Theor Chem Acc (2006) 115: 257–265
DOI 10.1007/s00214-005-0002-3

REGULAR ARTICLE

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Comparison between the frozen core and finite differences approximations for the generalized spin-dependent global and local reactivity descriptors in small molecules

Received: 12 April 2005 / Accepted: 28 July 2005 / Published online: 9 November 2005

Abstract Local and global reactivity descriptors defined within $\{N, N_S, \upsilon(\mathbf{r})\}$ and $\{N_\alpha, N_\beta, \upsilon(\mathbf{r})\}$ representations provide a remedy to the problem of inadequacy of hitherto-known reactivity descriptors in $\{N, \upsilon(\mathbf{r})\}$ representation in the analyses of situations where spin multiplicity changes are present. The tailor-made nature of the spin-dependent representations for specific processes is highlighted and a discussion on the convenience to use each representation is included. The connection between both representations is presented as a linear transformation. Generalized Fukui functions associated with processes where the number of electrons and/or the multiplicity change are calculated for closed-shell (NH_3, H_2O, HCOOH) and open-shell molecules (CH_2) with BLYP/aug-cc-pVTZ level of theory, using both the finite differences and the frozen core approximations. Chemical processes involving spin transfer require the explicitly spin-dependent reactivity descriptors whose definitions and domain of applicability are analyzed. The method of calculation of these quantities, using finite differences and frozen core approximations, highlights that these two techniques provide similar trends, however for cases where orbital relaxation is important, the finite differences approximation should be used.

1 Introduction

Chemical reactivity and selectivity have been successfully described by density functional theory (DFT) [1–5]. In the so-called $\{N, \upsilon(\mathbf{r})\}$ representation the chemical system is fully characterized by the total number of electrons, N, and the external potential, $\upsilon(\mathbf{r})$. In this representation the cardinal reactivity descriptors are electronegativity [3], χ, and hardness [4,5], η. They are defined as the following first [6] and second [7] derivatives of energy, E, with respect to N, at $\upsilon(\mathbf{r})$ fixed,

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

and

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\mathbf{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(\mathbf{r})}, \tag{2}$$

where μ is the chemical potential [6]. The global softness, S, is given by [1]

$$S = \frac{1}{\eta}, \tag{3}$$

and the electrophilicity is defined as [8]

$$\omega = \frac{\mu^2}{2\eta}. \tag{4}$$

Local reactivity descriptors are needed to explain the site selectivity in a molecule. The most widely used local descriptor is the Fukui function defined as [9]

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\upsilon(\mathbf{r})} = \left(\frac{\delta \mu}{\delta \upsilon(\mathbf{r})}\right)_N. \tag{5}$$

From the discontinuity in the $\rho(\mathbf{r})$ versus N curve, three different derivatives are usually defined,

$$f^\xi(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)^\xi_{\upsilon(\mathbf{r})}, \tag{6}$$

where the superscript ξ = +, − or 0, allows us to have three different types of Fukui functions, viz. $f^-(\mathbf{r})$ for electrophilic attack, $f^+(\mathbf{r})$ for nucleophilic attack and $f^0(\mathbf{r})$ for radical attack.

A local softness [10], $s^\xi(\mathbf{r})$, and a local philicity [11], $\omega^\xi(\mathbf{r})$, have also been proposed to analyze hard–soft and

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electrophile–nucleophile interactions respectively as given below,

$$s^{\xi}(\mathbf{r}) = S\, f^{\xi}(\mathbf{r}), \tag{7}$$

and

$$\omega^{\xi}(\mathbf{r}) = \omega\, f^{\xi}(\mathbf{r}). \tag{8}$$

Since $s^{\xi}(\mathbf{r})$ and the $\omega^{\xi}(\mathbf{r})$ are products of one global and one local reactivity indices they are supposed to explain the intermolecular reactivity better than $f^{\xi}(\mathbf{r})$. Condensed-to-atom variants of these descriptors are also known [2].

All these descriptors have been extensively used [2,12, 13] to understand a multitude of physico-chemical processes with or without spin multiplicity changes. Since these descriptors are unable to take into account the spin dependence, in the present work we apply global and local reactivity descriptors in $\{N, N_S, \upsilon(\mathbf{r})\}$ and $\{N_\alpha, N_\beta, \upsilon(\mathbf{r})\}$ representations within a spin polarized DFT [14–17] to analyze specific processes where there are multiplicity changes. Additionally, some descriptors are evaluated by using the finite differences approximation and frozen core approximation, which are widely used. Thus the pertinence to use of each approximation is discussed. The theoretical background is provided in Sect. 2 while Sect. 3 presents the computational details. Results and discussion are given in Sect. 4. Sect. 5 contains some concluding remarks and an appendix was included to present the connections between both representations.

2 Theoretical background

The electron density, $\rho(\mathbf{r})$, and the spin density, $\rho_S(\mathbf{r})$, are defined in terms of the spin-α and spin-β populations as,

$$\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r});\ \ \rho_S(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r}). \tag{9}$$

In an orbital formulation, like the Kohn-Sham (KS) approach, these spin densities are written in terms of the corresponding orbital densities as,

$$\rho_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \left|\varphi_{i,\sigma}(\mathbf{r})\right|^2 = \sum_{i=1}^{N_\sigma} \rho_{i,\sigma}(\mathbf{r});\ \ \sigma = \alpha,\ \beta, \tag{10}$$

which follow the normalization conditions

$$N_\sigma = \int \mathrm{d}\mathbf{r}\, \rho_\sigma(\mathbf{r});\ \ \sigma = \alpha,\ \beta. \tag{11}$$

Electron number, N, and spin number, N_S, are defined as

$$N = N_\alpha + N_\beta;\ N_S = N_\alpha - N_\beta. \tag{12}$$

2.1 Reactivity descriptors in $\{N, N_S, \upsilon(\mathbf{r})\}$ representation

In this representation the spin potential, μ_S, and a kind of chemical potential, μ_N, are given by [14–16]

$$\mu_N = \left(\frac{\partial E}{\partial N}\right)_{N_S,\upsilon(\mathbf{r})};\ \ \mu_S = \left(\frac{\partial E}{\partial N_S}\right)_{N,\upsilon(\mathbf{r})}. \tag{13}$$

