

# 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

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By means of the conceptual density functional theory, the so-called dual descriptor (DD) has been adapted to be used in any closed-shell molecule that presents degeneracy in its frontier molecular orbitals. The latter is of paramount importance because a correct description of local reactivity will allow to predict the most favorable sites on a molecule to undergo nucleophilic or electrophilic attacks; on the contrary, an incomplete description of local reactivity might have serious consequences, particularly for those experimental chemists that have the need of getting an insight about reactivity of chemical reagents before using them in synthesis to obtain a new compound. In the present work, the old approach based only on electronic densities of frontier molecular orbitals is replaced by the most accurate procedure that implies the use of total

electronic densities thus keeping consistency with the essential principle of the DFT in which the electronic density is the fundamental variable and not the molecular orbitals. As a result of the present work, the DD will be able to properly describe local reactivities only in terms of total electronic densities. To test the proposed operational formula, 12 very common molecules were selected as the original definition of the DD was not able to describe their local reactivities properly. The ethylene molecule was additionally used to test the capability of the proposed operational formula to reveal a correct local reactivity even in absence of degeneracy in frontier molecular orbitals. © 2016 Wiley Periodicals, Inc.

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## Introduction

When covalent interactions are more relevant than electrostatic ones, and within the framework of the Conceptual DFT,<sup>[1–6]</sup> Morell et al. have proposed the so-called dual descriptor (DD).<sup>[7]</sup> This is a local reactivity descriptor mathematically represented as  $f^{(2)}(\mathbf{r})$  within the context of closed-shell systems; from the point of view of the electronic density, this is a derivative of second order of  $\rho(\mathbf{r})$ , the electronic density, with respect to  $N$ , the number of electrons. From the point of view of  $E$ , the total energy, this descriptor is also understood as a derivative of third order that is computed as follows: first as a functional derivative of  $E$  with respect to  $v(\mathbf{r})$ , the external potential, thus resulting into the electronic density of the molecular system,  $\rho(\mathbf{r})$ ; and then an ordinary second-order derivative with respect to  $N$  is applied on  $\rho(\mathbf{r})$  coming from the first functional derivative.<sup>[8]</sup>

The main advantage of  $f^{(2)}(\mathbf{r})$  is to reveal, unambiguously, the most nucleophilic and electrophilic sites on a molecule at the same time as a three-dimensional (3D) picture, thus meaning that the DD reveals, simultaneously, the preferable sites for nucleophilic attacks when  $f^{(2)}(\mathbf{r}) > 0$  and the preferable sites for electrophilic attacks when  $f^{(2)}(\mathbf{r}) < 0$  on the molecular system at the point  $\mathbf{r}$ . Another mathematical interpretation points out that it corresponds to a derivative of the Fukui function,  $f(\mathbf{r})$ ,<sup>[4,9]</sup> with respect to  $N$ . The Maxwell relation allows one to understand this local reactivity descriptor as the variation of  $\eta$  (the molecular hardness which measures the resistance to

charge transfer<sup>[4,10,11]</sup>) with respect to the variation of  $v(\mathbf{r})$ . The definition of  $f^{(2)}(\mathbf{r})$  is shown as indicated by Morell et al.<sup>[7,12]</sup>:

$$f^{(2)}(\mathbf{r}) = \left( \frac{\partial^2 \rho(\mathbf{r})}{\partial N^2} \right)_{v(\mathbf{r})} = \left( \frac{\partial f(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} = \left[ \frac{\delta \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(\mathbf{r})}}{\delta v(\mathbf{r})} \right]_N = \left[ \frac{\delta \eta}{\delta v(\mathbf{r})} \right]_N \quad (1)$$

The robustness of the DD has been demonstrated through predicting specific sites of nucleophilic and electrophilic attacks in a much more efficient way than the Fukui function by itself.<sup>[13]</sup> As a proof of this characteristic behavior, some articles have been published to highlight the powerfulness of  $f^{(2)}(\mathbf{r})$  and all those local reactivity descriptors that depend on the DD.<sup>[14–21]</sup> For instance, the use of  $f^{(2)}(\mathbf{r})$  to assess the local

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reactivity of certain iron-based catalysts unveiled that Fe<sup>3+</sup> of a bis(imino)pyridyl iron is a more suitable oxidation state rather than Fe<sup>2+</sup> in the same organometallic compound to catalyze the polymerization of ethylene<sup>[22]</sup>; a more complete article involving theoretical thermodynamics calculations without using the DD supported this previous work aforementioned.<sup>[23]</sup> Another relevant study oriented toward organometallic complexes revealed that amphiphilic properties of some organic ligands can be retrieved through the use of the DD along with the use of molecular electrostatic potential.<sup>[24]</sup> Furthermore, a remarkable aspect of this work lies in the fact that the electronic density was obtained either from a DFT or post-Hartree-Fock calculation, thus recalling the reader that the DD and any reactivity descriptor that comes from the Conceptual DFT is independent on the level of theory, provided the electronic density has been correctly computed; that is to say that electron correlation has been taken into account in quantum chemical calculations.

An operational formula to obtain  $f^{(2)}(\mathbf{r})$  is given by the arithmetic difference between nucleophilic and electrophilic Fukui functions<sup>[7]</sup> as eq. (2) indicates. This is the most accurate mathematical expression to compute this descriptor as a scalar field, but from the point of view of pure mathematics, this procedure of computation is called the finite difference approximation (FDA) method because of the discrete nature of the variable  $N$ .<sup>[25]</sup> Even so the reader can convince himself or herself that the operational formula given by the eq. (2) is obtained as the most suitable definition to build up a 3D picture of the DD presenting an advantage over the nucleophilic and electrophilic Fukui functions,<sup>[13]</sup> but provided that there is no degeneracy in frontier molecular orbitals of the molecule under study. Notice that this expression leads to carry out three quantum chemical computations, with  $N - 1$ ,  $N + 1$ , and  $N$  electrons using the same optimized molecular geometry that is obtained with  $N$  electrons, in the ground state:

$$f^{(2)}(\mathbf{r}) = f^+(\mathbf{r}) - f^-(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - 2\rho_N(\mathbf{r}) + \rho_{N-1}(\mathbf{r}), \quad (2)$$

The position of subscripts is irrelevant, but for the sake of simplicity, we will choose the following notation:

$$f^{(2)}(\mathbf{r}) = f^+(\mathbf{r}) - f^-(\mathbf{r}) = \rho(\mathbf{r})_{N+1} - 2\rho(\mathbf{r})_N + \rho(\mathbf{r})_{N-1}, \quad (3)$$

In fact, as we are dealing with closed-shell molecular systems, the spin-multiplicity of a molecular system with  $N$  electrons (where  $N$  is an even number) is given by  $2S+1=1$  always, where  $S$  stands for the total spin and in this case  $S=0$ , meanwhile the spin-multiplicity of a couple of molecular systems based exactly on the same molecular geometry bearing  $N + 1$  and  $N - 1$  electrons, respectively and having one unpaired electron each, is given by  $2S+1=2$  where  $S=1$ , so that the eq. (3) can be written as follows:

$$f^{(2)}(\mathbf{r}) = f^+(\mathbf{r}) - f^-(\mathbf{r}) = \rho(\mathbf{r})_{N+1}^2 - 2\rho(\mathbf{r})_N^1 + \rho(\mathbf{r})_{N-1}^2, \quad (4)$$

where every superscript reveals the spin-multiplicity aforementioned. The  $\rho(\mathbf{r})_N^1$  central term represents an electronic density with a spin-multiplicity that is equals one always; in the original

definition given by the eq. (2), the spin-multiplicity is not indicated explicitly and the user has to know that a singlet spin-multiplicity must be used when dealing with closed-shell molecular systems, meanwhile for those open-shell molecular systems the procedure is not so simple because, on the one hand, the spin-multiplicity of the molecular system depends on the number of unpaired electrons and, on the other hand, the operational formula of the DD is not very clear yet. The case for open-shell molecular systems will not be broached here, but the mathematical formalism for definitions of the DDs has been well established, although their operation formulae have not been well defined yet.<sup>[26-31]</sup> However, it is important to remark that Tognetti et al. suggested an extension of the DD by means of the use of densities of the electronic excited states so demonstrating its usefulness in those cases where the Frontier Molecular Orbital Theory fails<sup>[32]</sup>; they coined the concept of "state specific dual descriptor." As the present work will be focused on modifications of the operational formula of the DD, hereafter we will refer to eq. (4) as the original operational formula which will be compared, mathematically and graphically, with the generalized operational formula that will be proposed.

As the chemical reactivity is driven by the most outer electrons and as they are located in the frontier molecular orbitals, the local reactivity of any molecular system should be well-described by a function like the DD provided that the phenomenon of degeneracy in frontier molecular orbitals has been taken into account too. In fact, the influence of molecular symmetry over the local reactivity has been demonstrated by means of the fact that Fukui function must conserve the symmetry,<sup>[33]</sup> in consequence, the DD also must do it.<sup>[34]</sup> Furthermore, an extended mathematical justification about the influence of degeneracy on local reactivity descriptors has been provided in previous publications.<sup>[35,36]</sup> Inasmuch as any degeneracy might arise in frontier molecular orbitals, operational formulae have been adapted to the molecular symmetry, but following the approximation based on the densities of frontier molecular orbitals<sup>[34,37,38]</sup> solely which is a drastic approximation that is well-known as the Frontier Molecular Orbital Approximation (FMOA) because it assumes that the remaining molecular orbitals do not experience any relaxation due the arrival or departure of an electron to or from the molecular system under analysis.

At the beginning of the Conceptual DFT, a reasonable justification to make use of operational formulae based on densities of frontier molecular orbitals was the computational cost to obtain the electronic density for the system having its original number of electrons  $N$  along with the electronic densities of the same molecular system having  $N + 1$  and  $N - 1$  electrons, respectively. Clearly the use of the FMOA needs only the electronic densities of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the molecular system bearing its original number of electrons,  $N$ , so that three quantum chemical calculations are reduced to just one and such an approximation was accepted in 2005<sup>[7]</sup> to compute the DD instead of using eq. (4). Nowadays, the computational power allows one to obtain electronic densities of different types of neutral and ionic systems without waiting too much time for retrieving the respective results. The latter has implied that the FMOA is needed no more,

thus allowing the use of the eq. (4) for describing local reactivities. The main problem lies in the fact that this operational formula does not take into account the degeneracy of frontier molecular orbitals that might appear in some molecules because of their symmetry. The aim of this work is to propose a more general operational formula based on total electronic densities and not on densities of frontier molecular orbitals, but by taking into account any possible degeneracy in frontier molecular orbitals.

This article is schematized as follows: first, the Introduction section will give the reader sufficient information about the DD; the second section is entitled A Deduction of a Generalized Operational Formula of  $f^{(2)}(\mathbf{r})$  and it shows us the origin of the proposed operational formula based on total electronic densities and adapted to the degeneracy in frontier molecular orbitals; in the third place, the Computational Details section explains the methodology that has been used to test the operational formula deduced in the previous section; the fourth section corresponds to Results and Discussions that provides the critical analysis concerning to the use of the proposed operational formula. Conclusions are given in the last section.

## A Deduction of a Generalized Operational Formula of $f^{(2)}(\mathbf{r})$

To understand this analysis, please refer to definitions of nucleophilic and electrophilic Fukui functions according to the pertinent and available bibliography.<sup>[3,4,7]</sup> Just for reminding to readers, the nucleophilic and electrophilic Fukui functions reveal the most preferable sites on a molecule when adding or removing an electron while the external potential is kept constant, meaning the position of the nuclei is frozen. The latter means that all quantum chemical calculations for the system with  $N + 1$ ,  $N$  and  $N - 1$  electrons must be performed with the same geometry that comes from a geometrical optimization of the system with  $N$  electrons in the ground state.

The Figure 1 shows us molecular orbitals diagram following an increasing energy order from down to up and that is focused on frontier molecular orbitals and their vicinity. As the nucleophilic Fukui function implies the hypothetical arrival of one electron on LUMO, we have the classical definition:

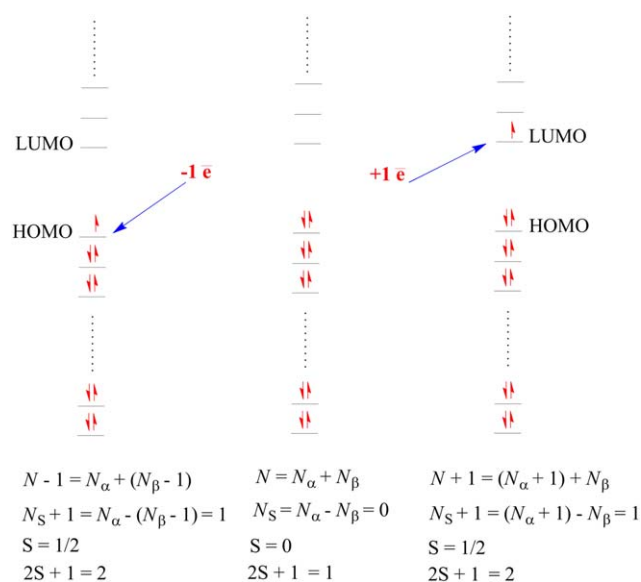
$$f^+(\mathbf{r}) = \rho(\mathbf{r})_{N+1} - \rho(\mathbf{r})_N, \quad (5)$$

Along with the operational formula given by the eq. (5), the electrophilic Fukui function implies the hypothetical departure of one electron from HOMO, as the eq. (6) reveals:

$$f^-(\mathbf{r}) = \rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-1}, \quad (6)$$

These mathematical expressions fail when trying to describe the local reactivities in molecular systems, where degeneracy is present in their frontier molecular orbitals, so leading to the suggested partial solution implying the use of a linear combination of electronic densities of frontier molecular orbitals.<sup>[34]</sup>

When degeneracy appears in frontier molecular orbitals as depicted by Figure 2 such that  $p$  is the degree of degeneracy in LUMO and  $q$  is the degree of degeneracy in HOMO, if only one of the degenerate LUMOs is taken into account, then the eq. (5) turns out to be an incomplete operational formula for



**Figure 1.** Molecular orbital diagrams (MOD). In the middle, an original molecular system presenting no degeneracy in its frontier molecular orbitals after a geometrical optimization with an even number of electrons  $N$  where  $N_\alpha = N_\beta = N/2$ . The construction of the operational formula for the nucleophilic Fukui function implies that LUMO is occupied by one electron as depicted by the MOD on the right under the same optimized molecular geometry. The construction of the operational formula for the electrophilic Fukui function implies that HOMO donates one electron as depicted by the MOD on the left under the same optimized molecular geometry.  $N$ ,  $N_S$ ,  $S$ , and  $2S + 1$  are: the total number of electrons, the spin-number, the total spin, and the spin-multiplicity, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the nucleophilic Fukui function,  $f^+(\mathbf{r})$ . The latter is due that the remaining  $p - 1$  LUMOs were excluded from this operational formula, thus leading to an incomplete 3D representation of the nucleophilic Fukui function. Similarly, when only one degenerate HOMO is taken into account, then the eq. (6) becomes an incomplete operational formula for the electrophilic Fukui function,  $f^-(\mathbf{r})$ . Again, as the remaining  $q - 1$  HOMOs have been excluded from this operational formula, the result is an incomplete 3D representation of the electrophilic Fukui function. As a consequence of these incorrect 3D representations of Fukui functions, an incomplete 3D representation of the DD is obtained too because the degeneracy has not been taken into account in its operational formula which depends upon the operational formulae of  $f^+(\mathbf{r})$  and  $f^-(\mathbf{r})$ .

Now, the main goal is to find a valid operational formula that takes into account the degeneracy in frontier molecular orbitals solely, but using the total electronic densities. To attain this objective, we will assume that the degeneracy among molecular orbitals will exist provided the difference in energy be equal or less than  $1 \cdot 10^{-4}$  hartrees. For instance, if we have a threefold degenerate HOMO then this will imply that one electron will be able to scape from HOMO, HOMO - 1, or HOMO - 2. A generalization with a  $q$ -fold degenerate HOMO will imply that one electron would scape from one of those HOMOs, it means that every of the  $q$  HOMOs has the same likelihood to donate an electron. Similarly, the arrival of one electron onto a molecular system

having a  $p$ -fold degenerate LUMO implies that there will be  $p$  available LUMOs with the same likelihood to receive one electron each. A graphical representation of this idea is depicted by Figure 3; the reader can notice that a nucleophilic attack implies that an electron will be able to arrive onto any of the  $p$  degenerate LUMOs meanwhile that an electrophilic attack implies that an electron will be able to depart from any of the  $q$  degenerate HOMOs. Figure 3 provides a clue to obtain an acceptable operational formula to generate a coherent 3D representation of the DD. All electrons that occupy either degenerate HOMOs or LUMOs will have upward spin; those electrons will be called alpha electrons. In our deduction, we will use  $K$  orthonormal spatial functions  $\{\psi_i(\mathbf{r})\}_{i=1}^K$  as molecular orbitals such that  $K \gg N/2$  to have several available degenerate LUMOs to be occupied by electrons.

