparison. When the attacker is very electrophilic (for example see H_3O^+) the $f_k^{A:B}$ values are close to the curve f_k^- (electrophilic attack); on the contrary, when the attacker is very nucleophilic (for example see OH^-) the $f_k^{A:B}$ values are close to the curve f_k^+ (nucleophilic attack). Where the attacker possesses an electronic chemical potential similar to CH_2CHCl (for example the dienes A–C) the $f_k^{A:B}$ values tend to curve f_k^0 (neutral or radical attack). Figure S2 in the supplementary material shows an enlargement of Fig. 4 where D–H dienes, H_2 , HCl and Cl_2 attackers have also been included (the data of Figs. 4 and S5 are shown in Table S1 in the supplementary material). Figures S6 to S10 of the Supplementary Material include some equivalent graphics for the CH_2CHCHO , CH_2CHNO_2 , CH_2CHCN , CH_2CHCH_3 and $\text{CH}_2\text{CHOCH}_3$ molecules (see Fig. S11) and the results are equivalent to those shown in Fig. 4. In addition, Figure S12 in the Supplementary Material includes an additional graphic achieved from “atoms in molecules” (AIM) [49–51] theory through the AIMAll software (<http://aim.tkgristmill.com/index.html>), Figure S13 includes a graphic achieved from natural population analysis and Fig. S14 a graphic achieved from Mulliken approximation with a minimal basis set [52, 53] for the CH_2CHCl reagent. The results, shown on these graphs, are qualitatively the same as those shown in Fig. 4. The comparison of all these methodologies led to the conclusion that the calculation method used to obtain the atomic populations does not change qualitatively the conclusions obtained.

Future perspectives

Our intention is to modify the UCA-FUKUI [28] software, based on “conceptual DFT” and specialized in the calculation of local reactivity indices, to introduce the new definition of Fukui’s function in some methodologies (bond-reactivity-indices calculation and improved-frontier-molecular-orbital approximation) implemented in the program [54–56]. Once the software works properly with the new definitions, we will make representative calculations in order to compare the results with those obtained from previous definitions.

Conclusions

A new way of calculating $f(\mathbf{r})$ and $f^{(2)}(\mathbf{r})$ has been developed, resulting in new operative formulas. The Fukui function has been obtained for those cases where one or both of the frontier

orbitals are degenerate, and a more general operative formula was obtained. The new formulae are in agreement with the usual formulae but only in cases without degeneracy. The new $f^{(2)}(\mathbf{r})$ function is identical to the previous formula of dual descriptor in all cases where the frontier molecular orbitals are not degenerate, and in those cases with degeneracy it has been found that they are proportional functions. Finally, a new way of applying the finite difference approximation has been developed that leads to more realistic results (with more physical meaning) than the usual formulas.

Acknowledgment Calculations were performed through CICA (Centro Informático Científico de Andalucía).