The corresponding hardness parameters are

$$\eta_{NN} = \left(\frac{\partial \mu_N}{\partial N}\right)_{N_S,\upsilon(\mathbf{r})}, \tag{14a}$$

$$\eta_{NS} = \left(\frac{\partial \mu_N}{\partial N_S}\right)_{N,\upsilon(\mathbf{r})} = \left(\frac{\partial \mu_S}{\partial N}\right)_{N_S,\upsilon(\mathbf{r})} = \eta_{SN}, \tag{14b}$$

and

$$\eta_{SS} = \left(\frac{\partial \mu_S}{\partial N_S}\right)_{N,\upsilon(\mathbf{r})}. \tag{14c}$$

Different Fukui functions are defined in this representation,

$$f_{NN}(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{N_S,\upsilon(\mathbf{r})}, \tag{15a}$$

$$f_{NS}(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N_S}\right)_{N,\upsilon(\mathbf{r})}, \tag{15b}$$

$$f_{SN}(\mathbf{r}) = \left(\frac{\partial \rho_S(\mathbf{r})}{\partial N}\right)_{N_S,\upsilon(\mathbf{r})}, \tag{15c}$$

and

$$f_{SS}(\mathbf{r}) = \left(\frac{\partial \rho_S(\mathbf{r})}{\partial N_S}\right)_{N,\upsilon(\mathbf{r})}. \tag{15d}$$

From these definitions it is clear that $\int \mathrm{d}\mathbf{r}\, f_{NN}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\, f_{SS}(\mathbf{r}) = 1$ and $\int \mathrm{d}\mathbf{r}\, f_{NS}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\, f_{SN}(\mathbf{r}) = 0$. Directional derivatives of all Fukui functions immediately come from the N-discontinuity.

Note that the derivatives of μ_N, equivalent to Eq. 5, are

$$\left(\frac{\delta \mu_N}{\delta \upsilon(\mathbf{r})}\right)_{N,N_S} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{N_S,\upsilon(\mathbf{r})} = f_{NN}(\mathbf{r}), \tag{16a}$$

$$\left(\frac{\delta \mu_S}{\delta \upsilon(\mathbf{r})}\right)_{N,N_S} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N_S}\right)_{N,\upsilon(\mathbf{r})} = f_{NS}(\mathbf{r}). \tag{16b}$$

By rewriting Eqs. 7 and 8 with the corresponding quantities from Eqs. 13–16, one can obtain the local softness and philicity variants in this representation. Some of these definitions have been used in recent years to analyze different chemical reactions involving changes in spin multiplicity [18–20].

2.2 Reactivity descriptors in $\{N_\alpha, N_\beta, \upsilon(\mathbf{r})\}$ representation

The chemical potentials for the spin up and spin down cases are written separately as follows [17]

$$\mu_\alpha = \left(\frac{\partial E}{\partial N_\alpha}\right)_{N_\beta,\upsilon(\mathbf{r})};\ \mu_\beta = \left(\frac{\partial E}{\partial N_\beta}\right)_{N_\alpha,\upsilon(\mathbf{r})}. \tag{17}$$

Associated hardness indices are

$$\eta_{\alpha\alpha} = \left(\frac{\partial \mu_\alpha}{\partial N_\alpha}\right)_{N_\beta,\upsilon(\mathbf{r})}, \tag{18a}$$

$$\eta_{\alpha\beta} = \left(\frac{\partial \mu_\alpha}{\partial N_\beta}\right)_{N_\alpha,\upsilon(\mathbf{r})} = \left(\frac{\partial \mu_\beta}{\partial N_\alpha}\right)_{N_\beta,\upsilon(\mathbf{r})} = \eta_{\beta\alpha}, \tag{18b}$$

and

$$\eta_{\beta\beta} = \left(\frac{\partial \mu_\beta}{\partial N_\beta}\right)_{N_\alpha, \upsilon(\mathbf{r})}. \tag{18c}$$

Corresponding Fukui functions similarly come,

$$f_{\alpha\alpha}(\mathbf{r}) = \left(\frac{\partial \rho_\alpha(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta, \upsilon(\mathbf{r})}, \tag{19a}$$

$$f_{\beta\beta}(\mathbf{r}) = \left(\frac{\partial \rho_\beta(\mathbf{r})}{\partial N_\beta}\right)_{N_\alpha, \upsilon(\mathbf{r})}, \tag{19b}$$

$$f_{\alpha\beta}(\mathbf{r}) = \left(\frac{\partial \rho_\alpha(\mathbf{r})}{\partial N_\beta}\right)_{N_\alpha, \upsilon(\mathbf{r})}, \tag{19c}$$

and

$$f_{\beta\alpha}(\mathbf{r}) = \left(\frac{\partial \rho_\beta(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta, \upsilon(\mathbf{r})}, \tag{19d}$$

where $\int d\mathbf{r}\, f_{\alpha\alpha}(\mathbf{r}) = \int d\mathbf{r}\, f_{\beta\beta}(\mathbf{r}) = 1$ and $\int d\mathbf{r}\, f_{\alpha\beta}(\mathbf{r}) = \int d\mathbf{r}\, f_{\beta\alpha}(\mathbf{r}) = 0$. Note that N-discontinuity leads to directional derivatives as in Eq. 6.

Derivatives of μ_α and μ_β are related with the previous quantities,

$$\left(\frac{\delta \mu_\alpha}{\delta \upsilon(\mathbf{r})}\right)_{N_\alpha, N_\beta} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta, \upsilon(\mathbf{r})} = f_{\alpha\alpha}(\mathbf{r}) + f_{\beta\alpha}(\mathbf{r}), \tag{20a}$$

$$\left(\frac{\delta \mu_\beta}{\delta \upsilon(\mathbf{r})}\right)_{N_\alpha, N_\beta} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N_\beta}\right)_{N_\alpha, \upsilon(\mathbf{r})} = f_{\alpha\beta}(\mathbf{r}) + f_{\beta\beta}(\mathbf{r}). \tag{20b}$$

Corresponding local softness and philicity can be defined easily using above definitions.

At a first glance it appears that the Fukui functions obtained from Eqs. 15 and 19 represent different processes. In fact this is true although they are connected, as it will be discussed below. The appendix contains the explicit connections between both representations.

2.3 Process when the number of electrons is changing

The process involving the determination of electron affinity is an example of a process where the number of electrons are changing. Consider the case when one alpha electron is added to the molecule, $\Delta N_\alpha = 1$ and $\Delta N_\beta = 0$.