### The nucleophilic Fukui function $f^+(\mathbf{r})$ in presence of a twofold degenerate LUMO

Without loss of generality, let us consider an hypothetical and electrically neutral molecular system that has only two electrons ( $N = 2$ ) in a closed-shell conformation and let us suppose that this system presents a twofold degenerate LUMO. In agreement with this initial example,  $p=2$  and  $q=1$ , such that just one of the two degenerate LUMOs can be occupied by one electron and the another is kept empty as depicted by Figure 2. The following Slater determinant<sup>[39]</sup> should be valid to represent this system:

$|\Psi\rangle = |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\rangle \equiv |\psi_1\bar{\psi}_1\rangle$ , therefore the total electronic density is:

$$\langle \psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2) | \hat{\rho}(\mathbf{r}) | \psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2) \rangle \\ = \langle \psi_1\bar{\psi}_1 | \hat{\rho}(\mathbf{r}) | \psi_1\bar{\psi}_1 \rangle = \rho(\mathbf{r})_N = 2|\psi_1(\mathbf{r})|_N^2.$$

Notice that the subscript  $N$  indicates that this is the electronic density of a molecular system having  $N$  electrons (in this example,  $N = 2$ , but we will keep the general subscript  $N$  for the sake of simplicity and to avoid any confusion concerning to the labelling of molecular orbitals). The density operator  $\hat{\rho}(\mathbf{r})_N$  has been used and it will be used every time the electronic density is requested; it is defined as:

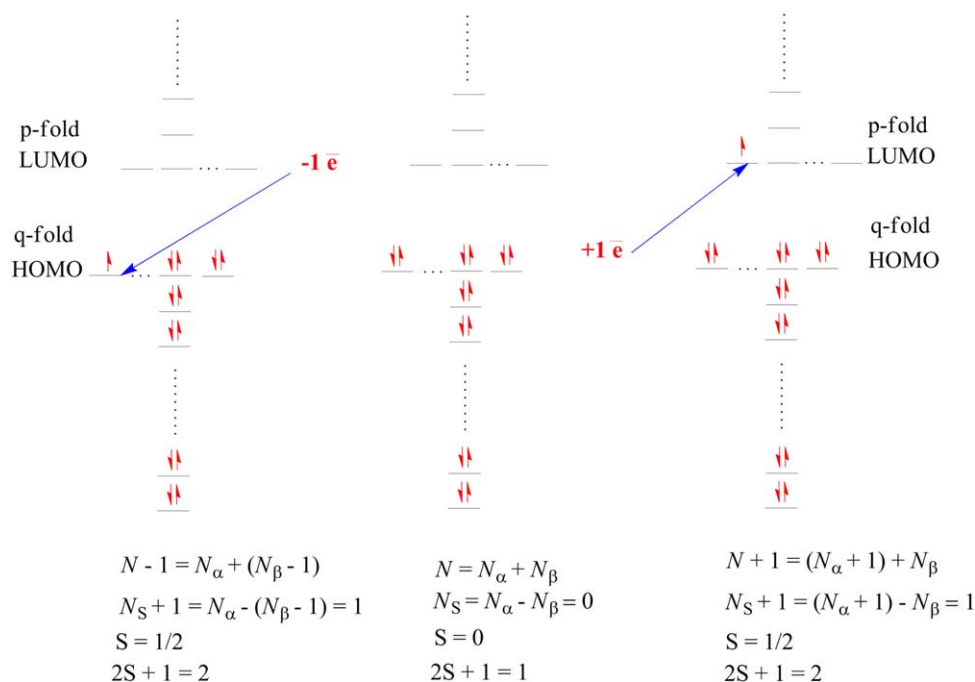
$$\hat{\rho}(\mathbf{r})_N = \sum_{j=1}^N \delta(\mathbf{r}_j - \mathbf{r})$$

As  $\psi_2(\mathbf{r})$  and  $\psi_3(\mathbf{r})$  are the two degenerate LUMOs able to receive an electron each, that is to say they have the same likelihood to receive one electron and to regard them both, we have two possible Slater determinants to represent this anionic system:

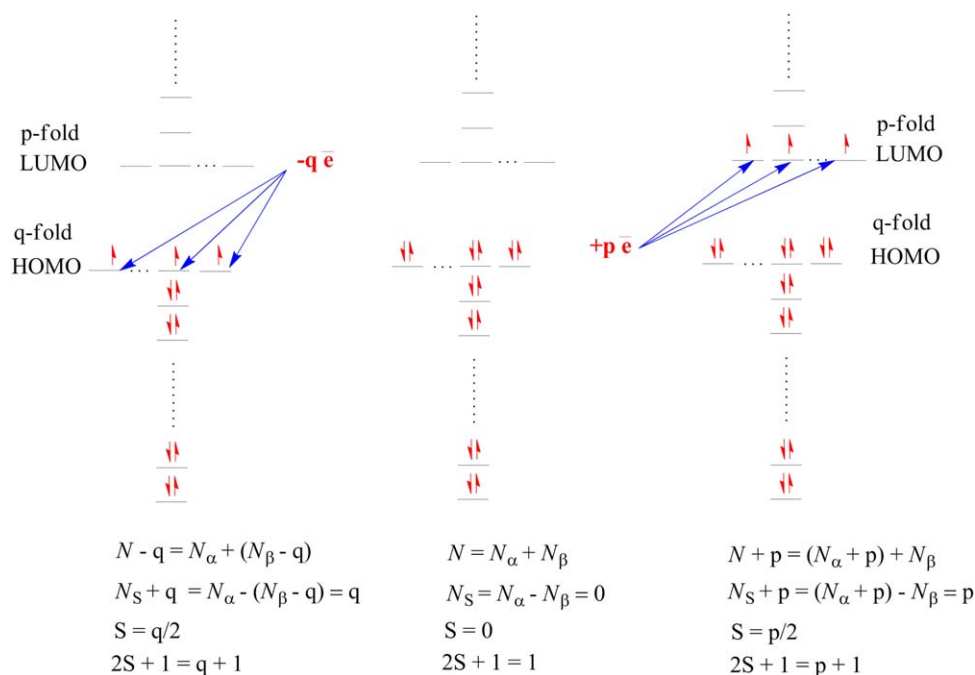
$$|\Psi_{\mathbf{a}}^-\rangle = |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_2(\mathbf{r}_3)\alpha(\omega_3)\rangle = |\psi_1\bar{\psi}_1\psi_2\rangle$$

and

$|\Psi_{\mathbf{b}}^-\rangle = |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_3(\mathbf{r}_3)\alpha(\omega_3)\rangle = |\psi_1\bar{\psi}_1\psi_3\rangle$  So that there are two linear combinations (I and II) to build up a



**Figure 2.** Molecular orbital diagrams (MOD). In the middle, an original molecular system presenting degeneracy in its frontier molecular orbitals after a geometrical optimization with an even number of electrons  $N$  where  $N_{\alpha} = N_{\beta} = N/2$ . The degree of degeneracy in LUMO is  $p$  (where  $p$  is a positive integer number always), thus implying that any of the  $p$  LUMOs is capable to receive one electron; similarly, the degree of degeneracy in HOMO is  $q$  (where  $q$  is a positive integer number always), thus implying that any of the  $q$  HOMOs is capable to donate one electron. The construction of an incomplete operational formula for the nucleophilic Fukui function implies that only one LUMO is occupied by one electron and the remaining  $p-1$  LUMOs are kept empty as depicted by the MOD on the right. The construction of an incomplete operational formula for the electrophilic Fukui function implies that only one HOMO is occupied by one electron and the remaining  $q-1$  HOMOs are kept doubly occupied as depicted by the MOD on the left. This way of facing the problem leads to incomplete 3D representations of the nucleophilic and electrophilic Fukui functions.  $N$ ,  $N_S$ ,  $S$ , and  $2S+1$  are: the total number of electrons, the spin-number, the total spin, and the spin-multiplicity, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** Molecular orbital diagrams (MOD). In the middle, an original molecular system presenting degeneracy in its frontier molecular orbitals after a geometrical optimization with an even number of electrons  $N$  where  $N_\alpha = N_\beta = N/2$ . Any of the  $p$  LUMOs is capable to receive one electron and any of the  $q$  HOMOs is capable to donate one electron, but the construction of a correct operational formula for the nucleophilic Fukui function implies the participation of all the LUMOs in the operational formula; the latter is achieved by means of an occupation of every degenerate LUMO by one electron with upward spin as depicted by this MOD on the right. The construction of a correct operational formula for the electrophilic Fukui function implies the participation of all the HOMOs in the operational formula; this can be achieved when every degenerate HOMO is being occupied by just one electron with upward spin as depicted by this MOD on the left. As a consequence of correct 3D representations of Fukui functions, a correct 3D representation of the DD is obtained too because the degeneracy has been taken into account in the operational formula.  $N$ ,  $N_S$ ,  $S$ , and  $2S+1$  are: the total number of electrons, the spin-number, the total spin, and the spin-multiplicity, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

complete Slater determinant for the anionic molecular system with three electrons (the two original electrons plus the electron that just arrived, thus turning the electrically neutral system into an anion):

$$|\Psi_I^- \rangle = 2^{-1/2} (|\Psi_a^- \rangle + |\Psi_b^- \rangle)$$

$$|\Psi_{II}^- \rangle = 2^{-1/2} (|\Psi_a^- \rangle - |\Psi_b^- \rangle)$$

where:

$$\langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle = 2|\psi_1(\mathbf{r})|_{N+1}^2 + |\psi_2(\mathbf{r})|_{N+1}^2$$

$$\langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle = 2|\psi_1(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2$$

$$\langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle = \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1}$$

$$\langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle = \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}$$

$$\text{and } \hat{\rho}(\mathbf{r})_{N+1} = \sum_{j=1}^{N=3} \delta(\mathbf{r}_j - \mathbf{r}).$$

The subscript  $N+1$  indicates that every molecular orbital has been generated within the framework of a  $(N+1)$ -electron molecular system. In this particular example,  $N+1=3$ . Taking into account the aforementioned mathematical expressions, the electronic density of the molecular system after receiving one electron can be written in terms of any of these linear combinations. The first linear combination given by  $|\Psi_I^- \rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N+1}^I$ :

$$\begin{aligned} \rho(\mathbf{r})_{N+1}^I &= \langle \Psi_I^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_I^- \rangle \\ &= 2^{-1/2} (\langle \Psi_a^- | + \langle \Psi_b^- |) \hat{\rho}(\mathbf{r})_{N+1} (|\Psi_a^- \rangle + |\Psi_b^- \rangle) 2^{-1/2} \\ &= 2^{-1} (\langle \Psi_a^- | + \langle \Psi_b^- |) \hat{\rho}(\mathbf{r})_{N+1} (|\Psi_a^- \rangle + |\Psi_b^- \rangle) \\ &= 2^{-1} (\langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle + \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle) \\ &= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} + \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{2} \end{aligned}$$

The second linear combination given by  $|\Psi_{II}^- \rangle$  leads to another expression for the electronic density that will be called  $\rho(\mathbf{r})_{N+1}^{II}$ :

$$\begin{aligned} \rho(\mathbf{r})_{N+1}^{II} &= \langle \Psi_{II}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{II}^- \rangle \\ &= 2^{-1/2} (\langle \Psi_{\mathbf{a}}^- | - \langle \Psi_{\mathbf{b}}^- |) \hat{\rho}(\mathbf{r})_{N+1} (| \Psi_{\mathbf{a}}^- \rangle - | \Psi_{\mathbf{b}}^- \rangle) 2^{-1/2} \\ &= 2^{-1} (\langle \Psi_{\mathbf{a}}^- | - \langle \Psi_{\mathbf{b}}^- |) \hat{\rho}(\mathbf{r})_{N+1} (| \Psi_{\mathbf{a}}^- \rangle - | \Psi_{\mathbf{b}}^- \rangle) \\ &= 2^{-1} (\langle \Psi_{\mathbf{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{a}}^- \rangle - \langle \Psi_{\mathbf{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{b}}^- \rangle - \langle \Psi_{\mathbf{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{a}}^- \rangle + \langle \Psi_{\mathbf{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{b}}^- \rangle) \\ &= 2 |\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 - \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} - \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{2} \end{aligned}$$

The electronic density of the molecular system can be written as an arithmetic average of  $\rho(\mathbf{r})_{N+1}^I$  and  $\rho(\mathbf{r})_{N+1}^{II}$  to delete the cross terms  $\psi_i^*(\mathbf{r})_{N+1} \cdot \psi_j(\mathbf{r})_{N+1}$  where  $i \neq j$ :

$$\begin{aligned} \rho(\mathbf{r})_{N+1}^{L.C.} &= 2^{-1} \{ \rho(\mathbf{r})_{N+1}^I + \rho(\mathbf{r})_{N+1}^{II} \} \\ &= 2 |\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2}{2} \end{aligned}$$

where L.C. means that this electronic density comes from the linear combinations deduced above. As a result, the electronic density of the molecular system with  $N+1=3$  electrons has been adapted to the degeneracy of LUMO and the nucleophilic Fukui function can be correctly written as follows:

$$\begin{aligned} f^+(\mathbf{r}) &= \rho(\mathbf{r})_{N+1}^{L.C.} - \rho(\mathbf{r})_N \\ &= 2 |\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2}{2} - 2 |\psi_1(\mathbf{r})|_N^2 \\ &= 2 \left\{ |\psi_1(\mathbf{r})|_{N+1}^2 - |\psi_1(\mathbf{r})|_N^2 \right\} + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2}{2} \end{aligned}$$

This corresponds to an operational formula to describe the nucleophilic Fukui function for a molecular system having a twofold degenerate LUMO. The normalization condition of  $f^+(\mathbf{r})$  is satisfied.

### The nucleophilic Fukui function $f^+(\mathbf{r})$ in presence of a threefold degenerate LUMO

In the case of a threefold degenerate LUMO, there are three degenerate LUMOs able to receive one electron each:  $\psi_2(\mathbf{r})$ ,  $\psi_3(\mathbf{r})$  and  $\psi_4(\mathbf{r})$ , such that the resulting molecular system after receiving one electron on one of these degenerate LUMOs can be expressed by any of these Slater determinants:

$$\begin{aligned} |\Psi_{\mathbf{a}}^- \rangle &= |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_2(\mathbf{r}_3)\alpha(\omega_3)\rangle = |\psi_1\bar{\psi}_1\psi_2\rangle \\ |\Psi_{\mathbf{b}}^- \rangle &= |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_3(\mathbf{r}_3)\alpha(\omega_3)\rangle = |\psi_1\bar{\psi}_1\psi_3\rangle \\ |\Psi_{\mathbf{c}}^- \rangle &= |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_4(\mathbf{r}_3)\alpha(\omega_3)\rangle = |\psi_1\bar{\psi}_1\psi_4\rangle \end{aligned}$$

thus leading to four plausible linear combinations as follows:

$$\begin{aligned} |\Psi_I^- \rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^- \rangle + |\Psi_{\mathbf{b}}^- \rangle + |\Psi_{\mathbf{c}}^- \rangle) \\ |\Psi_{II}^- \rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^- \rangle - |\Psi_{\mathbf{b}}^- \rangle + |\Psi_{\mathbf{c}}^- \rangle) \\ |\Psi_{III}^- \rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^- \rangle + |\Psi_{\mathbf{b}}^- \rangle - |\Psi_{\mathbf{c}}^- \rangle) \\ |\Psi_{IV}^- \rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^- \rangle - |\Psi_{\mathbf{b}}^- \rangle - |\Psi_{\mathbf{c}}^- \rangle) \end{aligned}$$

where

$$\begin{aligned} \langle \Psi_{\mathbf{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{a}}^- \rangle &= 2 |\psi_1(\mathbf{r})|_{N+1}^2 + |\psi_2(\mathbf{r})|_{N+1}^2 \\ \langle \Psi_{\mathbf{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{b}}^- \rangle &= 2 |\psi_1(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 \\ \langle \Psi_{\mathbf{c}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{c}}^- \rangle &= 2 |\psi_1(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2 \\ \langle \Psi_{\mathbf{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{b}}^- \rangle &= \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} \\ \langle \Psi_{\mathbf{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{a}}^- \rangle &= \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1} \\ \langle \Psi_{\mathbf{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{c}}^- \rangle &= \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} \\ \langle \Psi_{\mathbf{c}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{a}}^- \rangle &= \psi_4^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1} \\ \langle \Psi_{\mathbf{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{c}}^- \rangle &= \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} \\ \langle \Psi_{\mathbf{c}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\mathbf{b}}^- \rangle &= \psi_4^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} \end{aligned}$$

$$\text{and } \hat{\rho}(\mathbf{r})_{N+1} = \sum_{j=1}^{N=3} \delta(\mathbf{r}_j - \mathbf{r}).$$

Bearing in mind the possible linear combinations aforementioned, the electronic density when the molecular system receives one electron can be written in four possible ways.