References

1. Yang WT, Parr RG, Pucci R (1984) Electron density, Kohn-sham frontier orbitals, and Fukui functions. *J Chem Phys* 81:2862–2863
2. Parr RG, Yang W (1984) Density functional approach to the frontier-electron theory of chemical reactivity. *J Am Chem Soc* 106:4049
3. Ayers PW, Levy M (2000) Density functional approach to the frontierelectron theory of chemical reactivity. *Theor Chem Accounts* 103:353
4. Ayers PW, Yang WT, Bartolotti LJ (2009) The Fukui function. In: Chattaraj PK (ed) *Chemical reactivity theory: a density functional view*. CRC, Boca Raton, p 255
5. Yang W, Parr RG (1985) Hardness, softness, and the Fukui function in the electronic theory of metals and catalysis. *Proc Natl Acad Sci USA* 82:6723
6. Chandra AK, Nguyen MT (2008) Fukui function and local softness. In: Chattaraj PK (ed) *Chemical reactivity theory: a density-functional view*. Taylor and Francis, New York, pp 163–178
7. Geerlings P, Proft FD, Langenaeker W (2003) Conceptual density functional theory. *Chem Rev* 103:1793–1874
8. Parr R, Yang W (1989) *Density-functional theory of atoms and molecules*. Oxford University Press, Oxford
9. Perdew JP, Parr RG, Levy M, Balduz JL (1982) Density-functional theory for fractional particle number: derivative discontinuities of the energy. *Phys Rev Lett* 49:1691–1694
10. Yang WT, Zhang YK, Ayers PW (2000) Degenerate ground states and fractional number of electrons in density and reduced density matrix functional theory. *Phys Rev Lett* 84:5172–5175
11. Ayers PW (2008) The continuity of the energy and other molecular properties with respect to the number of electrons. *J Math Chem* 43: 285–303
12. Gázquez JL (2009) Chemical reactivity concepts in density functional theory. In: Chattaraj PK (ed) *Chemical reactivity theory: A density functional view*. CRC, Boca Raton, p 7
13. Morell C, Gázquez JL, Vela A, Guegan F, Chermette H (2014) Revisiting electroaccepting and electrodonating powers: proposals for local electrophilicity and local nucleophilicity descriptors. *Phys Chem Chem Phys* 16:26832
14. Robles A, Franco-Pérez M, Gázquez JL, Cárdenas C, Fuentealba P (2018) Local electrophilicity. *J Mol Model* 24:245
15. Morell C, Grand A, Toro-Labbe A (2005) New dual descriptor for chemical reactivity. *J Phys Chem A* 109:205–212
16. Morell C, Grand A, Toro-Labbe A (2006) Theoretical support for using the $\Delta f(r)$ descriptor. *Chem Phys Lett* 425:342–346
17. De Proft F, Ayers PW, Fias S, Geerlings P (2006) Woodward-Hoffmann rules in density functional theory: initial hardness response. *J Chem Phys* 125:214101–214109