It is clear that in this case the electron density is modified since the number of alpha electrons is changing. Thus, at first order the density changes can be written as

$$\Delta\rho(\mathbf{r}) \cong \left\{ \left(\frac{\partial \rho_\alpha(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta, \upsilon(\mathbf{r})} + \left(\frac{\partial \rho_\beta(\mathbf{r})}{\partial N_\alpha}\right)_{N_\beta, \upsilon(\mathbf{r})} \right\} \Delta N_\alpha, \tag{21}$$

or according to definition of Eqs. 19

$$\Delta\rho(\mathbf{r}) \cong \left\{ f_{\alpha\alpha}^{+}(\mathbf{r}) + f_{\beta\alpha}^{+}(\mathbf{r}) \right\} \Delta N_\alpha. \tag{22}$$

For this process within the $\{N_\alpha, N_\beta, \upsilon(\mathbf{r})\}$ representation two Fukui functions describe the changes on the electron density.

The changes up to first order in the total energy are expressed as

$$\Delta E \cong \left(\frac{\partial E}{\partial N_\alpha}\right)_{N_\beta, \upsilon(\mathbf{r})} \Delta N_\alpha, \tag{23}$$

or, from Eq. 17,

$$\Delta E \cong \mu_\alpha^{+} \Delta N_\alpha. \tag{24}$$

However, if we work in the $\{N, N_{\mathrm{S}}, \upsilon(\mathbf{r})\}$ representation, the electron affinity must be divided into several steps. In particular we can divide it into two processes: (1) Half of the electron is added to the alpha-electrons set and another half of the electron to the beta-electrons set, such that N_{S} is kept constant, $\Delta N_{\mathrm{S}}^{(1)} = 0$. In this way the change on the electron density is

$$\Delta\rho^{(1)}(\mathbf{r}) \cong \left(\frac{\partial \rho^{(1)}(\mathbf{r})}{\partial N}\right)_{N_{\mathrm{S}}, \upsilon(\mathbf{r})} \Delta N^{(1)}, \tag{25}$$

with $\Delta N^{(1)} = \Delta N_\alpha^{(1)} + \Delta N_\beta^{(1)} = \frac{1}{2} + \frac{1}{2} = 1$. (2) Now, the number of electrons is kept constant, $\Delta N^{(2)} = 0$, and N_{S} changes in such a way that the fraction of electron previously added to the beta set is transferred to the alpha one, $\Delta N_{\mathrm{S}}^{(2)} = \Delta N_\alpha^{(2)} - \Delta N_\beta^{(2)} = \frac{1}{2} - \left(-\frac{1}{2}\right) = 1$. For this case the change in the electron density is written as

$$\Delta\rho^{(2)}(\mathbf{r}) \cong \left(\frac{\partial \rho^{(2)}(\mathbf{r})}{\partial N_{\mathrm{S}}}\right)_{N, \upsilon(\mathbf{r})} \Delta N_{\mathrm{S}}^{(2)}. \tag{26}$$

The total change in the electron density is given by

$$\Delta\rho(\mathbf{r}) = \left(\frac{\partial \rho^{(1)}(\mathbf{r})}{\partial N}\right)_{N_{\mathrm{S}}, \upsilon(\mathbf{r})} \Delta N^{(1)} + \left(\frac{\partial \rho^{(2)}(\mathbf{r})}{\partial N_{\mathrm{S}}}\right)_{N, \upsilon(\mathbf{r})} \Delta N_{\mathrm{S}}^{(2)}, \tag{27}$$

or, in terms of the generalized Fukui functions (Eq. 15), it is obtained that

$$\Delta\rho(\mathbf{r}) \cong f_{NN}^{(1)+}(\mathbf{r})\, \Delta N^{(1)} + f_{NS}^{(2)+}(\mathbf{r})\, \Delta N_{\mathrm{S}}^{(2)}. \tag{28}$$

Note that Eqs. 22 and 28 become equal when Eq. 22 is evaluated at $\Delta N_\alpha = 1$ and Eq. 28 with $\Delta N^{(1)} = 1 = \Delta N_{\mathrm{S}}^{(2)}$ and the relations from the appendix are taken into account. It is clear that in both representations at least two Fukui functions are required. Although we use the electron affinity as example, the same ideas are applicable when an electron is removed in the ionization process.

For a closed-shell system, the additional electron will always be placed in an alpha orbital, however, in an open-shell molecule, a beta orbital could be involved, and the equations must be changed accordingly,

$$\Delta\rho(\mathbf{r}) \cong \left\{ f_{\alpha\beta}^{+}(\mathbf{r}) + f_{\beta\beta}^{+}(\mathbf{r}) \right\} \Delta N_\beta, \tag{29a}$$

$$\Delta E \cong \mu_\beta^{+} \Delta N_\beta. \tag{29b}$$

Similar equations are obtained when one electron is removed. In every case, we will assume that when one electron is added, it is placed on the lowest unoccupied orbital, while the removed electron comes from the highest occupied one.

Traditional Fukui function, defined by Eq. 5, can be approximated by $f(\mathbf{r}) \approx \left(\Delta\rho(\mathbf{r})/\Delta N\right)_{\upsilon}$, where $\Delta\rho(\mathbf{r})$ comes from Eq. 22 or 29a. In this case one has $f^{+}(\mathbf{r}) \approx \left(\Delta N_{\sigma}/\Delta N\right) \sum_{\sigma'} f^{+}_{\sigma'\sigma}$, where $\sigma, \sigma' = \alpha, \beta$. That is, the addition of one electron with a spin σ induces changes in both spin branches, one term is associated with the same spin type, $f^{+}_{\sigma\sigma}$, while the other, $f^{+}_{\sigma\sigma'}$, represents the relaxation of the other spin branch.