The first linear combination given by  $|\Psi_I^- \rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N+1}^I$ :

$$\begin{aligned}
 \rho(\mathbf{r})_{N+1}^I &= \langle \Psi_I^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_I^- \rangle \\
 &= 3^{-1/2} (\langle \Psi_a^- | + \langle \Psi_b^- | + \langle \Psi_c^- |) \hat{\rho}(\mathbf{r})_{N+1} (| \Psi_a^- \rangle + | \Psi_b^- \rangle + | \Psi_c^- \rangle) 3^{-1/2} \\
 &= 3^{-1} (\langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle + \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle \\
 &\quad + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle \\
 &\quad + \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle + \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle) \\
 &= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3} \\
 &\quad + \frac{\psi_2^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} + \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} + \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} + \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3} \\
 &\quad + \frac{\psi_4^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} + \psi_4^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3}
 \end{aligned}$$

The second linear combination given by  $|\Psi_{II}^- \rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N+1}^{II}$ :

$$\begin{aligned}
 \rho(\mathbf{r})_{N+1}^{II} &= \langle \Psi_{II}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{II}^- \rangle \\
 &= 3^{-1/2} (\langle \Psi_a^- | - \langle \Psi_b^- | + \langle \Psi_c^- |) \hat{\rho}(\mathbf{r})_{N+1} (| \Psi_a^- \rangle - | \Psi_b^- \rangle + | \Psi_c^- \rangle) 3^{-1/2} \\
 &= 3^{-1} (\langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle - \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle \\
 &\quad - \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle - \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle \\
 &\quad + \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle - \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle) \\
 &= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3} \\
 &\quad + \frac{\psi_2^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} - \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} - \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} - \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3} \\
 &\quad + \frac{-\psi_4^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} + \psi_4^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3}
 \end{aligned}$$

The third linear combination given by  $|\Psi_{III}^- \rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N+1}^{III}$ :

$$\begin{aligned}
 \rho(\mathbf{r})_{N+1}^{III} &= \langle \Psi_{III}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{III}^- \rangle \\
 &= 3^{-1/2} (\langle \Psi_a^- | + \langle \Psi_b^- | - \langle \Psi_c^- |) \hat{\rho}(\mathbf{r})_{N+1} (| \Psi_a^- \rangle + | \Psi_b^- \rangle - | \Psi_c^- \rangle) 3^{-1/2} \\
 &= 3^{-1} (\langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle + \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_a^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle \\
 &\quad - \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle + \langle \Psi_b^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle \\
 &\quad + \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_c^- \rangle - \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_b^- \rangle - \langle \Psi_c^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_a^- \rangle) \\
 &= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3} \\
 &\quad + \frac{-\psi_2^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} + \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} - \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} + \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3} \\
 &\quad + \frac{-\psi_4^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} - \psi_4^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3}
 \end{aligned}$$

The fourth linear combination given by  $|\Psi_{IV}^- \rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N+1}^{IV}$ :

$$\begin{aligned}
\rho(\mathbf{r})_{N+1}^{\text{IV}} &= \langle \Psi_{\text{IV}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{IV}}^- \rangle \\
&= 3^{-1/2} (\langle \Psi_{\text{a}}^- | - \langle \Psi_{\text{b}}^- | - \langle \Psi_{\text{c}}^- |) \hat{\rho}(\mathbf{r})_{N+1} (| \Psi_{\text{a}}^- \rangle - | \Psi_{\text{b}}^- \rangle - | \Psi_{\text{c}}^- \rangle) 3^{-1/2} \\
&= 3^{-1} (- \langle \Psi_{\text{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{c}}^- \rangle - \langle \Psi_{\text{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{b}}^- \rangle + \langle \Psi_{\text{a}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{a}}^- \rangle \\
&\quad + \langle \Psi_{\text{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{c}}^- \rangle + \langle \Psi_{\text{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{b}}^- \rangle - \langle \Psi_{\text{b}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{a}}^- \rangle \\
&\quad + \langle \Psi_{\text{c}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{c}}^- \rangle + \langle \Psi_{\text{c}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{b}}^- \rangle - \langle \Psi_{\text{c}}^- | \hat{\rho}(\mathbf{r})_{N+1} | \Psi_{\text{a}}^- \rangle) \\
&= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3} \\
&\quad + \frac{-\psi_2^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} - \psi_2^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} + \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_4(\mathbf{r})_{N+1} - \psi_3^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3} \\
&\quad + \frac{\psi_4^*(\mathbf{r})_{N+1} \cdot \psi_3(\mathbf{r})_{N+1} - \psi_4^*(\mathbf{r})_{N+1} \cdot \psi_2(\mathbf{r})_{N+1}}{3}
\end{aligned}$$

Again, to achieve a simpler operational formula of the nucleophilic Fukui function, the cross terms  $\psi_i^*(\mathbf{r})_{N+1} \cdot \psi_j(\mathbf{r})_{N+1}$  with  $i \neq j$  are naturally deleted through an arithmetic average of these four expressions  $\rho(\mathbf{r})_{N+1}^{\text{I}}$ ,  $\rho(\mathbf{r})_{N+1}^{\text{II}}$ ,  $\rho(\mathbf{r})_{N+1}^{\text{III}}$ , and  $\rho(\mathbf{r})_{N+1}^{\text{IV}}$  such that the following expression is obtained:

$$\begin{aligned}
\rho(\mathbf{r})_{N+1}^{\text{L.C.}} &= 4^{-1} \left\{ \rho(\mathbf{r})_{N+1}^{\text{I}} + \rho(\mathbf{r})_{N+1}^{\text{II}} + \rho(\mathbf{r})_{N+1}^{\text{III}} + \rho(\mathbf{r})_{N+1}^{\text{IV}} \right\} \\
&= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3}
\end{aligned}$$

and the nucleophilic Fukui function can be correctly written as follows:

$$\begin{aligned}
f^+(\mathbf{r}) &= \rho(\mathbf{r})_{N+1}^{\text{L.C.}} - \rho(\mathbf{r})_N \\
&= 2|\psi_1(\mathbf{r})|_{N+1}^2 + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3} - 2|\psi_1(\mathbf{r})|_N^2 \\
&= 2 \left\{ |\psi_1(\mathbf{r})|_{N+1}^2 - |\psi_1(\mathbf{r})|_N^2 \right\} + \frac{|\psi_2(\mathbf{r})|_{N+1}^2 + |\psi_3(\mathbf{r})|_{N+1}^2 + |\psi_4(\mathbf{r})|_{N+1}^2}{3}
\end{aligned}$$

As expected, the normalization condition of  $f^+(\mathbf{r})$  is satisfied by this operational formula.

#### The nucleophilic Fukui function $f^+(\mathbf{r})$ in presence of a $p$ -fold degenerate LUMO

This methodology is possible to be extended onto any molecular system having more than two electrons ( $N \geq 2$ ) and a  $p$ -fold degenerate LUMO because always we will be able to find a proper linear combination for the total electronic density in which the  $p$  degenerate LUMOs are taken into account. In terms of electronic densities of all of the occupied molecular orbitals, the eq. (7) is obtained:

$$f^+(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \left\{ |\psi_i(\mathbf{r})|_{N+1}^2 - |\psi_i(\mathbf{r})|_N^2 \right\} + \frac{1}{p} \sum_{i=N/2+1}^{N/2+p} |\psi_i(\mathbf{r})|_{N+1}^2 \quad (7)$$

The normalization condition of  $f^+(\mathbf{r})$  is satisfied by this operational formula. Nevertheless this procedure seems to be a little tedious to perform owing to its increasing complexity in the treatment of the respective linear combinations as the degree of degeneracy  $p$  is increased.

#### The proposal for a nucleophilic Fukui function $f^+(\mathbf{r})$ in presence of a $p$ -fold degenerate LUMO

With the aim to make easier the generation of a similar operational formula, the use of all of the  $p$  degenerate LUMOs in just one mathematical expression, rather than a linear combination of them, must lead to an operational formula that takes into account these LUMOs being occupied each by one electron with upward spin as depicted by Figure 3.

Let us start again with the simplest case: A two-electron molecular system with a twofold degenerate LUMO. In such a case, the both LUMOs will be occupied each by one alpha electron, in consequence the Slater determinant for this dianionic system will be given by:

$$\begin{aligned}
|\Psi^{-2}\rangle &= |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_2(\mathbf{r}_3)\alpha(\omega_3)\psi_3(\mathbf{r}_4)\alpha(\omega_4)\rangle \\
&= |\psi_1\bar{\psi}_1\psi_2\psi_3\rangle
\end{aligned}$$

According to the latter, after applying the respective density operator, the electronic density is written as follows:

$$\begin{aligned}
\langle \Psi^{-2} | \hat{\rho}(\mathbf{r})_{N+2} | \Psi^{-2} \rangle &= \langle \psi_1\bar{\psi}_1\psi_2\psi_3 | \hat{\rho}(\mathbf{r})_{N+2} | \psi_1\bar{\psi}_1\psi_2\psi_3 \rangle \\
&= \rho(\mathbf{r})_{N+2} \\
&= 2|\psi_1(\mathbf{r})|_{N+2}^2 + |\psi_2(\mathbf{r})|_{N+2}^2 + |\psi_3(\mathbf{r})|_{N+2}^2
\end{aligned}$$

The nucleophilic Fukui function,  $f^+(\mathbf{r})$ , must be obtained from the original definition given by the FDA:



$$\begin{aligned}
 f^+(\mathbf{r}) &= \frac{\langle \Psi^{-2} | \hat{\rho}_{N+2} | \Psi^{-2} \rangle - \langle \Psi | \hat{\rho}_N | \Psi \rangle}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_{N+2} - \rho(\mathbf{r})_N}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_{N+2} - \rho(\mathbf{r})_N}{N+2-N} \\
 &= \frac{\rho(\mathbf{r})_{N+2} - \rho(\mathbf{r})_N}{2} \\
 &= \frac{2|\psi_1(\mathbf{r})|_{N+2}^2 + |\psi_2(\mathbf{r})|_{N+2}^2 + |\psi_3(\mathbf{r})|_{N+2}^2 - 2|\psi_1(\mathbf{r})|_N^2}{2} \\
 &= |\psi_1(\mathbf{r})|_{N+2}^2 - |\psi_1(\mathbf{r})|_N^2 + \frac{|\psi_2(\mathbf{r})|_{N+2}^2 + |\psi_3(\mathbf{r})|_{N+2}^2}{2}
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_{N+2} = \sum_{j=1}^{N+4} \delta(\mathbf{r}_j - \mathbf{r})$  and  $\hat{\rho}(\mathbf{r})_N = \sum_{j=1}^{N+2} \delta(\mathbf{r}_j - \mathbf{r})$ .

Notice that this operational formula of  $f^+(\mathbf{r})$  satisfies the normalization condition as well.

This analysis can be extended to a molecular system having a threefold degenerate LUMO, thus implying a Slater determinant of a tri-anion that leads to the following expression for its electronic density:

$$\begin{aligned}
 \langle \Psi^{-3} | \hat{\rho}_{N+3} | \Psi^{-3} \rangle &= \langle \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \bar{\psi}_4 | \hat{\rho}_{N+3} | \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \bar{\psi}_4 \rangle \\
 &= \rho(\mathbf{r})_{N+3} \\
 &= 2|\psi_1(\mathbf{r})|_{N+3}^2 + |\psi_2(\mathbf{r})|_{N+3}^2 + |\psi_3(\mathbf{r})|_{N+3}^2 + |\psi_4(\mathbf{r})|_{N+3}^2
 \end{aligned}$$

and the nucleophilic Fukui function following the same aforementioned procedure is:

$$\begin{aligned}
 f^+(\mathbf{r}) &= \frac{\langle \Psi^{-3} | \hat{\rho}_{N+3} | \Psi^{-3} \rangle - \langle \Psi | \hat{\rho}_N | \Psi \rangle}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_{N+3} - \rho(\mathbf{r})_N}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_{N+3} - \rho(\mathbf{r})_N}{N+3-N} \\
 &= \frac{\rho(\mathbf{r})_{N+3} - \rho(\mathbf{r})_N}{3} \\
 &= \frac{2|\psi_1(\mathbf{r})|_{N+3}^2 + |\psi_2(\mathbf{r})|_{N+3}^2 + |\psi_3(\mathbf{r})|_{N+3}^2 + |\psi_4(\mathbf{r})|_{N+3}^2 - 2|\psi_1(\mathbf{r})|_N^2}{3} \\
 &= \frac{2|\psi_1(\mathbf{r})|_{N+3}^2 - 2|\psi_1(\mathbf{r})|_N^2}{3} + \frac{|\psi_2(\mathbf{r})|_{N+3}^2 + |\psi_3(\mathbf{r})|_{N+3}^2 + |\psi_4(\mathbf{r})|_{N+3}^2}{3}
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_{N+3} = \sum_{j=1}^{N+5} \delta(\mathbf{r}_j - \mathbf{r})$  and  $\hat{\rho}(\mathbf{r})_N = \sum_{j=1}^{N+2} \delta(\mathbf{r}_j - \mathbf{r})$ . It can be checked that the normalization condition of  $f^+(\mathbf{r})$  is satisfied by this operational formula. This analysis was developed on a molecular system having 2 electrons ( $N=2$ ) and a threefold degenerate LUMO. A generalization is achieved by following the same procedure for a system with  $N$  electrons (where  $N$  is an even number with  $N \geq 2$ ) and presenting a  $p$ -fold degenerate LUMO, thus leading to define a Slater determinant for an anion with a net electric charge of  $-p$ ,  $|\Psi^{-p}\rangle$ . As a result, the respective operational formula for the nucleophilic Fukui function is written as follows:

$$\begin{aligned}
 f^+(\mathbf{r}) &= \frac{\langle \Psi^{-p} | \hat{\rho}_{N+p} | \Psi^{-p} \rangle - \langle \Psi | \hat{\rho}_N | \Psi \rangle}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_{N+p} - \rho(\mathbf{r})_N}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_{N+p} - \rho(\mathbf{r})_N}{N+p-N} \\
 &= \frac{\rho(\mathbf{r})_{N+p} - \rho(\mathbf{r})_N}{p} \\
 &= \frac{1}{p} \left\{ \rho(\mathbf{r})_{N+p} - \rho(\mathbf{r})_N \right\} \\
 &= \frac{1}{p} \left\{ 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|_{N+p}^2 + \sum_{i=N/2+1}^{N/2+p} |\psi_i(\mathbf{r})|_{N+p}^2 - 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|_N^2 \right\} \\
 &= \frac{2}{p} \sum_{i=1}^{N/2} \left\{ |\psi_i(\mathbf{r})|_{N+p}^2 - |\psi_i(\mathbf{r})|_N^2 \right\} + \frac{1}{p} \sum_{i=N/2+1}^{N/2+p} |\psi_i(\mathbf{r})|_{N+p}^2 \quad (8)
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_{N+p} = \sum_{j=1}^{N+p} \delta(\mathbf{r}_j - \mathbf{r})$  and  $\hat{\rho}(\mathbf{r})_N = \sum_{j=1}^N \delta(\mathbf{r}_j - \mathbf{r})$ . Notice that the normalization condition of  $f^+(\mathbf{r})$  is satisfied by this operational formula. Observe that  $\rho(\mathbf{r})_{N+p}$  was split into two sums:

$$\rho(\mathbf{r})_{N+p} = \sum_{i=1}^{N/2} 2|\psi_i(\mathbf{r})|_{N+p}^2 + \sum_{i=N/2+1}^{N/2+p} |\psi_i(\mathbf{r})|_{N+p}^2$$

It can be noticed there is a resemblance between eqs. (7) and (8) so that in absence of molecular orbital relaxation, a strong approximation  $|\psi_i(\mathbf{r})|_{N+p}^2 \approx |\psi_i(\mathbf{r})|_N^2$  arises in these both equations thus leading to the well-known nucleophilic Fukui function adapted to the  $p$ -fold degenerate LUMO<sup>[34]</sup>; but in such an approximation the nucleophilic Fukui function is only written in terms of the electronic densities of these degenerate frontier molecular orbitals, with the risk of giving an inaccurate 3D picture of the local reactivity.

### The electrophilic Fukui function $f^-(\mathbf{r})$ in presence of a twofold degenerate HOMO

Following the same stream of analysis and without loss of generality, let us now focus our attention on the case of the electrophilic Fukui function, where an hypothetical and electrically neutral molecular system has only ten electrons ( $N=10$ ) in a closed-shell conformation such that:  $|\Psi\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \bar{\psi}_4 \psi_5 \bar{\psi}_5\rangle$

Through the use of the density operator  $\hat{\rho}(\mathbf{r})_N$  the electronic density for this system is obtained as follows:

$$\begin{aligned}
 \langle \Psi | \hat{\rho}(\mathbf{r})_N | \Psi \rangle &= \langle \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \bar{\psi}_4 \psi_5 \bar{\psi}_5 | \\
 &\quad \hat{\rho}(\mathbf{r})_N | \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \bar{\psi}_4 \psi_5 \bar{\psi}_5 \rangle \\
 &= \rho(\mathbf{r})_N \\
 &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_N^2
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_N = \sum_{j=1}^{N=10} \delta(\mathbf{r}_j - \mathbf{r})$ . Let us suppose that this system presents a twofold HOMO, thus meaning that spatial functions

$\psi_4(\mathbf{r})$  and  $\psi_5(\mathbf{r})$  have the same likelihood to release one electron each. According to this initial example,  $p=1$  and  $q=2$ , such that just one of the two degenerate HOMOs can be occupied by one electron with upward spin (by one alpha electron) and the another HOMO is doubly occupied (by one alpha electron and one beta electron), as depicted by Figure 2. As a result, any of these two Slater determinants should be valid to represent this system as follows:

$$\begin{aligned} |\Psi_a^+\rangle &= |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_2(\mathbf{r}_3)\alpha(\omega_3)\psi_2(\mathbf{r}_4)\beta(\omega_4)\dots \\ &\quad \psi_4(\mathbf{r}_7)\alpha(\omega_7)\psi_4(\mathbf{r}_8)\beta(\omega_8)\psi_5(\mathbf{r}_9)\alpha(\omega_9)\rangle \\ &= |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\psi_4\bar{\psi}_4\psi_5\rangle \end{aligned}$$

and

$$\begin{aligned} |\Psi_b^+\rangle &= |\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_1(\mathbf{r}_2)\beta(\omega_2)\psi_2(\mathbf{r}_3)\alpha(\omega_3) \\ &\quad \psi_2(\mathbf{r}_4)\beta(\omega_4)\dots\psi_4(\mathbf{r}_7)\alpha(\omega_7)\psi_5(\mathbf{r}_8)\alpha(\omega_8)\psi_5(\mathbf{r}_9)\beta(\omega_9)\rangle \\ &= |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\psi_4\psi_5\bar{\psi}_5\rangle \\ &= -|\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\psi_4\bar{\psi}_5\psi_5\rangle \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_{N-1} = \sum_{j=1}^{N-9} \delta(\mathbf{r}_j - \mathbf{r})$ .