18. Ayers PW, Morell C, De Proft F, Geerlings P (2007) Understanding the Woodward–Hoffmann rules by using changes in Electron density. *Chem Eur J* 13:8240–8247
19. Cárdenas AC, Ayers PW, Cedillo A (2011) Reactivity indicators for degenerate states in the density-functional theoretic chemical reactivity theory. *J Chem Phys* 134:174103–13
20. Bultinck P, Cardenas C, Fuentealba P, Johnson PA, Ayers PW (2013) Atomic charges and the electrostatic potential are ill-defined in degenerate ground states. *J Chem Theory Comp* 9: 4779–4788
21. Bultinck P, Cardenas C, Fuentealba P, Johnson PA, Ayers PW (2014) How to compute the Fukui matrix and function for systems with (quasi-)degenerate states. *J Chem Theory Comp* 10:202–210
22. Bultinck P, Jayatilaka D, Cardenas C (2015) A problematic issue for atoms in molecules: impact of (quasi-)degenerate states on quantum theory atoms in molecules and Hirshfeld-I properties. *Comput Theor Chem* 1053:106–111
23. Martínez-Araya JI (2016) A generalized operational formula based on Total electronic densities to obtain 3D pictures of the dual descriptor to reveal nucleophilic and electrophilic sites accurately on closed-Shell molecules. *J Comput Chem* 37:2279–2303
24. Martínez-Araya JI (2015) Why is the dual descriptor a more accurate local reactivity descriptor than Fukui functions? *J Math Chem* 53:451–465
25. Becke AD (1993) Density-functional thermochemistry. III the role of exact exchange. *J Chem Phys* 98:5648–5652
26. Frisch MJ, Pople JA, Binkley JS (1984) Self-consistent molecular orbital methods. 25. Supplementary functions for gaussian basis sets. *J Chem Phys* 80:3265–3269
27. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, Revision A.02. Gaussian, Inc., Wallingford CT
28. Sánchez-Márquez J, Zorrilla D, Sánchez-Coronilla AM, de los Santos D, Navas J, Fernández-Lorenzo C, Alcántara R, Martín-Calleja J (2014) Introducing UCA-FUKUI software: reactivity-index calculations. *J Mol Model* 20:2492
29. Bultinck P et al (2007) Critical thoughts on computing atom condensed Fukui functions. *J Chem Phys* 127:034102–034111
30. Nalewajski RF, Parr RG (2000) Information theory, atoms in molecules, and molecular similarity. *Proc Natl Acad Sci USA* 97:8879–8882
31. Heidar-Zadeh F, Ayers PW, Verstraelen T, Vinogradov I, Vöhringer-Martinez E, Bultinck P (2018) Information-theoretic approaches to atoms-in-molecules: Hirshfeld family of partitioning schemes. *J Phys Chem A* 122:4219–4245
32. Roy RK, Pal S, Hirao K (1999) On non-negativity of Fukui function indices. *J Chem Phys* 110:8236–8245
33. Yang WT, Mortier WJ (1986) The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines. *J Am Chem Soc* 108:5708–5711
34. Hirshfeld FL (1977) Bonded-atom fragments for describing molecular charge densities. *Theor Chem Accounts* 44:129–138
35. Ritchie JP (1985) Electron density distribution analysis for nitromethane, nitromethide, and nitramide. *J Am Chem Soc* 107:1829–1837
36. Ritchie JP, Bachrach SM (1987) Some methods and applications of electron density distribution analysis. *J Comp Chem* 8:499–509
37. Mulliken RS (1955) Electronic population analysis on LCAO–MO molecular wave functions I. *J Chem Phys* 23:1833
38. Reed AE, Weinhold F (1983) Natural bond orbital analysis of near-Hartree-Fock water dimer. *J Chem Phys* 78:4066
39. Reed AE, Weinstock RB, Weinhold F (1985) Natural population analysis. *J Chem Phys* 83:735
40. Reed AE, Weinhold F (1985) Natural localized molecular orbitals. *J Chem Phys* 83:1736
41. Orozco-Valencia U, Gazquez JL, Vela A (2018) Global and local charge transfer in electron donor-acceptor complexes. *J Mol Model* 24:250
42. Orozco-Valencia U, Gazquez JL, Vela A (2018) Role of reaction conditions in the global and local two parabolas charge transfer model. *J Phys Chem A* 122:1796–1806
43. Parr RG, Pearson RG (1983) Absolute hardness: companion parameter to absolute electronegativity. *J Am Chem Soc* 105:7512–7516
44. Parr RG, Bartolotti LJ (1982) On the geometric mean principle for electronegativity equalization. *J Am Chem Soc* 104:3801–3803
45. Heidar-Zadeh F (2016) When is the Fukui function not normalized? The danger of inconsistent energy interpolation models in density functional theory. *J Chem Theory Comp*. 12:5777–5787
46. Heidar-Zadeh F, Richer M, Fias S, Miranda-Quintana RA, Chan M, Franco-Pérez M, González-Espinoza CE, Kim TD, Lanssens C, Patel AHG, Yang XD, Vöhringer-Martinez E, Cárdenas C, Verstraelen T, Ayers PW (2016) *Chem Phys Lett* 660:307–312
47. Franco-Perez M, Gázquez JL, Ayers PW, Vela A (2018) Thermodynamic justification for the parabolic model for reactivity indicators with respect to Electron number and a rigorous definition for the Electrophilicity: the essential role played by the electronic entropy. *J Chem Theory Comp* 14:597–606
48. Dennington R, Keith T, Millam J (2009) Gauss View 5.0. Semichem Inc, Shawnee Mission, KS 7
49. Bader RFW (1990) *Atoms in molecules: a quantum theory*. Oxford University Press, Oxford
50. Matta CF, Boyd RJ (2007) *The quantum theory of atoms in molecules: from solid state to DNA and drug design*. WILEY-VCH, Weinham
51. Bader RFW (2005) The quantum mechanical basis for conceptual chemistry. *Monatsh Chem* 136:819–854
52. Montgomery JA, Frisch MJ, Ochterski JW, Petersson GA (1999) A complete basis set model chemistry. VI. Use of density functional geometries and frequencies. *J Chem Phys* 110:2822
53. Montgomery JA, Frisch MJ, Ochterski JW, Petersson GA (2000) A complete basis set model chemistry. VII. Use of the minimum population localization method. *J Chem Phys* 112:6532
54. Sánchez-Márquez J (2016) Introducing new reactivity descriptors: “bond reactivity indices.” comparison of the new definitions and atomic reactivity indices. *J Chem Phys* 145:194105–194112
55. Sánchez-Márquez J, Zorrilla D, García V, Fernández M (2018) Introducing a new bond reactivity index: Philicities for natural bond orbitals. *J Mol Model* 24:25
56. Sánchez-Márquez J, Zorrilla D, García V, Fernández M (2018) Introducing a new methodology for the calculation of local philicity and multiphilic descriptor: an alternative to the finite difference approximation. *Mol Phys* 116:1737–1748

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.