2.4 Process when the number of electrons is kept constant

In order to avoid holes in the electron configuration, when the electrons are moved from one spin set to the other, we only consider processes between the lowest states of two different multiplicities. Consider the case when an electron is transferred from a beta orbital to an alpha one, for this process the spin number changes,

$$\begin{aligned} N_{\mathrm{S}} &= N_{\alpha} - N_{\beta} = N^{0}_{\alpha} + 1 - (N^{0}_{\beta} - 1) \\ &= N^{0}_{\mathrm{S}} + 2, \quad \Delta N_{\mathrm{S}} = 2. \end{aligned}$$

In this case, the $\{N, N_{\mathrm{S}}, \upsilon(\mathbf{r})\}$ representation is more convenient since only one variable is modified. The corresponding change in the electron density is given by

$$\Delta\rho(\mathbf{r}) \cong \left(\frac{\partial\rho(\mathbf{r})}{\partial N_{\mathrm{S}}}\right)_{N,\upsilon(\mathbf{r})} \Delta N_{\mathrm{S}}, \tag{30}$$

or in terms of the Fukui function,

$$\Delta\rho(\mathbf{r}) \cong f^{+}_{N\mathrm{S}}\ \Delta N_{\mathrm{S}}. \tag{31}$$

In this case the energy change up to first order is given by

$$\Delta E \cong \left(\frac{\partial E}{\partial N_{\mathrm{S}}}\right)_{N,\upsilon(\mathbf{r})} \Delta N_{\mathrm{S}}, \tag{32}$$

or in terms of the spin potential,

$$\Delta E \cong \mu^{+}_{\mathrm{S}} \Delta N_{\mathrm{S}}. \tag{33}$$

For the same process, in $\{N_{\alpha}, N_{\beta}, \upsilon(\mathbf{r})\}$ representation we need at least two steps: (A) One electron is added to the alpha electrons set, such that $\Delta N^{(A)}_{\alpha} = 1$ and $\Delta N^{(A)}_{\beta} = 0$. In this way

$$\Delta\rho^{(A)}(\mathbf{r}) = \left\{\left(\frac{\partial\rho_{\alpha}(\mathbf{r})}{\partial N_{\alpha}}\right)_{N_{\beta},\upsilon(\mathbf{r})} + \left(\frac{\partial\rho_{\beta}(\mathbf{r})}{\partial N_{\alpha}}\right)_{N_{\beta},\upsilon(\mathbf{r})}\right\}\Delta N^{(A)}_{\alpha}. \tag{34}$$

(B) One electron is removed from the set of beta electrons, $\Delta N^{(B)}_{\beta} = -1$, keeping N_{α} constant, i.e., $\Delta N^{(B)}_{\alpha} = 0$. For this trajectory, the electron density change is given by

$$\Delta\rho^{(B)}(\mathbf{r}) = \left\{\left(\frac{\partial\rho_{\alpha}(\mathbf{r})}{\partial N_{\beta}}\right)_{N_{\alpha},\upsilon(\mathbf{r})} + \left(\frac{\partial\rho_{\beta}(\mathbf{r})}{\partial N_{\beta}}\right)_{N_{\alpha},\upsilon(\mathbf{r})}\right\}\Delta N^{(B)}_{\beta}. \tag{35}$$

From Eqs. 34 and 35, we obtain the total change in the electron density as

$$\Delta\rho(\mathbf{r}) \cong \Delta\rho^{(A)}(\mathbf{r}) + \Delta\rho^{(B)}(\mathbf{r}). \tag{36}$$

In terms of the generalized Fukui functions (Eq. 19), we have

$$\begin{aligned} \Delta\rho(\mathbf{r}) \cong &\left\{f^{+}_{\alpha\alpha}(\mathbf{r}) + f^{+}_{\beta\alpha}(\mathbf{r})\right\}\ \Delta N^{(A)}_{\alpha} \\ &+ \left\{f^{-}_{\alpha\beta}(\mathbf{r}) + f^{-}_{\beta\beta}(\mathbf{r})\right\}\ \Delta N^{(B)}_{\beta}. \end{aligned} \tag{37}$$

It is evident that the $\{N, N_{\mathrm{S}}, \upsilon(\mathbf{r})\}$ representation is the natural representation for this process.

For an open-shell system we can increase or decrease the multiplicity, while in the closed-shell molecules, it only increases. Also note that the equivalence between Eqs. 31 and 37 directly comes from the relationships obtained in the appendix.

It is worthy to note that in this case there is not a quantity that is equivalent to the traditional Fukui function, Eq. 5, since the number of electrons is not changing. For this kind of process, the new quantities are necessary to characterize the reactivity.

The main point we want to emphasize here is that there is one representation where the corresponding Fukui functions can be computed easily, since they only involve one step. The present analysis provides an important insight: the best representation to analyze a given process depends on the particular features of the process. This work shows the differences in the use of different representations and tries to give guidelines to choose a suitable representation for the concerned processes.

3 Computational details

Those Fukui functions appearing in the processes previously described are calculated for both closed- (NH_3, H_2O and HCOOH) and open-shell molecules (CH_2 in the triplet state) using the generalized gradient approximation BLYP [21,22] with the basis set aug-cc-pVTZ [23,24], and two types of approximations, viz., the finite differences approximation and the frozen core approximation. The electronic structure and the full optimization of the geometries of the systems considered in this work were obtained with the code NWChem v4.5 [25].

If it is not possible to use fractional occupancy, there are two ways to evaluate the Fukui functions. The first one is related to the finite differences approximation (FDA). For this case a derivative, for example, $\frac{\partial F}{\partial N}$ is approximated by

$$\frac{\partial F}{\partial N} \cong \frac{F^{\mathrm{Final}} - F^{\mathrm{Initial}}}{N^{\mathrm{Final}} - N^{\mathrm{Initial}}} \tag{38}$$

With this approximation, the Fukui functions of Eq. 22, which were obtained for the case when $\Delta N_{\alpha} = 1$ and $\Delta N_{\beta} = 0$, are approximated by

$$\begin{aligned} f^{+}_{\alpha\alpha}(\mathbf{r}) &\cong \frac{\rho^{\mathrm{Anion}}_{\alpha}(\mathbf{r}) - \rho^{\mathrm{Neutral}}_{\alpha}(\mathbf{r})}{N^{0}_{\alpha} + 1 - N^{0}_{\alpha}} \\ &= \rho^{\mathrm{Anion}}_{\alpha}(\mathbf{r}) - \rho^{\mathrm{Neutral}}_{\alpha}(\mathbf{r}), \end{aligned} \tag{39}$$

$$\begin{aligned} f^{+}_{\beta\alpha}(\mathbf{r}) &\cong \frac{\rho^{\mathrm{Anion}}_{\beta}(\mathbf{r}) - \rho^{\mathrm{Neutral}}_{\beta}(\mathbf{r})}{N^{0}_{\alpha} + 1 - N^{0}_{\alpha}} \\ &= \rho^{\mathrm{Anion}}_{\beta}(\mathbf{r}) - \rho^{\mathrm{Neutral}}_{\beta}(\mathbf{r}), \end{aligned} \tag{40}$$

and the chemical potential μ_α^+ of Eq. 24 by

$$\mu_\alpha^+ \cong \frac{E^{\text{Anion}} - E^{\text{Neutral}}}{N_\alpha^0 + 1 - N_\alpha^0} = E^{\text{Anion}} - E^{\text{Neutral}}. \tag{41}$$