Then, the presence of two possible HOMOs,  $\psi_4(\mathbf{r})$  and  $\psi_5(\mathbf{r})$ , capable to donate one electron each with the same likelihood leads to two possible linear combinations to build up the Slater determinant for the molecular system with nine electrons (the molecule turns into a cation):

$$\begin{aligned} |\Psi^+\rangle &= 2^{-1/2}(|\Psi_a^+\rangle + |\Psi_b^+\rangle) \\ |\Psi_{\parallel}^+\rangle &= 2^{-1/2}(|\Psi_a^+\rangle - |\Psi_b^+\rangle) \end{aligned}$$

where:

$$\begin{aligned} \langle \Psi_a^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_a^+ \rangle &= 2 \sum_{i=1}^4 |\psi_i(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2 \\ &\equiv 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_5(\mathbf{r})|_{N-1}^2 \\ \langle \Psi_b^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_b^+ \rangle &= 2 \sum_{i=1, j \neq 4}^5 |\psi_i(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 \\ &\equiv 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_4(\mathbf{r})|_{N-1}^2 \\ \langle \Psi_a^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_b^+ \rangle &= -\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} \\ \langle \Psi_b^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_a^+ \rangle &= -\psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} \end{aligned}$$

In alignment with the anionic case that led us to the general expression for the nucleophilic Fukui function, we can follow the same procedure for the electrophilic Fukui function by taking into account the linear combinations  $|\Psi_a^+\rangle$  and  $|\Psi_b^+\rangle$  which are the two Slater determinants plausible to be used for describing the cationic state of  $|\Psi\rangle$ . The first linear

combination given by  $|\Psi_{\parallel}^+\rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N-1}^{\parallel}$ :

$$\begin{aligned} \rho(\mathbf{r})_{N-1}^{\parallel} &= \langle \Psi_{\parallel}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\parallel}^+ \rangle \\ &= 2^{-1/2} (\langle \Psi_a^+ | + \langle \Psi_b^+ |) \hat{\rho}(\mathbf{r})_{N-1} (|\Psi_a^+\rangle + |\Psi_b^+\rangle) 2^{-1/2} \\ &= 2^{-1} (\langle \Psi_a^+ | + \langle \Psi_b^+ |) \hat{\rho}(\mathbf{r})_{N-1} (|\Psi_a^+\rangle + |\Psi_b^+\rangle) \\ &= 2^{-1} (\langle \Psi_a^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_a^+\rangle + \langle \Psi_a^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_b^+\rangle + \\ &\quad \langle \Psi_b^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_a^+\rangle + \langle \Psi_b^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_b^+\rangle) \\ &= 2^{-1} \left( 4 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_4(\mathbf{r})|_{N-1}^2 - |\psi_5(\mathbf{r})|_{N-1}^2 \right. \\ &\quad \left. - \psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} - \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} \right) \\ &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{2} \\ &\quad - \frac{\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1}}{2} \end{aligned}$$

The second linear combination given by  $|\Psi_{\perp}^+\rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N-1}^{\perp}$ :

$$\begin{aligned} \rho(\mathbf{r})_{N-1}^{\perp} &= \langle \Psi_{\perp}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\perp}^+ \rangle \\ &= 2^{-1/2} (\langle \Psi_a^+ | - \langle \Psi_b^+ |) \hat{\rho}(\mathbf{r})_{N-1} (|\Psi_a^+\rangle - |\Psi_b^+\rangle) 2^{-1/2} \\ &= 2^{-1} (\langle \Psi_a^+ | - \langle \Psi_b^+ |) \hat{\rho}(\mathbf{r})_{N-1} (|\Psi_a^+\rangle - |\Psi_b^+\rangle) \\ &= 2^{-1} (\langle \Psi_a^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_a^+\rangle - \langle \Psi_a^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_b^+\rangle - \\ &\quad \langle \Psi_b^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_a^+\rangle + \langle \Psi_b^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_b^+\rangle) \\ &= 2^{-1} \left( 4 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_4(\mathbf{r})|_{N-1}^2 - |\psi_5(\mathbf{r})|_{N-1}^2 \right. \\ &\quad \left. + \psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} \right) \\ &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{2} \\ &\quad + \frac{\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1}}{2} \end{aligned}$$

The electronic density of the molecular system can be written as an arithmetic average of  $\rho(\mathbf{r})_{N-1}^{\perp}$  and  $\rho(\mathbf{r})_{N-1}^{\parallel}$  to cancel those cross terms of the type  $\psi_i^*(\mathbf{r})_{N-1} \cdot \psi_j(\mathbf{r})_{N-1}$  where  $i \neq j$ :

$$\begin{aligned} \rho(\mathbf{r})_{N-1}^{\text{L.C.}} &= 2^{-1} \left\{ \rho(\mathbf{r})_{N-1}^{\perp} + \rho(\mathbf{r})_{N-1}^{\parallel} \right\} \\ &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{2} \end{aligned}$$

As a result, the electronic density of the molecular system with  $N-1=9$  electrons has been adapted to the degeneracy of HOMO and the electrophilic Fukui function can be correctly written as follows:

$$\begin{aligned}
 f^-(\mathbf{r}) &= \rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-1}^{\text{L.C.}} \\
 &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_N^2 - 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 + \frac{|\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{2} \\
 &= 2 \sum_{i=1}^5 \left\{ |\psi_i(\mathbf{r})|_N^2 - |\psi_i(\mathbf{r})|_{N-1}^2 \right\} + \frac{|\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{2}
 \end{aligned}$$

This corresponds to an operational formula to describe the electrophilic Fukui function for a molecular system having a twofold degenerate HOMO; it is easy to check that the normalization condition is satisfied by this mathematical expression.

### The electrophilic Fukui function $f^-(\mathbf{r})$ in presence of a threefold degenerate HOMO

Let us examine the case for a threefold degenerate HOMO for the electrically neutral molecular system having  $N = 10$  electrons, meaning that  $\psi_3(\mathbf{r})$ ,  $\psi_4(\mathbf{r})$ , and  $\psi_5(\mathbf{r})$  are the three degenerate HOMOs. In such a case, any of these three HOMOs are capable to donate one electron each with the same likelihood; hence, any of these three Slater determinants can represent the resulting cationic system:

$$\begin{aligned}
 |\Psi_{\mathbf{a}}^+\rangle &= |\psi_1 \overline{\psi_1} \overline{\psi_2} \overline{\psi_2} \overline{\psi_3} \overline{\psi_3} \psi_4 \overline{\psi_4} \psi_5 \rangle \\
 &= -|\psi_1 \overline{\psi_1} \overline{\psi_2} \overline{\psi_2} \psi_3 \overline{\psi_3} \psi_4 \psi_5 \overline{\psi_4} \rangle \\
 &= -|\psi_1 \overline{\psi_1} \overline{\psi_2} \overline{\psi_2} \psi_3 \psi_4 \overline{\psi_4} \psi_5 \overline{\psi_3} \rangle \\
 |\Psi_{\mathbf{b}}^+\rangle &= |\psi_1 \overline{\psi_1} \overline{\psi_2} \overline{\psi_2} \overline{\psi_3} \overline{\psi_3} \psi_4 \psi_5 \overline{\psi_5} \rangle \\
 &= -|\psi_1 \overline{\psi_1} \overline{\psi_2} \overline{\psi_2} \psi_3 \psi_4 \overline{\psi_3} \psi_5 \overline{\psi_5} \rangle \\
 |\Psi_{\mathbf{c}}^+\rangle &= |\psi_1 \overline{\psi_1} \overline{\psi_2} \overline{\psi_2} \overline{\psi_3} \psi_4 \overline{\psi_4} \psi_5 \overline{\psi_5} \rangle
 \end{aligned}$$

Therefore, the following linear combinations can be used for this cationic system:

$$\begin{aligned}
 |\Psi_{\mathbf{I}}^+\rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^+\rangle + |\Psi_{\mathbf{b}}^+\rangle + |\Psi_{\mathbf{c}}^+\rangle) \\
 |\Psi_{\mathbf{II}}^+\rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^+\rangle - |\Psi_{\mathbf{b}}^+\rangle + |\Psi_{\mathbf{c}}^+\rangle) \\
 |\Psi_{\mathbf{III}}^+\rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^+\rangle + |\Psi_{\mathbf{b}}^+\rangle - |\Psi_{\mathbf{c}}^+\rangle) \\
 |\Psi_{\mathbf{IV}}^+\rangle &= 3^{-1/2} (|\Psi_{\mathbf{a}}^+\rangle - |\Psi_{\mathbf{b}}^+\rangle - |\Psi_{\mathbf{c}}^+\rangle)
 \end{aligned}$$

where

$$\begin{aligned}
 \langle \Psi_{\mathbf{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{a}}^+ \rangle &= 2 \sum_{i=1}^4 |\psi_i(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2 \\
 &\equiv 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_5(\mathbf{r})|_{N-1}^2 \\
 \langle \Psi_{\mathbf{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{b}}^+ \rangle &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_4(\mathbf{r})|_{N-1}^2 \\
 \langle \Psi_{\mathbf{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{c}}^+ \rangle &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - |\psi_3(\mathbf{r})|_{N-1}^2 \\
 \langle \Psi_{\mathbf{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{b}}^+ \rangle &= -\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} \\
 \langle \Psi_{\mathbf{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{a}}^+ \rangle &= -\psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} \\
 \langle \Psi_{\mathbf{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{c}}^+ \rangle &= -\psi_3^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} \\
 \langle \Psi_{\mathbf{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{a}}^+ \rangle &= -\psi_5^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1} \\
 \langle \Psi_{\mathbf{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{c}}^+ \rangle &= -\psi_3^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} \\
 \langle \Psi_{\mathbf{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{b}}^+ \rangle &= -\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1}
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_{N-1} = \sum_{j=1}^{N-9} \delta(\mathbf{r}_j - \mathbf{r})$ . Bearing in mind these four possible linear combinations, the electronic density when the molecular system donates one electron can be written in these four possible ways.

The first linear combination given by  $|\Psi_{\mathbf{I}}^+\rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N-1}^{\mathbf{I}}$ :

$$\begin{aligned}
 \rho(\mathbf{r})_{N-1}^{\mathbf{I}} &= \langle \Psi_{\mathbf{I}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{I}}^+ \rangle \\
 &= 3^{-1/2} (\langle \Psi_{\mathbf{a}}^+ | + \langle \Psi_{\mathbf{b}}^+ | + \langle \Psi_{\mathbf{c}}^+ |) \hat{\rho}(\mathbf{r})_{N-1} (|\Psi_{\mathbf{a}}^+\rangle + |\Psi_{\mathbf{b}}^+\rangle + |\Psi_{\mathbf{c}}^+\rangle) 3^{-1/2} \\
 &= 3^{-1} (\langle \Psi_{\mathbf{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{a}}^+ \rangle + \langle \Psi_{\mathbf{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{b}}^+ \rangle + \langle \Psi_{\mathbf{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{c}}^+ \rangle \\
 &\quad + \langle \Psi_{\mathbf{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{a}}^+ \rangle + \langle \Psi_{\mathbf{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{b}}^+ \rangle + \langle \Psi_{\mathbf{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{c}}^+ \rangle \\
 &\quad + \langle \Psi_{\mathbf{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{a}}^+ \rangle + \langle \Psi_{\mathbf{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{b}}^+ \rangle + \langle \Psi_{\mathbf{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\mathbf{c}}^+ \rangle) \\
 &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3} \\
 &\quad - \frac{\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} + \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1} + \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} + \psi_4^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1}}{3}
 \end{aligned}$$

The second linear combination given by  $|\Psi_{\mathbf{II}}^+\rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N-1}^{\mathbf{II}}$ :

$$\begin{aligned}
\rho(\mathbf{r})_{N-1}^{\text{II}} &= \langle \Psi_{\text{II}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{II}}^+ \rangle \\
&= 3^{-1/2} (\langle \Psi_{\text{a}}^+ | - \langle \Psi_{\text{b}}^+ | + \langle \Psi_{\text{c}}^+ |) \hat{\rho}(\mathbf{r})_{N-1} (| \Psi_{\text{a}}^+ \rangle - | \Psi_{\text{b}}^+ \rangle + | \Psi_{\text{c}}^+ \rangle) 3^{-1/2} \\
&= 3^{-1} (\langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle - \langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle + \langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle \\
&\quad - \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle + \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle - \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle \\
&\quad + \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle - \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle + \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle) \\
&= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3} \\
&+ \frac{\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} - \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} + \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1}}{3} \\
&\quad + \frac{-\psi_5^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1} + \psi_4^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1}}{3}
\end{aligned}$$

The third linear combination given by  $|\Psi_{\text{III}}^+\rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N-1}^{\text{III}}$ :

$$\begin{aligned}
\rho(\mathbf{r})_{N-1}^{\text{III}} &= \langle \Psi_{\text{III}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{III}}^+ \rangle \\
&= 3^{-1/2} (\langle \Psi_{\text{a}}^+ | + \langle \Psi_{\text{b}}^+ | - \langle \Psi_{\text{c}}^+ |) \hat{\rho}(\mathbf{r})_{N-1} (| \Psi_{\text{a}}^+ \rangle + | \Psi_{\text{b}}^+ \rangle - | \Psi_{\text{c}}^+ \rangle) 3^{-1/2} \\
&= 3^{-1} (\langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle + \langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle - \langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle \\
&\quad + \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle + \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle - \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle \\
&\quad - \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle - \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle + \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle) \\
&= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3} \\
&+ \frac{-\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} - \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} + \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1}}{3} \\
&\quad + \frac{\psi_5^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1} + \psi_4^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1}}{3}
\end{aligned}$$

And the fourth linear combination given by  $|\Psi_{\text{IV}}^+\rangle$  leads to an electronic density that will be called  $\rho(\mathbf{r})_{N-1}^{\text{IV}}$ :

$$\begin{aligned}
\rho(\mathbf{r})_{N-1}^{\text{IV}} &= \langle \Psi_{\text{IV}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{IV}}^+ \rangle \\
&= 3^{-1/2} (\langle \Psi_{\text{a}}^+ | - \langle \Psi_{\text{b}}^+ | - \langle \Psi_{\text{c}}^+ |) \hat{\rho}(\mathbf{r})_{N-1} (| \Psi_{\text{a}}^+ \rangle - | \Psi_{\text{b}}^+ \rangle - | \Psi_{\text{c}}^+ \rangle) 3^{-1/2} \\
&= 3^{-1} (\langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle - \langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle - \langle \Psi_{\text{a}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle \\
&\quad - \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle + \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle + \langle \Psi_{\text{b}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle \\
&\quad - \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{a}}^+ \rangle + \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{b}}^+ \rangle + \langle \Psi_{\text{c}}^+ | \hat{\rho}(\mathbf{r})_{N-1} | \Psi_{\text{c}}^+ \rangle) \\
&= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3} \\
&+ \frac{\psi_4^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_5(\mathbf{r})_{N-1} + \psi_5^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1} - \psi_3^*(\mathbf{r})_{N-1} \cdot \psi_4(\mathbf{r})_{N-1}}{3} \\
&\quad + \frac{\psi_5^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1} - \psi_4^*(\mathbf{r})_{N-1} \cdot \psi_3(\mathbf{r})_{N-1}}{3}
\end{aligned}$$

The arithmetic average of these four expressions leads to an expression free of cross terms of the type  $\psi_i^*(\mathbf{r})_{N-1} \cdot \psi_j(\mathbf{r})_{N-1}$  where  $i \neq j$ :

$$\begin{aligned}
\rho(\mathbf{r})_{N-1}^{\text{L.C.}} &= 4^{-1} \{ \rho(\mathbf{r})_{N-1}^{\text{I}} + \rho(\mathbf{r})_{N-1}^{\text{II}} + \rho(\mathbf{r})_{N-1}^{\text{III}} + \rho(\mathbf{r})_{N-1}^{\text{IV}} \} \\
&= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 - \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3}
\end{aligned}$$

and the electrophilic Fukui function can be correctly written as follows:

$$\begin{aligned}
 f^-(\mathbf{r}) &= \rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-1}^{\text{L.C.}} \\
 &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_N^2 - 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-1}^2 \\
 &\quad + \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3} \\
 &= 2 \sum_{i=1}^5 \left\{ |\psi_i(\mathbf{r})|_N^2 - |\psi_i(\mathbf{r})|_{N-1}^2 \right\} \\
 &\quad + \frac{|\psi_3(\mathbf{r})|_{N-1}^2 + |\psi_4(\mathbf{r})|_{N-1}^2 + |\psi_5(\mathbf{r})|_{N-1}^2}{3}
 \end{aligned}$$

The normalization condition of  $f^-(\mathbf{r})$  is satisfied by this operational formula.

### The electrophilic Fukui function $f^-(\mathbf{r})$ in presence of a $q$ -fold degenerate HOMO

A generalization of this methodology implies to extend it onto any closed-shell molecular system having  $N$  electrons (being  $N$  an even number) and presenting a  $q$ -fold degenerate HOMO because always there will be a proper linear combination capable to lead to an expression for the total electronic density in which the  $q$  degenerate HOMOs are taken into account:

$$f^-(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \left\{ |\psi_i(\mathbf{r})|_N^2 - |\psi_i(\mathbf{r})|_{N-1}^2 \right\} + \frac{1}{q} \sum_{i=N/2+1-q}^{N/2} |\psi_i(\mathbf{r})|_{N-1}^2 \quad (9)$$

It can be noticed that the normalization condition of  $f^-(\mathbf{r})$  is satisfied by this operational formula. Alike the case of the nucleophilic Fukui function, this procedure is tedious to perform owing to its increasing complexity in the treatment of the respective linear combinations as the degree of degeneracy  $q$  is increased.

### The proposal for an electrophilic Fukui function $f^-(\mathbf{r})$ in presence of a $q$ -fold degenerate HOMO

Alternatively, the use of all of the  $q$  degenerate HOMOs instead of using a linear combination of them should lead to an expression where each HOMO is occupied by one electron with upward spin as depicted by Figure 3. Again, starting with the case of a 10-electron molecular system with a twofold degenerate HOMO, then both HOMOs will be occupied by one alpha electron each and as a consequence the respective Slater determinant for this di-cationic system will be described by the following Slater determinant:  $|\Psi^{+2}\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \psi_5\rangle$  According to the latter, after applying the respective density operator, the electronic density is given by:

$$\begin{aligned}
 \langle \Psi^{+2} | \hat{\rho}(\mathbf{r})_{N-2} | \Psi^{+2} \rangle &= \langle \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \psi_5 | \hat{\rho}(\mathbf{r}) \\
 &\quad | \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \bar{\psi}_3 \psi_4 \psi_5 \rangle \\
 &= \rho(\mathbf{r})_{N-2} \\
 &= 2 \sum_{i=1}^3 |\psi_i(\mathbf{r})|_{N-2}^2 + |\psi_4(\mathbf{r})|_{N-2}^2 + |\psi_5(\mathbf{r})|_{N-2}^2 \\
 &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-2}^2 - |\psi_4(\mathbf{r})|_{N-2}^2 - |\psi_5(\mathbf{r})|_{N-2}^2
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_{N-2} = \sum_{j=1}^{N=8} \delta(\mathbf{r}_j - \mathbf{r})$ .

The electrophilic Fukui function must be obtained from the original definition given by the FDA:

$$\begin{aligned}
 f^-(\mathbf{r}) &= \frac{\langle \Psi | \hat{\rho}(\mathbf{r})_N | \Psi \rangle - \langle \Psi^{+2} | \hat{\rho}(\mathbf{r})_{N-2} | \Psi^{+2} \rangle}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-2}}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-2}}{N - (N-2)} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-2}}{2} \\
 &= \frac{2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_N^2 - 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-2}^2 + |\psi_4(\mathbf{r})|_{N-2}^2 + |\psi_5(\mathbf{r})|_{N-2}^2}{2} \\
 &= \sum_{i=1}^5 \left\{ |\psi_i(\mathbf{r})|_N^2 - |\psi_i(\mathbf{r})|_{N-2}^2 \right\} + \frac{|\psi_4(\mathbf{r})|_{N-2}^2 + |\psi_5(\mathbf{r})|_{N-2}^2}{2}
 \end{aligned}$$

Notice that this operational formula satisfies the normalization condition of  $f^-(\mathbf{r})$ . A threefold degenerate HOMO systems leads to a calculation involving a tri-cation, so that the  $|\Psi^{+3}\rangle$  Slater determinant must be used:

$$\begin{aligned}
 \langle \Psi^{+3} | \hat{\rho}(\mathbf{r})_{N-3} | \Psi^{+3} \rangle &= \langle \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \psi_4 \psi_5 | \\
 &\quad \hat{\rho}(\mathbf{r})_{N-3} | \psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_3 \psi_4 \psi_5 \rangle \\
 &= \rho(\mathbf{r})_{N-3} \\
 &= 2 \sum_{i=1}^2 |\psi_i(\mathbf{r})|_{N-3}^2 + |\psi_3(\mathbf{r})|_{N-3}^2 + |\psi_4(\mathbf{r})|_{N-3}^2 + |\psi_5(\mathbf{r})|_{N-3}^2 \\
 &= 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-3}^2 - |\psi_3(\mathbf{r})|_{N-3}^2 - |\psi_4(\mathbf{r})|_{N-3}^2 - |\psi_5(\mathbf{r})|_{N-3}^2
 \end{aligned}$$

where

$$\hat{\rho}(\mathbf{r})_{N-3} = \sum_{j=1}^{N=7} \delta(\mathbf{r}_j - \mathbf{r})$$

The respective electrophilic Fukui function is obtained from the original definition given by the FDA:

$$\begin{aligned}
 f^-(\mathbf{r}) &= \frac{\langle \Psi | \hat{\rho}(\mathbf{r})_N | \Psi \rangle - \langle \Psi^{+3} | \hat{\rho}(\mathbf{r})_{N-3} | \Psi^{+3} \rangle}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-3}}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-3}}{N - (N-3)} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-3}}{3} \\
 &= \frac{2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_N^2 - 2 \sum_{i=1}^5 |\psi_i(\mathbf{r})|_{N-3}^2 + |\psi_3(\mathbf{r})|_{N-3}^2 + |\psi_4(\mathbf{r})|_{N-3}^2 + |\psi_5(\mathbf{r})|_{N-3}^2}{3} \\
 &= \frac{2}{3} \sum_{i=1}^5 \left\{ |\psi_i(\mathbf{r})|_N^2 - |\psi_i(\mathbf{r})|_{N-3}^2 \right\} + \frac{|\psi_3(\mathbf{r})|_{N-3}^2 + |\psi_4(\mathbf{r})|_{N-3}^2 + |\psi_5(\mathbf{r})|_{N-3}^2}{3}
 \end{aligned}$$

Notice that the normalization condition of  $f^-(\mathbf{r})$  is satisfied by this operational formula. This analysis was developed on a molecular system having 10 electrons ( $N = 10$ ) and a threefold degenerate HOMO. However, the same analysis will allow to obtain a general expression to be applied on a system with  $N$  electrons (where  $N$  is an even number with  $N \geq 2$ ) and presenting a  $q$ -fold degenerate HOMO. The latter leads to define a Slater determinant for a cation with a net electric charge of  $+q$ ,  $|\Psi^{+q}\rangle$ . As a result, the respective operational formula for the electrophilic Fukui function is written as follows:

$$\begin{aligned}
 f^-(\mathbf{r}) &= \frac{\langle \Psi | \hat{\rho}(\mathbf{r})_N | \Psi \rangle - \langle \Psi^{+q} | \hat{\rho}(\mathbf{r})_{N-q} | \Psi^{+q} \rangle}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-q}}{\Delta N} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-q}}{N - (N-q)} \\
 &= \frac{\rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-q}}{q} \\
 &= \frac{1}{q} \left\{ \rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-q} \right\} \\
 &= \frac{1}{q} \left\{ 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|_N^2 - 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2 + \sum_{i=N/2+1-q}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2 \right\} \\
 &= \frac{2}{q} \sum_{i=1}^{N/2} \left\{ |\psi_i(\mathbf{r})|_N^2 - |\psi_i(\mathbf{r})|_{N-q}^2 \right\} + \frac{1}{q} \sum_{i=N/2+1-q}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2 \quad (10)
 \end{aligned}$$

where  $\hat{\rho}(\mathbf{r})_N = \sum_{j=1}^N \delta(\mathbf{r}_j - \mathbf{r})$  and  $\hat{\rho}(\mathbf{r})_{N-q} = \sum_{j=1}^{N-q} \delta(\mathbf{r}_j - \mathbf{r})$ . Notice that this operational formula satisfies the normalization condition of  $f^-(\mathbf{r})$ .

The reader can notice there is a resemblance between eqs. (9) and (10). They both are plausible operational formulae, but eq. (10) is obtained easier than eq. (9). In absence of molecular orbital relaxation, the strong approximation  $|\psi_i(\mathbf{r})|_N^2 \approx |\psi_i(\mathbf{r})|_{N-q}^2$  arises in these both equations thus leading to the well-known electrophilic Fukui function adapted to the  $q$ -fold degenerate HOMO<sup>[34]</sup>; but in such an approximation the electrophilic Fukui function is only written in terms of the

electronic densities of these degenerate frontier molecular orbitals, with the risk of giving an inaccurate 3D picture of the local reactivity. Observe that  $\rho(\mathbf{r})_{N-q}$  was split into two sums which were rearranged as an arithmetic difference of two sums:

$$\begin{aligned}
 \rho(\mathbf{r})_{N-q} &= 2 \sum_{i=1}^{N/2-q} |\psi_i(\mathbf{r})|_{N-q}^2 + \sum_{i=N/2-q+1}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2 \\
 &= 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2 - \sum_{i=N/2-q+1}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2
 \end{aligned}$$

For all reasons previously explained, the use of eqs. (5) and (6) will not be useful because the description of local reactivity will be incomplete for those molecules presenting degeneracies in their frontier molecular orbitals. Hence, these operational formulae must be replaced the operational formulae given by eqs. (11) and (12) which are supported by the definitions given in terms of all involved molecular orbitals as eqs. (10) and (8) have demonstrated.

The eq. (11) is a generalized nucleophilic Fukui function and it tell us that there are  $p$  possible LUMOs where one electron can arrive. Then, the calculation of the electronic density of the molecular system with  $N+p$  electrons,  $\rho(\mathbf{r})_{N+p}$ , must be computed with the maximum value of spin-multiplicity associated to the unpaired electrons located at the  $p$  degenerate LUMOs. The latter leads to obtain a value of spin-multiplicity equal to  $p+1$ . The arithmetic difference between the electronic density  $\rho(\mathbf{r})_{N+p}$  and the original electronic density  $\rho(\mathbf{r})_N$  must be divided by  $p$  to conserve the normalization condition of the nucleophilic Fukui function:

$$f^+(\mathbf{r}) = \frac{1}{p} \left\{ \rho(\mathbf{r})_{N+p} - \rho(\mathbf{r})_N \right\}, \quad (11)$$

Along with the operational formula given by the eq. (11), the generalized electrophilic Fukui function is given by eq. (12). It tell us there are  $q$  possible HOMOs from where one electron can depart from the molecular system. This leads to compute the electronic density of the molecular system with  $N-q$  electrons,  $\rho(\mathbf{r})_{N-q}$ , in its maximum value of spin-multiplicity associated to the unpaired electrons located at the  $q$  degenerate HOMOs. The latter allows us to obtain a value of spin-

multiplicity equal to  $q+1$ . This electronic density obtained so is subtracted to the original electronic density  $\rho(\mathbf{r})_N$  and this arithmetic difference is divided by  $q$  with the aim to conserve the normalization condition of the electrophilic Fukui function:

$$f^-(\mathbf{r}) = \frac{1}{q} \left\{ \rho(\mathbf{r})_N - \rho(\mathbf{r})_{N-q} \right\}, \quad (12)$$

As the DD is defined as the arithmetic difference between eqs. (11) and (12), the latter leads to:

$$f^{(2)}(\mathbf{r}) = \frac{q \cdot \rho(\mathbf{r})_{N+p} - (p+q) \cdot \rho(\mathbf{r})_N + p \cdot \rho(\mathbf{r})_{N-q}}{p \cdot q}, \quad (13)$$

To emphasize the values of spin-multiplicities that must be used when computing the electronic densities for the system with  $N+p$  and  $N-q$  electrons, the eq. (13) can be re-written in the following way:

$$f^{(2)}(\mathbf{r}) = \frac{q \cdot \rho(\mathbf{r})_{N+p}^{p+1} - (p+q) \cdot \rho(\mathbf{r})_N^1 + p \cdot \rho(\mathbf{r})_{N-q}^{q+1}}{p \cdot q}, \quad (14)$$

Notice that whenever the calculation be performed for the molecule with  $N+p$  and  $N-q$  electrons, maxima values of the spin-multiplicities are taken into account ( $p+1$  and  $q+1$ , respectively), thus being an application of The Hund's Rule of Maximum Multiplicity due to the consequence of the degeneracy that is presented in frontier molecular orbitals. To end this analysis, it is important to mention that the proposed operational formula satisfies the characteristic normalization condition of the DD<sup>[7]</sup> which can be easily demonstrated by pen and hand:

$$\int_{\text{all space}} d\mathbf{r} f^{(2)}(\mathbf{r}) = 0$$

In more detail, we can examine the eq. (14) in terms of densities of molecular orbitals through the analysis of the arithmetic difference between eqs. (8) and (10):

$$f^{(2)}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \left\{ \frac{q \cdot |\psi_i(\mathbf{r})|_{N+p}^2 - (p+q) \cdot |\psi_i(\mathbf{r})|_N^2 + p \cdot |\psi_i(\mathbf{r})|_{N-q}^2}{p \cdot q} \right\} + \frac{1}{p} \sum_{i=N/2+1}^{N/2+p} |\psi_i(\mathbf{r})|_{N+p}^2 - \frac{1}{q} \sum_{i=N/2+1-q}^{N/2} |\psi_i(\mathbf{r})|_{N-q}^2 \quad (15)$$

When  $p=q=1$ , the eq. (2) [or eq. (3) because they are the same in practice] is recovered which can be written in terms of densities of molecular orbitals:

$$f^{(2)}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \left\{ |\psi_i(\mathbf{r})|_{N+1}^2 - 2|\psi_i(\mathbf{r})|_N^2 + |\psi_i(\mathbf{r})|_{N-1}^2 \right\} + |\psi_{N/2+1}(\mathbf{r})|_{N+1}^2 - |\psi_{N/2}(\mathbf{r})|_{N-1}^2$$

And when the orbital relaxation is not relevant, thus meaning that  $|\psi_i(\mathbf{r})|_{N+1}^2 \approx |\psi_i(\mathbf{r})|_N^2 \approx |\psi_i(\mathbf{r})|_{N-1}^2$ , this expression is

reduced to the primitive operational formula suggested in terms of electronic densities of HOMO and LUMO:

$$f^{(2)}(\mathbf{r}) \approx |\psi_{N/2+1}(\mathbf{r})|_N^2 - |\psi_{N/2}(\mathbf{r})|_N^2 \equiv |\psi_{\text{LUMO}}(\mathbf{r})|_N^2 - |\psi_{\text{HOMO}}(\mathbf{r})|_N^2$$

where the  $N/2+1$  and  $N/2$  subscripts mean LUMO and HOMO, respectively<sup>[7]</sup> so that only one quantum chemical calculation is required for the original system with  $N$  electrons. Anyway, more simple than eq. (15) is to use the generalized operational formula given by eq. (14) thus indicating that the computation of the electronic densities of the system with  $N$ ,  $N+p$ , and  $N-q$  electrons with the values of spin-multiplicities ( $1$ ,  $p+1$ , and  $q+1$ , respectively) is sufficient to obtain the most accurate operational formula of the DD for a molecular system having or not a degree of degeneracy in HOMO, LUMO, or both. Of course the operational formula also works well for the case  $p=q=1$  as we demonstrated above and as exposed in the Results and Discussion section through an example given by the ethylene molecule which has no degeneracy in its frontier molecular orbitals.

## Computational Details

The eq. (14) has been tested with the following molecules:  $\text{C}_2\text{H}_4$  (ethylene);  $\text{CO}$  (carbon monoxide);  $\text{CO}_2$  (carbon dioxide);  $\text{HCN}$  (hydrogen cyanide);  $\text{C}_2\text{F}_2$  (difluoroacetylene);  $\text{C}_2\text{H}_2$  (acetylene);  $\text{PCl}_5$  (phosphorus pentachloride);  $\text{SF}_6$  (sulfur hexafluoride);  $\text{C}_6\text{H}_6$  (benzene);  $\text{C}_6\text{F}_6$  (hexafluorobenzene);  $\text{P}_4\text{O}_{10}$  (phosphorus pentoxide);  $\text{Cr}(\text{CO})_6$  (chromium hexacarbonyl), and  $\text{C}_{60}$  (Buckminsterfullerene).