For this approximation, two calculations are required. In particular the calculation for anions could be a difficult task. In order to avoid the problem of obtaining the anion electronic structure, an additional approximation can be made on the Fukui function and the chemical potential. This approximation is known as the frozen core approximation (FCA). Essentially, this approximation does not allow relaxation on the orbitals when a change in the occupancy occurs, and then the change in the density corresponds to the orbital density of the new orbital. As a consequence, the difference of Eq. 39 is approximated by the lowest alpha unoccupied molecular orbital (LUMO, α) density of the neutral system. In this way the Fukui function $f_{\alpha\alpha}^+(\mathbf{r})$ is approximated by

$$f_{\alpha\alpha}^+(\mathbf{r}) \cong \left|\varphi_{\text{LUMO},\alpha}(\mathbf{r})\right|^2. \tag{42}$$

Within this approximation the cross Fukui function $f_{\beta\alpha}^+(\mathbf{r})$ is zero, since no relaxation is allowed.

The chemical potential of Eq. 41 in the FCA (a Koopmans-like approximation) is approximated by the LUMO energy

$$\mu_\alpha^+ \cong \varepsilon_{\text{LUMO},\alpha}. \tag{43}$$

For the open-shell system considered in this work, the triplet state of CH_2, when an electron is added to the molecule it is placed on the beta set, then, $\Delta N_\alpha = 0$ and $\Delta N_\beta = 1$. Therefore, two Fukui functions, $f_{\alpha\beta}^+(\mathbf{r})$ and $f_{\beta\beta}^+(\mathbf{r})$, must be computed since alpha and beta densities are not equal, and within the FDA they are obtained from

$$f_{\alpha\beta}^+(\mathbf{r}) \cong \frac{\rho_\alpha^{\text{Anion}}(\mathbf{r}) - \rho_\alpha^{\text{Neutral}}(\mathbf{r})}{N_\beta^0 + 1 - N_\beta^0} = \rho_\alpha^{\text{Anion}}(\mathbf{r}) - \rho_\alpha^{\text{Neutral}}(\mathbf{r}), \tag{44}$$

$$f_{\beta\beta}^+(\mathbf{r}) \cong \frac{\rho_\beta^{\text{Anion}}(\mathbf{r}) - \rho_\beta^{\text{Neutral}}(\mathbf{r})}{N_\beta^0 + 1 - N_\beta^0} = \rho_\beta^{\text{Anion}}(\mathbf{r}) - \rho_\beta^{\text{Neutral}}(\mathbf{r}). \tag{45}$$

The corresponding chemical potential is

$$\mu_\beta^+ \cong \frac{E^{\text{Anion}} - E^{\text{Neutral}}}{N_\beta^0 + 1 - N_\beta^0} = E^{\text{Anion}} - E^{\text{Neutral}}. \tag{46}$$

Within the FCA, the Fukui function $f_{\alpha\beta}^+(\mathbf{r})$ is zero and

$$f_{\beta\beta}^+(\mathbf{r}) \cong \left|\varphi_{\text{LUMO},\beta}(\mathbf{r})\right|^2. \tag{47}$$

In this approximation μ_β^+ is related with the LUMO of the beta occupation,

$$\mu_\beta^+ \cong \varepsilon_{\text{LUMO},\beta} \tag{48}$$

At this point, it is interesting to compare the Fukui functions and the chemical potential obtained from FDA and from FCA. Furthermore, it is interesting to see if the $f_{\beta\alpha}^+(\mathbf{r})$ and $f_{\alpha\beta}^+(\mathbf{r})$ are zero or close to zero with the FDA. In this way the reliability of the frozen core approximation can be established in systems of small size.

Another Fukui function and chemical potential are considered in this work, namely $f_{\beta\beta}^-(\mathbf{r})$ and μ_β^-, which are involved in the ionization process for a closed-shell system, $\Delta N_\alpha = 0$ and $\Delta N_\beta = -1$. With the FDA these quantities are approximated by

$$f_{\beta\beta}^-(\mathbf{r}) \cong -[\rho_\beta^{\text{Cation}}(\mathbf{r}) - \rho_\beta^{\text{Neutral}}(\mathbf{r})], \tag{49}$$

and

$$\mu_\beta^- \cong -[E^{\text{Cation}} - E^{\text{Neutral}}] \tag{50}$$

or with the FCA by

$$f_{\beta\beta}^-(\mathbf{r}) \cong \left|\varphi_{\text{HOMO},\beta}(\mathbf{r})\right|^2, \tag{51}$$

and

$$\mu_\beta^- \cong \varepsilon_{\text{HOMO},\beta}. \tag{52}$$

The last relation is valid for the exact exchange-correlation energy functional, which is self-interaction free. However the previous equation does not hold for many of the approximate functionals currently used [26].

For the ionization potential, in the open-shell molecule, one has $\Delta N_\alpha = -1$ and $\Delta N_\beta = 0$ and the involved Fukui function is $f_{\alpha\alpha}^-(\mathbf{r})$. In the FDA one gets

$$f_{\alpha\alpha}^-(\mathbf{r}) \cong -[\rho_\alpha^{\text{Cation}}(\mathbf{r}) - \rho_\alpha^{\text{Neutral}}(\mathbf{r})], \tag{53}$$

while in the FCA it can be written as

$$f_{\alpha\alpha}^-(\mathbf{r}) \cong \left|\varphi_{\text{HOMO},\alpha}(\mathbf{r})\right|^2. \tag{54}$$