All of them possess a degree of degeneracy that is equal to 2 or more at least at one frontier molecular orbital (HOMO or LUMO or both), with the exception of ethylene. Geometrical optimizations were performed by means of the M062X meta-GGA functional designed by Zhao and Truhlar<sup>[40]</sup> and using the 6-311 + G(d) Pople basis set<sup>[41-53]</sup> excepting for: ethylene, acetylene, hydrogen cyanide, and benzene where the 6-311 + G(d,p) Pople basis set was used, meanwhile for the Buckminsterfullere the 6-31G(d)<sup>[53-59]</sup> Pople basis was used and for the chromium hexacarbonyl the metallic atom was described by means of the LANL2TZ+ pseudopotential<sup>[60]</sup> and non-metal atoms by means of the 6-311 + G(d) Pople basis set.

Frequency calculations were then performed to identify the obtained stationary points as minima.<sup>[61]</sup> Next and to use of the operational formula given by the eq. (14), single point calculations for all the geometrically optimized molecules and their respective ions (cations and anions) were performed by means of the same M062X functional and using the 6-311 + G(d) Pople basis set excepting for ethylene, acetylene, hydrogen cyanide, and benzene where the 6-311 + G(d,p) Pople basis set was used, meanwhile for the Buckminsterfullere the 6-31 + G(d) Pople basis was used; for the chromium hexacarbonyl the same level of theory used for the geometrical optimization was used in all its single point calculations. The respective spin-multiplicities  $p+1$  and  $q+1$  were imposed during the calculation of the respective ions. As a

consequence the electronic densities were obtained for the following anions:  $C_2H_4^-$ ;  $CO^-$ ;  $CO_2^-$ ;  $CO_2^{2-}$ ;  $HCN^-$ ;  $C_2F_2^-$ ;  $C_2H_2^-$ ;  $PCl_5^-$ ;  $SF_6^-$ ;  $C_6H_6^-$ ;  $C_6F_6^-$ ;  $P_4O_{10}^-$ ;  $Cr(CO)_6^-$ ;  $Cr(CO)_6^{3-}$ ;  $C_{60}^-$ ; and  $C_{60}^{3-}$  and for the following cations:  $C_2H_4^+$ ;  $CO^+$ ;  $CO_2^+$ ;  $HCN^+$ ;  $HCN^{2+}$ ;  $CO_2^{2+}$ ;  $C_2F_2^+$ ;  $C_2F_2^{2+}$ ;  $C_2H_2^+$ ;  $C_2H_2^{2+}$ ;  $PCl_5^+$ ;  $PCl_5^{2+}$ ;  $SF_6^+$ ;  $SF_6^{3+}$ ;  $C_6H_6^+$ ;  $C_6H_6^{2+}$ ;  $C_6F_6^+$ ;  $C_6F_6^{2+}$ ;  $P_4O_{10}^+$ ;  $P_4O_{10}^{3+}$ ;  $Cr(CO)_6^+$ ;  $Cr(CO)_6^{3+}$ ;  $C_{60}^+$ ; and  $C_{60}^{5+}$ . Notice that every cation coming from a molecule with a  $q$ -fold degenerate HOMO and every anion coming from a molecule with a  $p$ -fold degenerate LUMO, has a net electric charge of  $+q$  (written as a superscript in the manner  $q+$ ) and  $-p$  (written as a superscript in the manner  $p-$ ), respectively. These ions were computed with the purpose of obtaining 3D pictures of electronic densities in agreement with eq. (14). In addition, mono-cations and mono-anions were computed too for all these molecules independently of the presence or absence of degeneracy in their frontier molecular orbitals with the aim of using the eq. (4) and compare the resulting 3D pictures with those obtained through eq. (14). The use of diffuse functions has been required in all quantum chemical calculations to build up the DD for each molecule because, for every molecule that has been analyzed here, this local reactivity descriptor depends on an anionic electronic density.

All calculations were carried out using the Gaussian 09<sup>[62]</sup> software package. All of the 3D pictures of the DD were visualized by means of GaussView 5.0.9.<sup>[63]</sup> The cubegen program allowed us to generate the respective cubes to plot the 3D electronic densities of neutral and ionic molecular systems and all of the arithmetical operations among cubes were carried out by means of the cubman program. Both cubegen and cubman programs are included in the Gaussian 09 software suite.

## Results and Discussions

After performing the quantum chemical calculations described in the previous section, results concerning to energy values of HOMO, LUMO, and their respective degeneracies are exposed in Tables 1 and 2. The Buckminster fullerene exhibited the

**Table 1.** Energies (expressed in hartrees) of the lowest unoccupied molecular orbitals (LUMOs) and their respective degree of degeneracy which is represented by  $p$ .

Molecule	LUMO	LUMO +1	LUMO +2	$p$
$C_2H_4$	0.00701	-	-	1
CO	0.01077	0.01077	-	2
$CO_2$	-0.00144	-	-	1
HCN	0.00039	-	-	1
$C_2F_2$	0.00527	-	-	1
$C_2H_2$	0.00796	-	-	1
$PCl_5$	-0.11708	-	-	1
$SF_6$	-0.04644	-	-	1
$C_6H_6$	-0.00017	-	-	1
$C_6F_6$	-0.03017	-	-	1
$P_4O_{10}$	-0.05496	-	-	1
$Cr(CO)_6$	-0.01225	-0.01225	-0.01225	3
$C_{60}$	-0.11221	-0.11215	-0.11215	3

An arbitrary and reasonable threshold value for considering a case of degenerate orbitals is given by a value of difference in energy of  $1 \cdot 10^{-4}$  hartree.

**Table 2.** Energies (expressed in hartrees) of the highest occupied molecular orbitals (HOMOs) and their respective degree of degeneracy which is represented by  $q$ .

Molecule	HOMO	HOMO -1	HOMO -2	HOMO -3	HOMO -4	$q$
$C_2H_4$	-0.33588	-	-	-	-	1
CO	-0.45189	-	-	-	-	1
$CO_2$	-0.45413	-0.45413	-	-	-	2
HCN	-0.43716	-0.43716	-	-	-	2
$C_2F_2$	-0.36102	-0.36102	-	-	-	2
$C_2H_2$	-0.35838	-0.35838	-	-	-	2
$PCl_5$	-0.37855	-0.37855	-	-	-	2
$SF_6$	-0.55537	-0.55537	-0.55537	-	-	3
$C_6H_6$	-0.30956	-0.30958	-	-	-	2
$C_6F_6$	-0.34556	-0.34565	-	-	-	2
$P_4O_{10}$	-0.46895	-0.46895	-0.46898	-	-	3
$Cr(CO)_6$	-0.30331	-0.30331	-0.30331	-	-	3
$C_{60}$	-0.27713	-0.27715	-0.27716	-0.27717	-0.27720	5

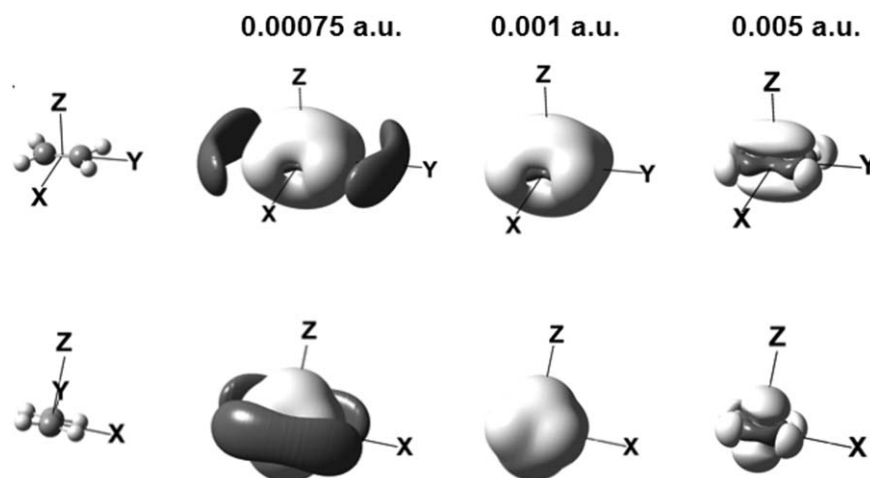
An arbitrary and reasonable threshold value for considering a case of degenerate orbitals is given by a value of difference in energy of  $1 \cdot 10^{-4}$  hartree.

maximum number of degeneracies in its frontier molecular orbitals ( $p=3$  and  $q=5$ ), therefore, the quoted tables show until LUMO +2 and HOMO -4, respectively.

All of the 3D pictures of isosurfaces of the DD defined by the eqs. (4) and (14) are depicted by Figures 4–16. These isosurfaces are characterized by lobes which are divided into two types: dark-colored lobes corresponding to the positive phase of the DD ( $f^{(2)}(\mathbf{r}) > 0$ ) and white-colored lobes corresponding to the negative phase of the DD ( $f^{(2)}(\mathbf{r}) < 0$ ). Once defined the color code, we analyzed the local reactivity belonging to the selected molecules from the perspective of the DD. A way to test the quality of the eq. (14) to properly reveal the local reactivity is given by the fact that the 3D picture must belong to the respective totally symmetric irreducible representation of the symmetry group of the respective molecule under analysis. In every figure that is displayed, the DD is represented as a 3D picture of an isosurface at specific cuts expressed in atomic units (a.u.); isosurfaces given by means of the eq. (4) are depicted on zone (a), isosurfaces given by means of the eq. (14) are depicted on zone (b). The respective degrees of degeneracy ( $p$  and  $q$ ) were extracted from Tables 1 and 2 to be used on eq. (14).

The  $C_2H_4$  molecule, displayed by Figure 4, has two carbon atoms and four hydrogen atoms; the two carbon atoms are chemically equivalent each other and the hydrogen atoms are chemically equivalent among them too, so that the DD must be able to reveal the same information, but graphically through a 3D picture of an isosurface at certain values. Inasmuch as  $p=q=1$ , the use of the operational formula given by eq. (14) is equivalent to use the original operational formula given by eq. (4). According to Figure 4,  $\pi$  electrons are more favorable to undergo an electrophilic attack rather than a nucleophilic attack on hydrogen atoms; hence, we expect a predominance of electrophilic attacks on this molecule along the Z axis mainly with: (i) a maximum likelihood on the double bond between the two carbon atoms; (ii) and a smaller likelihood along the X axis as depicted by Figure 4. Nucleophilic

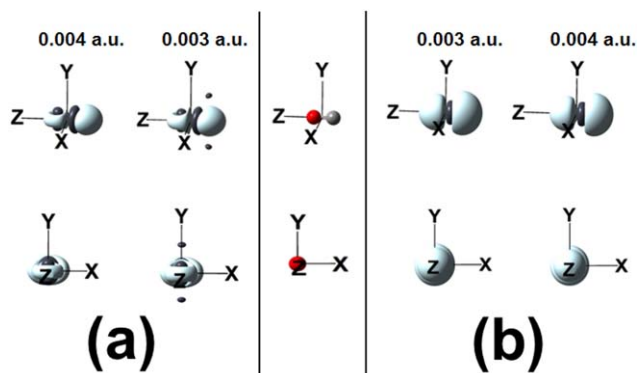




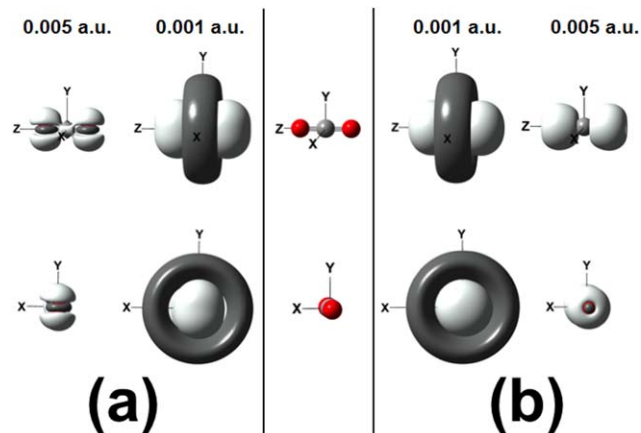
**Figure 4.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $C_2H_4$  molecule; isosurfaces of the DD have been depicted at values of 0.00075 a.u.; 0.001 a.u. and 0.005 a.u. and they were generated through the use of either both equations: eq. (4) or (14). Gray-colored spheres represent carbon atoms and white-colored spheres represent hydrogen atoms. On the top: a front perspective view, on the bottom: a side perspective view. Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region.

attacks are relevant along the Y axis at an isosurface value of 0.00075 a.u., thus meaning that this type of reactivity is secondary. Notice that the operational formula of the DD given by the eq. (4) provides an isosurface that belongs to the  $A_g$  totally symmetric irreducible representation ( $D_{2h}$  symmetry point group) and as  $p=q=1$  for ethylene, we can notice that the DD for this molecule is correctly represented either by eq. (4) or eq. (14) because there is no degeneracy in frontier molecular orbitals, being sufficient the use of the original operational formula given by eq. (2). So far, using any of these two operational formulae is irrelevant.

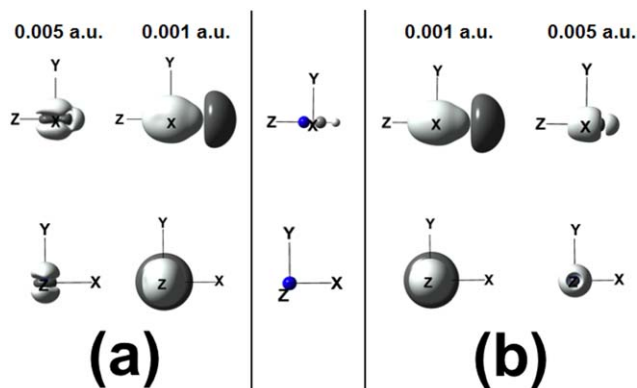
The CO molecule is depicted by Figure 5. The operational formula given by eq. (4) is displayed at isosurface values of 0.003 a.u. and 0.004 a.u. by Figure 5a. This operational formula fails because it reveals an incomplete local reactivity on this molecule around the Z axis. In addition, there are some small positive phases of the DD that appear as dark points over and below the X-Z plane near the carbon atom; these isosurfaces do not belong to the  $A_1$  totally symmetric irreducible representation ( $C_{\infty v}$  symmetry point group). Let us analyze the



**Figure 5.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the CO molecule; isosurfaces of the DD have been depicted at values of 0.003 a.u. and 0.004 a.u.; the red-colored sphere represents an oxygen atom and the gray-colored sphere represents a carbon atom. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

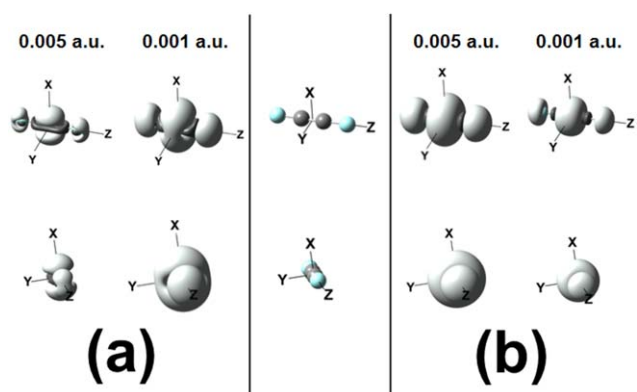


**Figure 6.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $CO_2$  molecule; isosurfaces of the DD have been depicted at values of 0.001 a.u. and 0.005 a.u.; red-colored spheres represent oxygen atoms and the gray-colored sphere represents the carbon atom. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

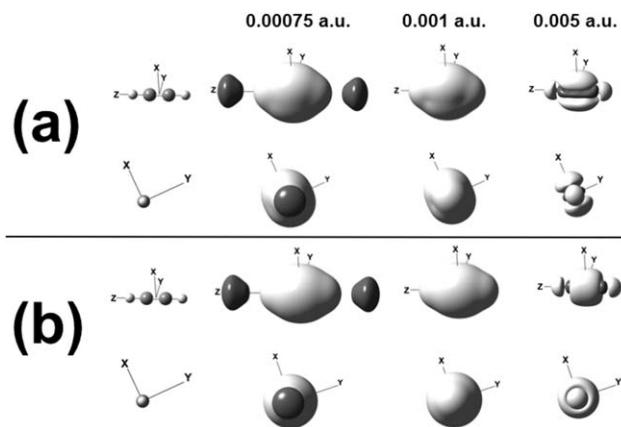


**Figure 7.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the HCN molecule; isosurfaces of the DD have been depicted at values of 0.001 a.u. and 0.005 a.u.; blue-colored sphere represents a nitrogen atom, the gray-colored sphere represents a carbon atom and the white-colored sphere corresponds to an hydrogen atom. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

operational formula given by eq. (14) and displayed by Figure 5b. It reveals that the carbon atom is more susceptible to undergo an electrophilic attack rather than the oxygen atom because it is observed that the white-colored lobe surrounding the carbon atom is bigger than the white-colored lobe that surrounds the oxygen atom. And the positive phase of this descriptor is represented by a dark-colored little lobe which is located along the Z axis that surrounds the carbon atom.

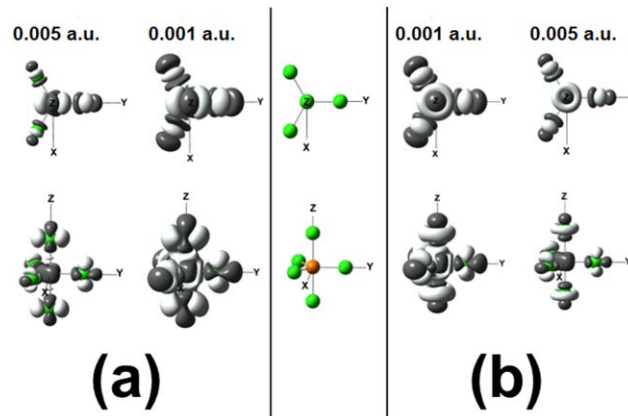


**Figure 8.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $C_2F_2$  molecule; isosurfaces of the DD have been depicted at values of 0.001 a.u. and 0.005 a.u.; pale blue-colored spheres represent fluorine atoms and gray-colored spheres represent carbon atoms. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

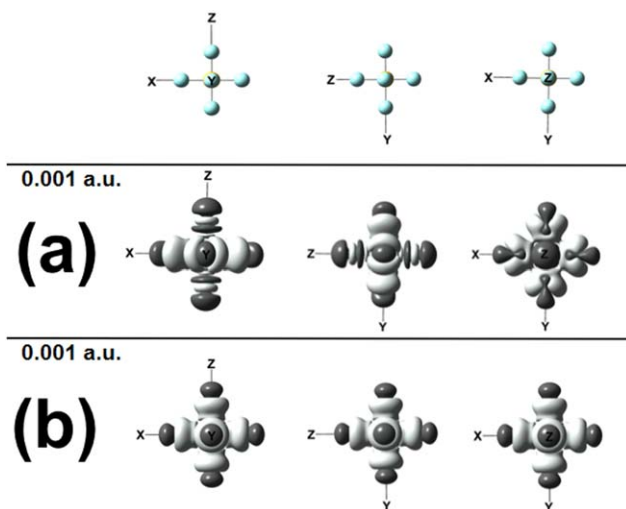


**Figure 9.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $C_2H_2$  molecule; isosurfaces of the DD have been depicted at values of 0.00075 a.u., 0.001 a.u. and 0.005 a.u.; gray-colored spheres represent the carbon atoms and white-colored spheres represent hydrogen atoms. (a) On the top: front and side perspective views of the DD given by eq. (4). (b) On the bottom: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region.

Anyway we can claim there is a predominance of electrophilic attacks on this molecule, meaning that this descriptor reveals that this molecule behaves as a strong electron-donor. The eq. (14) leads to a 3D picture of the DD that correctly belongs to the  $A_1$  totally symmetric irreducible representation, so implying a correct 3D description of this local reactivity descriptor for this molecule as explained above.

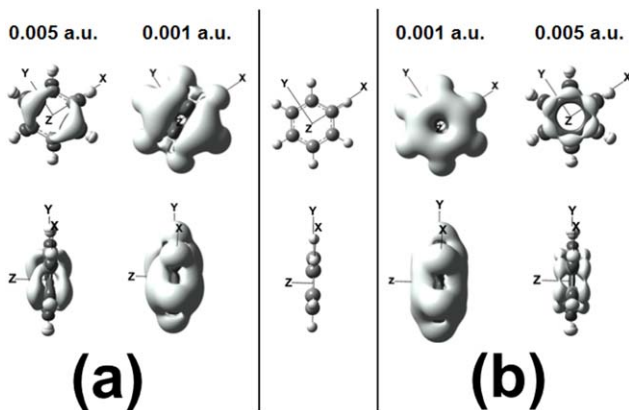


**Figure 10.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $PCl_5$  molecule; isosurfaces of the DD have been depicted at values of 0.001 a.u. and 0.005 a.u.; green-colored spheres represent chlorine atoms and the orange-colored sphere represents the phosphorus atom. (a) On the left: top and side perspective views of the DD given by eq. (4). (b) On the right: top and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

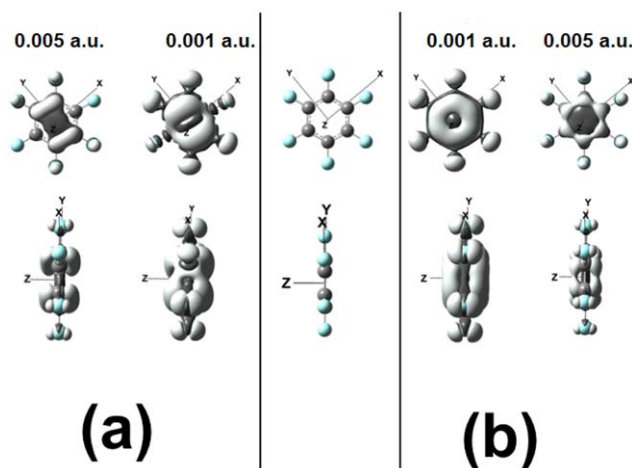


**Figure 11.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $\text{SF}_6$  molecule; isosurface of the DD has been depicted at a value of 0.001 a.u.; pale blue-colored spheres represent fluorine atoms and the yellow-colored sphere represents the sulfur atom (however, it is not possible to observe the sulfur atom because it is surrounded by fluorine atoms). (a) In the middle: front, top, and side perspective views of the DD given by eq. (4). (b) On the bottom: front, top, and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The  $\text{CO}_2$  molecule is depicted by Figure 6. When observing Figures 6a and 6b, it is tempting to claim that the operational formulae given by eqs. (4) and (14), respectively, at an isosurface

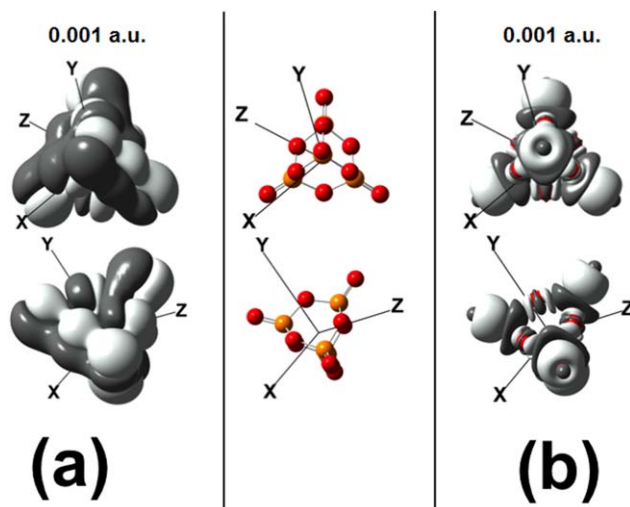


**Figure 12.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $\text{C}_6\text{H}_6$  molecule; isosurfaces of the DD have been depicted at values of 0.001 a.u. and 0.005 a.u.; gray-colored spheres represent carbon atoms and white-colored spheres represent hydrogen atoms. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

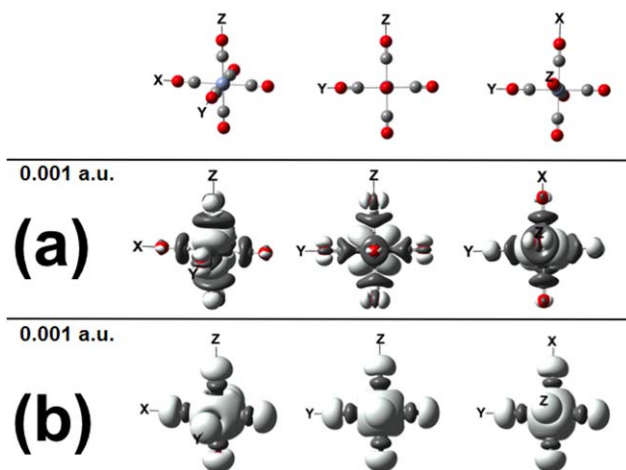


**Figure 13.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $\text{C}_6\text{F}_6$  molecule; isosurfaces of the DD have been depicted at values of 0.001 a.u. and 0.005 a.u.; gray-colored spheres represent carbon atoms and pale blue-colored spheres represent fluorine atoms. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

value of 0.001 a.u. do not differ each other because they both describe the same local reactivity: the positive phase of the DD represented by a dark-colored ring-shaped lobe is surrounding

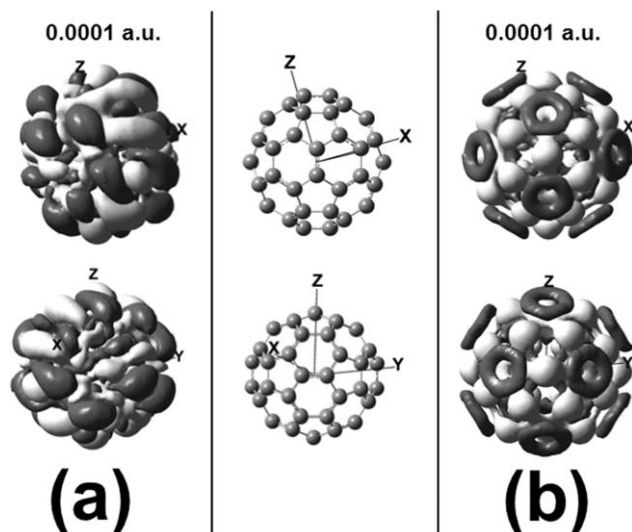


**Figure 14.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $\text{P}_4\text{O}_{10}$  molecule; isosurface of the DD has been depicted at a value of 0.001 a.u.; red-colored spheres represent oxygen atoms and orange-colored spheres represent phosphorus atoms. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 15.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $\text{Cr}(\text{CO})_6$  molecule; isosurface of the DD has been depicted at a value of 0.001 a.u.; the pale purple-colored central sphere represents a chromium atom; gray-colored spheres represent carbon atoms and red-colored spheres represent oxygen atoms (however, the chromium atom is not possible to see from all the perspectives). (a) In the middle: front, top, and side perspective views of the DD given by eq. (4). (b) On the bottom: front, top, and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the carbon atom along the  $X$ - $Y$  plane, meanwhile the negative phase of the DD represented by a white-colored lobe is located along the  $Z$  axis, just on the positions of oxygen atoms. But,



**Figure 16.** Molecular structure including cartesian axis along with the respective 3D picture of the DD for the  $\text{C}_{60}$  molecule; isosurface of the DD has been depicted at a value of 0.0001 a.u.; gray-colored spheres represent carbon atoms. (a) On the left: front and side perspective views of the DD given by eq. (4). (b) On the right: front and side perspective views of the DD given by eq. (14). Color code for a correct interpretation of the DD is explained as follows: Positive values of the DD are indicated by dark-colored lobes, thus revealing a preference to undergo nucleophilic attacks there; negative values of the DD are indicated by white-colored lobes, thus revealing a preference to undergo electrophilic attacks in such a region.

after a more detailed analysis by a simple observation through a side perspective view, we can realize that the negative phase of the DD depicted by Figure 6a is narrower in the  $X$ - $Y$  plane than the negative phase of the DD depicted by Figure 6b, so that the latter is a more representative picture of the local reactivity of this molecule.

To break down this subtle difference, the 3D picture at an isosurface value of 0.005 a.u. immediately reveals that eq. (4) is not good enough for a correct description of local reactivity of carbon dioxide because it reveals an erroneous local reactivity on this molecule around the  $Z$  axis as depicted by Figure 6a, in addition this 3D picture does not belong to the  $\Sigma_g^+$  totally symmetric irreducible representation ( $D_{\infty h}$  symmetry point group). As this molecule has two oxygen atoms, electrophilic attacks preferably would occur on them, while nucleophilic attacks will occur on the carbon atom preferably. The local reactivity as expected is well-described by the DD given by eq. (14) as Figure 6b indicates: The operational formula given by the eq. (14) builds up a 3D picture of the DD that correctly belongs to the  $\Sigma_g^+$  totally symmetric irreducible representation so that this is the correct 3D representation of the DD for the  $\text{CO}_2$  molecule.

Similarly to the previous molecule, the HCN is also a three-member molecule that is depicted by Figure 7. Again, when the DD is displayed at an isosurface value of 0.001 a.u., we are not able to realize that operational formulae given by eqs. (4) and (14) have differences as depicted by Figure 7a and 7b, however the negative phase of the DD according to eq. (4) is a little bit narrower in the  $Y$ - $Z$  plane in comparison with the same negative phase of the DD given by eq. (14). To make sure that eq. (4) leads to an incomplete 3D picture of the DD it is sufficient to change the cut of this local reactivity descriptor. After selecting the isosurface value of 0.005 a.u., the difference between these two operational formulae becomes evident, so that we can correctly describe the local reactivity according to the 3D representation of the DD exposed in Figure 7b: electrophilic attacks are expected to occur preferably on carbon and nitrogen elements with a maximum likelihood onto the  $X$ - $Y$  plane, specifically between these two atoms:  $\pi$  electrons are more susceptible to undergo the electrophilic attack aforementioned. Three-dimensional pictures of the DD based on the eq. (14) belong to the  $A_1$  totally symmetric irreducible representation ( $C_{\infty v}$  symmetry point group).

The  $\text{C}_2\text{F}_2$  molecule is depicted by Figure 8. The operational formula given by eq. (4) is displayed by Figure 8a, so revealing an incorrect description of the local reactivity at isosurface values of 0.001 and 0.005 a.u. because the displayed pictures of the zone (a) do not belong to the  $\Sigma_g^+$  totally symmetric irreducible representation. On the contrary, the operational formula given by eq. (14) provides an isosurface of the DD that is exhibited by Figure 8b showing that it belongs to the  $\Sigma_g^+$  totally symmetric irreducible representation ( $D_{\infty h}$  symmetry point group). We observe a clear predominance of electrophilic attacks on this molecule whose maximum value is reached on the  $X$ - $Y$  plane surrounding the triple bond. As fluorine atoms are electron-withdrawing groups, they concentrate electrons on them such that electrophilic attacks are possible to

occur on them, but having a lower likelihood to be performed in comparison with possible electrophilic attacks on the triple carbon–carbon bond. On the other hand, there is no a predominance of nucleophilic attacks on this molecule.

The  $C_2H_2$  molecule is depicted by Figure 9. We expect that nucleophilic attacks can be more favorable to occur on hydrogen atoms, while electrophilic attacks are more susceptible to occur on carbon atoms. The operational formula given by eq. (4) is displayed by Figure 9a and the operational formula given by eq. (14) is depicted by Figure 9b.

When comparing zones (a) and (b), we notice some similarities between both isosurfaces at values of 0.00075 a.u. and 0.001 a.u. However, a certain narrowness is detected on the negative phase of the DD when observing the  $X$ – $Z$  plane from the side perspective view of Figure 9a. This difference between eqs. (4) and (14) is noticeably remarked at an isosurface value of 0.005 a.u. because this value reveals that eq. (4) does not belong to the  $\Sigma_g^+$  totally symmetric irreducible representation ( $D_{\infty h}$  symmetry point group), thus supporting again the use of the operational formula given by eq. (14) instead of eq. (4). The reader can check that the local reactivity of this molecule was predicted through an approximated mathematical expression in which a weighted linear combination of densities of molecular orbitals was proposed in 2012 to plot a 3D picture of the DD,<sup>[64]</sup> nevertheless the level of theory that was used in that work and in particular the basis set differs from the one used in the present work. It seems that a trend is evidenced as follows: the larger the basis set, the farther are the positive lobes located from the hydrogen atoms along the  $Z$  axis. To check this comparison, please refer to the respective bibliography along with the pictures included there.<sup>[64]</sup>

The  $PCl_5$  molecule depicted by Figure 10 has five chlorine atoms which are divided into two types: The axial ones (located at the  $Z$  axis) and the equatorial ones (located on the  $X$ – $Y$  plane), so that these two types of atoms are not chemically equivalent each other. This expected local reactivity must be well described by the DD. Let us then examine the performance of the operational formulae given by eqs. (4) and (14). The Figure 10a shows us this distinction and one would think that the operational formula given by eq. (4) is good enough to be used on this molecule. However, according to this figure, the equatorial chlorine atoms are not equivalent each other; the reader has to remind that all of studied molecules have been geometrically optimized on their respective ground state, so that interatomic distances belong to an equilibrium condition; hence, the distance between phosphorus and each equatorial chlorine atom is exactly the same; there is no reason to expect a difference of reactivity among these three chlorine atoms. But the chlorine atom localized just on the  $Y$  axis exhibits a certain difference on its negative phase of the DD in comparison with negative phase of the same DD of the remaining two equatorial chlorine atoms. In fact, this distinction is much better visualized when comparing the top perspective view with the side perspective view depicted by Figure 10a: the negative phase of the DD on the chlorine atom located at the  $Y$  axis is a little bigger than the negative phase of the DD on the remaining equatorial chlorine atoms which are also located

on the  $X$ – $Y$  plane, and this supports the decision to discard the use of the operational formula given by the eq. (4). Conversely, the top and side perspective views depicted by Figure 10b at isosurface values of 0.001 a.u. and 0.005 a.u. correctly shows that the equatorial chlorine atoms have the same reactivity each other, but different reactivity in comparison to the reactivity exhibited by the axial chlorine atoms as should be expected. The axial chlorine atoms have the same reactivity each other, thus supporting the use of the operational formula given by eq. (14) which indicates that in the case of the axial chlorine atoms, they both would undergo nucleophilic attacks along the  $Z$  axis preferably, meanwhile electrophilic attacks are more favorable to occur along parallel planes to the  $X$ – $Y$  plane passing through every axial chlorine atom. On the contrary, the three equatorial chlorine atoms are favored to undergo nucleophilic attacks in certain directions along the  $X$ – $Y$  plane, and any possible electrophilic attack can preferably occur above and below this cartesian plane. Notice this double type of local reactivity on an as electronegative atom as chlorine; this type of reactivity will be broached at more depth for the next molecule. Although the phosphorus atom is theoretically favored to be attacked by a nucleophilic reagent, this type of attack would be hampered by a steric hindrance due the chlorine atoms, hence it is expected that phosphorus be less reactive than chlorine atoms in practice. The operational formula given by eq. (14) generates an isosurface of the DD that belongs to the  $A_1'$  totally symmetric irreducible representation ( $D_{3h}$  symmetry point group).