For this process the corresponding chemical potential is obtained from

$$\mu_\alpha^- \cong -[E^{\text{Cation}} - E^{\text{Neutral}}] \tag{55}$$

or

$$\mu_\alpha^- \cong \varepsilon_{\text{HOMO},\alpha}. \tag{56}$$

Finally, FDA estimations to the Fukui function $f_{NS}^+(\mathbf{r})$ and the chemical potential μ_S^+, in a closed-shell system ($\Delta N = 0$, $\Delta N_S = 2$), are given by

$$f_{NS}^+(\mathbf{r}) \cong \frac{1}{2}\left[\rho^{\text{Triplet}}(\mathbf{r}) - \rho^{\text{Singlet}}(\mathbf{r})\right], \tag{57}$$

and

$$\mu_S^+ \cong \frac{1}{2}\left[E^{\text{Triplet}} - E^{\text{Singlet}}\right]. \tag{58}$$

And from the FCA [14–16] by

$$f_{NS}^+(\mathbf{r}) \cong \frac{1}{2}\left[\left|\varphi_{\text{LUMO},\alpha}(\mathbf{r})\right|^2 - \left|\varphi_{\text{HOMO},\beta}(\mathbf{r})\right|^2\right], \tag{59}$$

and

$$\mu_S^+(\mathbf{r}) \cong \frac{1}{2}\left[\varepsilon_{\text{LUMO},\alpha} - \varepsilon_{\text{HOMO},\beta}\right] \tag{60}$$

For the open-shell system CH_2, the process from the triplet to the singlet state was considered, then $\Delta N = 0$ and

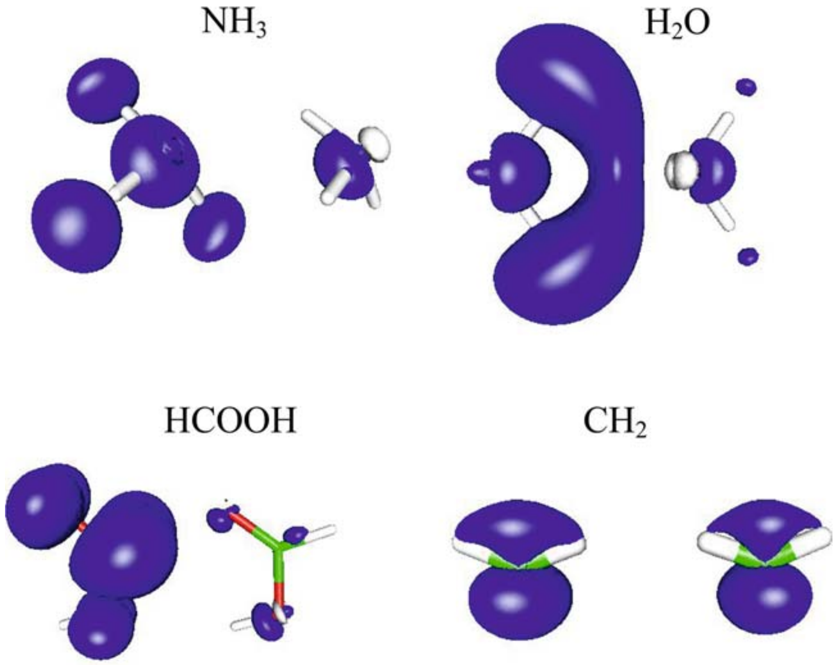

Fig. 1 $f^{+}_{\alpha\alpha}$ for NH_3, H_2O and HCOOH and $f^{+}_{\beta\beta}$ for CH_2 obtained with BLYP/aug-cc-pVTZ. The isosurface on the *left side* of each picture represents the frozen core approximation (FCA) and the *right side* is the finite differences approximation (FDA). The isosurfaces for $f^{+}_{\alpha\alpha}$ were done at a value of ±0.002 and for $f^{+}_{\beta\beta}$ at ±0.008. The *dark color* represents positive values.

$\Delta N_S = -2$. In this case, the corresponding Fukui function can be obtained within the FDA from

$$f^{-}_{NS}(\mathbf{r}) \cong \frac{1}{2}\left[\rho^{\text{Triplet}}(\mathbf{r}) - \rho^{\text{Singlet}}(\mathbf{r})\right], \qquad (61)$$

or, using the FCA, it becomes

$$f^{-}_{NS}(\mathbf{r}) \cong \frac{1}{2}\left[\left|\varphi_{\text{HOMO},\alpha}(\mathbf{r})\right|^2 - \left|\varphi_{\text{LUMO},\beta}(\mathbf{r})\right|^2\right], \qquad (62)$$

where both orbitals come from the triplet state calculation. The chemical potential for this process is also obtained from both the approximated schemes. In the FDA it takes the form

$$\mu^{-}_{S} \cong \frac{1}{2}\left[E^{\text{Triplet}} - E^{\text{Singlet}}\right], \qquad (63)$$

while from the FCA,

$$\mu^{-}_{S} \cong \frac{1}{2}\left[\varepsilon_{\text{HOMO},\alpha} - \varepsilon_{\text{LUMO},\beta}\right]. \qquad (64)$$

4 Results and discussion

In Fig. 1, the Fukui function obtained from Eqs. 39 and 42 is depicted for the closed-shell systems NH_3, H_2O and HCOOH. Also the Fukui function obtained from Eqs. 45 and 47 for the CH_2 is included.

According to Eqs. 22 and 29a, the increase in the electron density is commanded by positive values of the Fukui function. In Fig. 1, the positive values are shown in dark color. For the closed-shell systems studied in this work, just a small dark region is present with the FDA, while the LUMO density (FCA) is located in the same atoms as the FDA, but in more extended regions, as a consequence of the delocalized nature of the orbitals from unoccupied shells. Thus, there are large differences in the spread between FDA and FCA in the process where one electron is added to these systems, coming from the relaxation. However, for the open-shell system the LUMO density is very similar to the Fukui function obtained with the FDA. This behavior may come from the fact that the opposite spin partner of the orbital used to describe the Fukui function in the FCA (LUMO,β), is an occupied one. Estimations of the electron affinity predict a positive value for CH_2 and a negative one for the closed-shell systems.[1] Precisely for the CH_2 system, the Fukui function $f^{+}_{\beta\beta}(\mathbf{r})$ is very similar between FDA and FCA.

Fukui functions $f^{+}_{\beta\alpha}(\mathbf{r})$ and $f^{+}_{\alpha\beta}(\mathbf{r})$ obtained by the FDA are depicted in Fig. 2.

In this figure the nodal isosurface is plotted. In all the cases studied in this work, the negative region is enclosed into this isosurface, indicating that this region is more localized than the positive one. Note that this Fukui function presents very small values. For example, the H_2O exhibits one of the biggest values for $f^{+}_{\beta\alpha}(\mathbf{r})$, with a maximum value of +0.0013 and a minimum value of −0.0140. It suggests that the FCA, $f^{+}_{\beta\alpha}(\mathbf{r})$=$f^{+}_{\alpha\beta}(\mathbf{r})$=0, can be thought as a good estimation of this quantity.

A comparison between Eqs. 49 and 51, for the closed-shell systems, and between Eqs. 53 and 54, for the open-shell system, is made in Fig. 3.

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[1] Electron affinities obtained with BLYP/aug-cc-pVTZ for NH_3, H_2O, HCOOH and CH_2 are −0.0196, −0.185, −0.0207 and 0.0137 hartrees, respectively

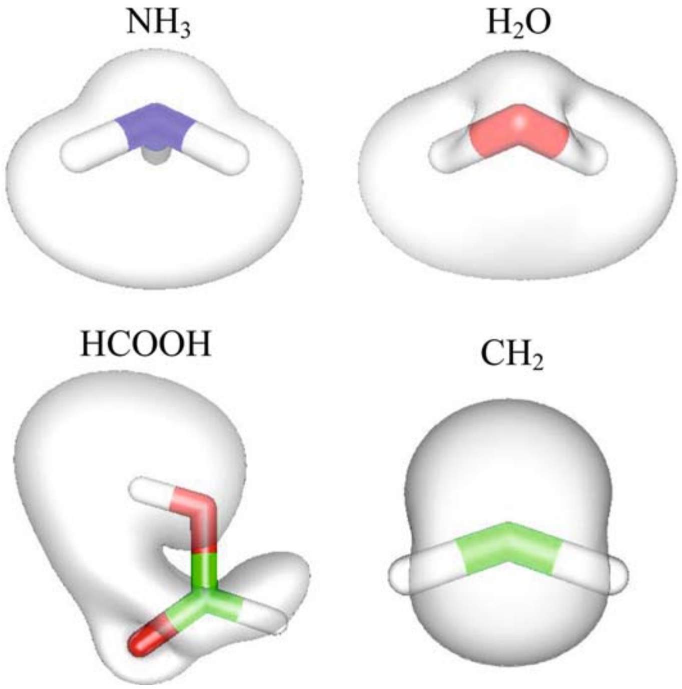

Fig. 2 $f^{+}_{\beta\alpha}$ for NH$_3$, H$_2$O and HCOOH and $f^{+}_{\alpha\beta}$ for CH$_2$ obtained with BLYP/aug-cc-pVTZ, using the FDA. All isosurfaces were done at a value of 0.0. Regions with a negative value of the Fukui function are located *inside* the isosurface.

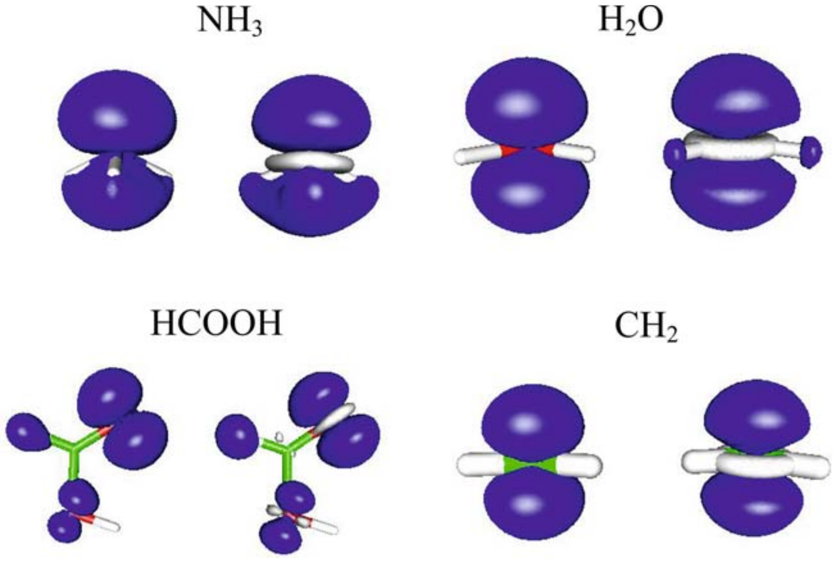

Fig. 3 $f^{-}_{\beta\beta}$ for NH$_3$, H$_2$O and HCOOH and $f^{-}_{\alpha\alpha}$ for CH$_2$ obtained with BLYP/aug-cc-pVTZ. The isosurface on the *left side* of each picture represents the FCA and the *right side* is the FDA. All isosurfaces were done at a value of ±0.008. The *dark color* represents positive values.

From this figure it is clear that the HOMO density gives a better approximation to the Fukui function $f^{-}_{\beta\beta}(\mathbf{r})$ or $f^{-}_{\alpha\alpha}(\mathbf{r})$ than the LUMO density to the Fukui functions $f^{+}_{\alpha\alpha}(\mathbf{r})$ and $f^{+}_{\beta\beta}(\mathbf{r})$. This is in agreement with the fact that the HOMO is always more reliable than the LUMO in a self-consistent field calculation.

The Fukui functions $f^{+}_{N\mathrm{S}}(\mathbf{r})$ and $f^{-}_{N\mathrm{S}}(\mathbf{r})$ calculated from the FDA (Eqs. 57 and 61) and the FCA (Eqs. 59 and 62) are presented in Fig. 4.

Without any doubt, the FCA gives similar results to those obtained with the FDA for the singlet–triplet or triplet–singlet excitation process, as it is shown in Fig. 4.