The Figure 11 shows us the  $SF_6$  molecule having six fluorine atoms that are chemically equivalent. The operational formula given by eq. (4) is displayed by Figure 11a at an isosurface value of 0.001 a.u. showing the front, top, and side perspective views. It is easy to observe a noticeable difference when comparing this isosurface with that obtained by the operational formula given by eq. (14) as depicted by Figure 11b so that the latter is a 3D picture of the DD that belongs to the  $A_{1g}$  totally symmetric irreducible representation ( $O_h$  symmetry point group). According to the molecular geometry, it should not be possible to distinguish among the fluorine atoms, but the DD based on the eq. (4) generates an erroneous distinction among the fluorine atoms. This distinction is an artifact, while the eq. (14), correctly describes the local reactivity of this molecule, so revealing no distinction among fluorine atoms as should be expected, meaning that this operational formula meets this requirement, in fact it shows us a reactivity that is a little more complicated as expected. As depicted by Figure 11b, an electrophilic attack is more favorable to be performed on fluorine atoms and chemical bonds defined between each fluorine atom and the sulfur atom on the cartesian planes:  $X$ – $Y$ ,  $Y$ – $Z$ , and  $Z$ – $X$ . Nevertheless, contrary to what one would expect, a nucleophilic attack on each fluorine atom is also favorable to occur along each cartesian axis, which is chemically counter-intuitive due to the electronegativity of fluorine. As fluorine is an electronegative atom, one would think there is no chance for nucleophilic attacks on it, however depending on how the local reactivity varies around the atom as the DD reveals, a nucleophilic attack is also possible to

occur, this implies a double kind of reactivity that is possible to be carried out on the same atom. In fact Rogachev and Hoffman have revealed this double type of reactivity on electronegative atoms like those forming the iodine molecule through the use of the Perturbation Theory within the natural bond orbital framework.<sup>[65]</sup> That study revealed that iodine molecule is able to accept and donate electrons. The latter indicates that the operational formula of the DD given by eq. (14) should be able to reveal possible nucleophilic and electrophilic attacks on each atom of the iodine molecule. The reader can notice that these researchers found that the double nature of the reactivity of iodine aforementioned depends on the geometrical orientation of the attacking reagent, thus supporting the idea that the DD is even able to reveal a double reactivity around an atom in a molecule as the case of each fluorine atom in SF<sub>6</sub> (and each chlorine atom in PCl<sub>5</sub>).

The C<sub>6</sub>H<sub>6</sub> molecule has six hydrogen atoms and six carbon atoms, as depicted by Figure 12. Therefore, there must be one type of reactivity for each type of atom, because all of the hydrogen atoms are chemically equivalent each other and all of the carbon atoms are chemically equivalent each other too, so that a proper operational formula of the DD must lead to this same conclusion. The operational formula given by eq. (4) does not support this expected trivial result. Figure 12a immediately reveals that C<sub>6</sub>H<sub>6</sub> has two types of carbon atoms at isosurface values of 0.001 a.u. and 0.005 a.u. which is incorrect. In addition, that isosurface of the DD does not belong to the A<sub>1g</sub> totally symmetric irreducible representation (D<sub>6h</sub> symmetry point group). This fail in producing a correct representation of local reactivity disappears when using the operational formula given by eq. (14) as depicted by Figure 12b because the latter belongs to the A<sub>1g</sub> totally symmetric irreducible representation, so exhibiting just one type of carbon atom as expected. As a consequence, each carbon atom shows the same capability to undergo a preferable nucleophilic attack in certain directions along the X–Y plane at an isosurface value of 0.005 a.u., meanwhile there are some parallel planes located in front of and behind the X–Y plane on which electrophilic attacks are preferable to occur owing to the presence of π-electrons. Besides each hydrogen atom seems to be also able to undergo an electrophilic attack. As can be checked, the 3D picture that is displayed by Figure 12b clearly reveals π-electrons rings in front and behind the X–Y plane that are the responsible of this type of local reactivity. Notice that these two different cuts of isosurface values for the DD were used to appreciate how the π-cloud occupies space around the nuclei that conform this molecule. As observed, both values of isosurfaces of the DD reveal that there would be a predominance of electrophilic attacks, mainly on carbon atoms and second on hydrogen atoms, instead of nucleophilic attacks on this molecule. In other words, a small likelihood of electrophilic attacks on hydrogen atoms is a consequence of the expansion of the π-cloud.

The C<sub>6</sub>F<sub>6</sub> molecule has six fluorine atoms and six carbon atoms as Figure 13 depicts. Similarly to the benzene molecule, there must be one type of reactivity for each type of atom, because all of the fluorine atoms are chemically equivalent

each other and all of the carbon atoms are chemically equivalent each other too. Hence, an operational formula of the DD must lead to this conclusion. Figure 13a depicts the operational formula given by eq. (4) at isosurface values of 0.001 a.u. and 0.005 a.u. and easily we can check that the local reactivity is described erroneously because, according to this picture, there are two types of carbon atoms and two types of hydrogen atoms, which is incorrect. On the contrary, the operational formula given by eq. (14) that is displayed at isosurface values of 0.001 a.u. and 0.005 a.u. by Figure 13b allows us to observe a local reactivity that exhibits some resemblance with the local reactivity of benzene. But there are some differences that are worthwhile to mention; unlike to C<sub>6</sub>H<sub>6</sub>, the DD applied on C<sub>6</sub>F<sub>6</sub> reveals that this molecule is able to undergo a nucleophilic attack in the middle of the carbon ring with a higher likelihood than the likelihood of a nucleophilic attack in the middle of the carbon ring of the C<sub>6</sub>H<sub>6</sub> molecule. The latter is a consequence of the high electronegative nature of the fluorine atom: due to its capability to withdraw electrons, the carbon-atom ring is more available to undergo nucleophilic attacks in the middle as Figure 13b depicts. It reveals that the π-cloud is more confined to be located on the carbon atoms than the π-cloud of benzene (Fig. 12b), hence, there are two possible electrophilic attacks well-distinguished: those ones possible to occur on the π-ring (like onto the benzene molecule) and those that are possible to occur on each fluorine atom. The latter means that each fluorine atom can experience its own electrophilic attack independently of electrophilic attacks that the carbon-atom ring can undergo. According to Figure 13b, the 3D picture of the DD given by eq. (14) belongs to the A<sub>1g</sub> totally symmetric irreducible representation too (D<sub>6h</sub> symmetry point group).

The Figure 14 depicts the P<sub>4</sub>O<sub>10</sub> molecule, which has four phosphorus atoms chemically equivalent among them and structurally two types of oxygen atoms and then they are chemically different each other: four oxygen atoms at the vertex positions and six bridge oxygen atoms. The operational formula given by eq. (4) is depicted by Figure 13a at an isosurface value of 0.001 a.u. that reveals, at a simple glance, an incomplete information concerning to the local reactivity of this molecule that does not deserve a deeper analysis. Besides, this 3D picture of the DD does not belong to the A<sub>1</sub> totally symmetric irreducible representation (T<sub>d</sub> symmetry point group). Without a doubt, this operational formula must be replaced by the operational formula given by eq. (14) whose isosurface is depicted by Figure 14b that belongs to the A<sub>1</sub> totally symmetric irreducible representation and it clearly reveals a particular reactivity for oxygen atoms located at the vertex positions. According to the operational formula of the DD given by eq. (14), this descriptor indicates that the oxygen atoms located at vertices are the most exposed to electrophilic attacks in comparison to phosphorus atoms where nucleophilic attacks are more favorable to happen. On the contrary, the bridging oxygen atoms are the least likely to undergo nucleophilic and electrophilic attacks. It is possible to claim that the negative phase of the DD focuses mainly on those oxygen atoms that are located at vertices while the positive phase

focuses on phosphorus atoms. The contribution to the local reactivity given by the bridging oxygen atoms is not too much relevant.

The Figure 15 shows us the structure of the  $\text{Cr}(\text{CO})_6$  organometallic molecule which presents a remarkable similarity with the  $\text{SF}_6$  molecule (Fig. 11), such that a similar analysis performed on the  $\text{SF}_6$  molecule can be done concerning to the local reactivity of the  $\text{Cr}(\text{CO})_6$  molecule. As can be noticed, there is one type of oxygen atom, one type of carbon atom and the chromium atom. The operational formula given by eq. (4) is displayed at an isosurface value of 0.001 a.u. which is depicted by Figure 15a in three perspectives: front, top, and side views. It allows us to realize that this operational formula shows an incorrect description of the local reactivity for the  $\text{Cr}(\text{CO})_6$  molecule because it reveals different reactivities on the oxygen and carbon atoms, which is not true. After discarding and replacing this operational formula by that given by eq. (14) whose isosurface is depicted by Figure 15b at an isosurface value of 0.001 a.u. in the same three perspectives, we notice that the local reactivity is correctly described because the oxygen atoms have the same reactivity each other and the carbon atoms have the same reactivity each other too; the chromium atom shows its own reactivity. This information tell us there is predominance of electrophilic attacks on this molecule because oxygen atoms are the most susceptible to undergo an attack of this type; second, the chromium atom also has a susceptibility to be undergone electrophilic attacks and carbon atoms are susceptible to undergo a nucleophilic attack, but at a lower importance in comparison to electrophilic attacks that could occur on the oxygen atoms and the chromium atom. This is easy to notice because the negative phase of the DD (white colored lobes) predominates over the positive lobes of the DD (black colored lobes). The 3D picture of the DD depicted by Figure 15b belongs to the  $A_{1g}$  totally symmetric irreducible representation ( $O_h$  symmetry point group).

To end this discussion concerning to local reactivity in molecules with degeneracies in their frontier molecular orbitals through the use of the generalized operational formula suggested in the present work to build up a 3D picture of the DD, the emblematic  $\text{C}_{60}$  molecule, depicted by Figure 16, is analyzed. Chemically there is only one type of carbon atom; however, structurally there are two types of carbon-carbon bonds: those ones shared by two six-member rings (which are also known as [6,6] bonds) and those ones that are shared by one five-member ring and one six-member ring (which are also known as [5,6] bonds). Clearly it is expected a different reactivity between these two types of chemical bonds. The first time that the DD was applied in describing local reactivity of  $\text{C}_{60}$  was published in 2009; however, at that moment, the FMOA adapted to the molecular symmetry was used to build up a 3D picture of the isosurface of the DD for this molecule,<sup>[37]</sup> so that the total electronic densities were not used at all as suggested in the present work.

The latter implied that any possible relaxation of the remaining molecular orbitals was ignored by this previous publication. Following the same sequence of analysis, we first used the operational formula given by eq. (4), so generating a 3D

picture of the DD at an isosurface value of 0.0001 a.u. as depicted by Figure 16a. At a simple glance, it can be seen that the distinction between the two types of chemical bonds is not possible to perform with this original operational formula. In fact, the description of local reactivity is incorrect because there are [5,6] bonds that are not chemically equivalent among them along with [6,6] bonds that are not chemically equivalent among them either. Again the solution to this problem of description of the local reactivity lies in the fact of using the operational formula given by eq. (14) with the aim to give rise a correct 3D representation of this local reactivity descriptor at an isosurface value of 0.0001 a.u. as Figure 16b depicts. Now the two types of chemical bonds are nicely revealed, so providing a marked nucleophilic character for the [6,6] bonds, meaning they are susceptible to undergo an electrophilic attack, and a noticeable electrophilic character for the [5,6] bonds, meaning they are susceptible to undergo a nucleophilic attack. Furthermore, thanks to this present work, we confirmed that the use of the FMOA is good enough to obtain a qualitative picture of local reactivity of the Buckminster fullerene, thus validating the approximation applied in 2009 in this same molecule in spite of using a different level of theory. It is important to mention that a complete work concerning to the local reactivity of  $\text{C}_{60}$  was performed by Fernández et al.<sup>[66]</sup> They concluded that there is a preference for [6,6] over [5,6] bonds in cycloaddition reactions involving  $\text{C}_{60}$ . The analysis of the Activation Strain Model along the reaction profiles,<sup>[67,68]</sup> and the Molecular Orbital Theory along with the Energy Decomposition Analysis<sup>[69]</sup> were the conceptual tools that these authors used in their research. The DD in its more general expression proposed here offers another complementary explanation: chemical bonds that conform six-member rings exhibit an alternation between nucleophilic and electrophilic nature on  $\text{C}_{60}$  that promotes a favorable interaction with a diene. This alternation is not present in five-member rings, thus preventing interaction with a diene. Finally, we notice that the operational formula of the DD given by eq. (14) generates an isosurface that belongs to the  $A_g$  totally symmetric irreducible representation ( $I_h$  symmetry point group).

## Conclusions

A more general operational formula to build up a 3D picture of the DD given by the eq. (14) has been proposed for closed-shell molecules, so that any degeneracy in their frontier molecular orbitals has been taken into account, provided that a threshold value of energy difference among frontier molecular orbitals has been pre-established: in the present work, a reasonable value of  $1 \cdot 10^{-4}$  hartree is recommended as a threshold value according to the obtained results for different cuts of isosurfaces of the DD.

As the total electronic density is the main and only variable that has been taken into account to generate the 3D pictures of the DD through the use of one functional (M062X), it is expected that any other functional can also be good enough to produce suitable isosurfaces of the DD, so that the type of functional should be generally irrelevant provided that total

electronic density has been well-described by it. Notice that when the degree of degeneracy is  $p=q=1$ , the classical definition for the DD is retrieved as originally defined.

This is the first time that an operational formula for building up a 3D picture of the DD has been proposed in terms of total electronic densities in the ground state including any possible degeneracy in frontier molecular orbitals, thus leading to abandon the old approximation based only on the use of electronic densities of frontier molecular orbitals or the total electronic densities that do not include the degeneracy of frontier molecular orbitals.

Emblematic and very common molecules were used to test the capability of this proposed generalized operational formula with the aim to obtain the DD to reveal the truly nucleophilic and electrophilic regions of molecules properly with no risk in representing local reactivity as could happen with the original operational formula. As the molecules broached in this work are electrically neutral, in all single point calculations to obtain the DD there was an anionic system involved, hence the use of a basis set including diffuse functions was necessary during the use of the operational formula given by eq. (14). However, the net electric charge on a molecular system is irrelevant if it corresponds to a closed-shell system. The latter statement means that, in spite of using only electrically neutral molecules in the present work, the operational formula given by eq. (14) should be possible to apply on not only electrically neutral molecular systems but also on cationic and anionic molecular systems, provided they are closed-shell systems, for instance: cyanide anion ( $\text{CN}^-$ ) or nitrosyl cation ( $\text{NO}^+$ ).

And from the computational point of view, the DD can be implemented as a computational code through the use of eq. (14) to be applied on a wide variety of new molecules and all those molecules whose local reactivities have not been correctly described by the original operational formula of the DD given by eq. (4), provided that the degree of degeneracy in their frontier molecular orbitals is known through the respective results generated by any standard software of quantum chemistry as follows:

- i. Optimize the geometry of the electrically neutral closed-shell molecule under study at its ground state and identify the degree of degeneracy in LUMO and HOMO ( $p$  and  $q$ , respectively).
- ii. Use the same optimized geometry to perform single point calculations of: (a) the molecular system at its ground state with values of spin-multiplicity and net electric charge equal 1 and 0, respectively; (b) the molecular system with values of spin-multiplicity and net electric charge equal  $p+1$  and  $-p$ , respectively (the anionic system); (c) the molecular system with values of spin-multiplicity and net electric charge equal  $q+1$  and  $+q$ , respectively (the cationic system).
- iii. Generate the respective cube files of the electronic densities of the neutral, anionic, and cationic systems:  $\rho(\mathbf{r})_N^1$ ,  $\rho(\mathbf{r})_{N+p}^{p+1}$ ; and  $\rho(\mathbf{r})_{N-q}^{q+1}$ , where the subscripts represent the total number of electrons on each molecular system and

the superscript indicates the respective value of spin-multiplicity.

- iv. Perform the arithmetic operations as eq. (14) indicates to generate the cube file from which the 3D picture of the DD can be built up through a proper visualizer.

These steps should be valid for ions and not only for electrically neutral molecules, provided that the respective ion be a closed-shell system.

This is not the only most accurate operational formula to obtain a correct description of the DD because the single occupation of  $p$  degenerate LUMOs and  $q$  degenerate HOMOs can be replaced by a double-occupation of LUMOs and HOMOs to keep constant the spin-number; although the latter is not a mandatory requirement in the conceptual density functional theory, it is a mandatory requirement within the framework of the spin-polarized conceptual density functional theory. This study is in progress.

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**Keywords:** dual descriptor · conceptual density functional theory · degeneracy in frontier molecular orbitals · symmetric molecules · nucleophilic Fukui function · electrophilic Fukui function · total electronic densities · electronic densities

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