The chemical potentials associated with each process are reported in Table 1. We can see from this table that the FCA gives different results to those obtained from the FDA. For the closed-shell systems the estimation of μ^{+}_{α} presents a different sign. We can attribute this behavior to the trend of the KS orbital energies obtained with the GGA exchange-correlation

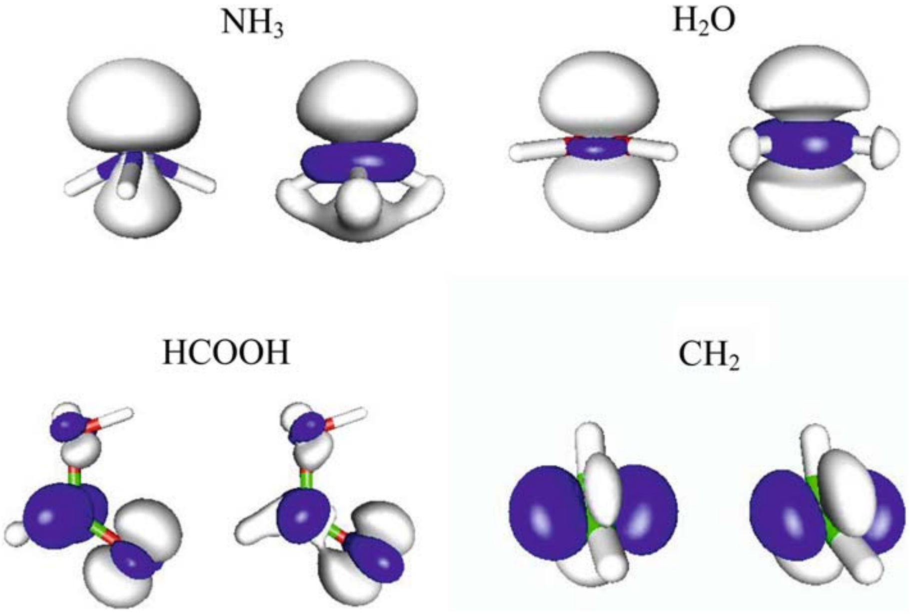

Fig. 4 f_{NS}^{+} for NH_3, H_2O and HCOOH and f_{NS}^{-} for CH_2 obtained with BLYP/aug-cc-pVTZ. The isosurface on the *left side* of each picture represents the frozen core approximation and the *right side* is the finite differences approximation. All isosurfaces were done at a value of ±0.008. The *dark color* represents positive values.

Table 1 Different chemical potentials estimated by the finite difference approximation (FDA) and the frozen core approximation (FCA) for NH_3, H_2O, HCOOH and CH_2.

System	μ_α^+		μ_β^-		μ_S^+	
	FDA	FCA	FDA	FCA	FDA	FCA
NH_3	0.0196	−0.0312	−0.4006	−0.2242	0.1117	0.0965
H_2O	0.0185	−0.0404	−0.4672	−0.2640	0.1281	0.1118
HCOOH	0.0207	−0.0589	−0.4528	−0.2548	0.0953	0.0979
	μ_β^+		μ_α^-		μ_S^-	
	FDA	FCA	FDA	FCA	FDA	FCA
CH_2	−0.0137	−0.1293	−0.3789	−0.2015	−0.0182	−0.0361

All quantities are in hartrees

functionals. It is known that if the exchange-correlation potential shows a good asymptotic behavior, then the orbital energies will be deeper. [27–29] Unfortunately this is not the case for the BLYP functional. Additionally, a physical meaning has been associated to the HOMO–LUMO gap and the HOMO energy obtained within KS approach, [30,31] but there is no physical meaning for the LUMO energy obtained with this method. Thus this orbital energy cannot be associated to the electron affinity process. On the other hand, both approximations, FDA and FCA, yield different values in the estimation of μ_β^-, however both show the same trend, in contrast with the calculation of μ_α^+ and μ_S^+, where the LUMO energy is involved. Clearly the open-shell system exhibits a different behavior than that presented for the closed-shell system since the chemical potentials predicted by FDA or FCA have the same sign.

5 Concluding remarks

Chemical reactivity descriptors like chemical potential, hardness and Fukui function defined in $\{N, \upsilon(\mathbf{r})\}$ representation are not suitable tools in the understanding of reactivity and selectivity trends in some chemical processes that involve spin polarization effects. To overcome this difficulty, several local and global reactivity descriptors from the $\{N, Ns, \upsilon(\mathbf{r})\}$ and $\{N_\alpha, N_\beta, \upsilon(\mathbf{r})\}$ representations are used. Two processes are considered to highlight the fact that the best representation to be used is determined by the features of the process under consideration. Spin polarized generalization of the Fukui functions are calculated for these processes using two widely used procedures; namely the FDA and FCA.

In general, we found that the FCA gives very similar results when the involved orbital corresponds to an occupied shell. The use of virtual orbitals in the FCA, especially when both the alpha and beta are unoccupied, usually leads to noticeable differences with respect to the FDA. This fact becomes evident when we compare the local behavior of both approximations in Fig. 1 with those in Fig. 3.

The importance of spin-dependent global and local reactivity descriptors and two different techniques of their calculations are highlighted. This generalization is necessary in the understanding of chemical processes like spin catalysis, mostly involving radicals and electron deficient species like carbenes. For any process associated with a change in the spin number, even when the number of electrons and the external potential remain constant, the conventional $\{N, \upsilon(\mathbf{r})\}$ representation becomes inadequate. Two different spin-dependent representations, viz., $\{N, N_S, \upsilon(\mathbf{r})\}$ and $\left\{N_\alpha, N_\beta, \upsilon(\mathbf{r})\right\}$ as well as their interconnections, are discussed and it is shown that the choice of the representation depends on the process under consideration. Both approaches, FDA and FCA, are approximate techniques. But the former is more reliable because the latter does not take care of the relaxation effects, which are more evident in the addition of one electron to a closed-shell molecule. Relaxation effects can also be important in the HOMO density, as it was recently reported. [32] FDA and FCA provide identical trends for the ionization potential, but, for the electron affinity, the use of the FCA is not recommended. For processes involving just multiplicity changes FDA and FCA give close results, but trends are not the same, mainly because the LUMO orbital energy is involved.

Appendix. Relationship between the reactivity parameters in $\{N, N_S, v(\mathbf{r})\}$ and $\{N_\alpha, N_\beta, v(\mathbf{r})\}$ representations

Equation (12) defines a linear transformation between the basic variables of the two representations and it can be written in the following form,

$$\begin{pmatrix} N \\ N_S \end{pmatrix} = \mathbf{P}\begin{pmatrix} N_\alpha \\ N_\beta \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} N_\alpha \\ N_\beta \end{pmatrix}. \tag{65}$$

This transformation is characterized by matrix $\mathbf{P}$ whose inverse is proportional to itself, $\mathbf{P}^{-1} = \frac{1}{2}\mathbf{P}$, then

$$\begin{pmatrix} N_\alpha \\ N_\beta \end{pmatrix} = \mathbf{P}^{-1}\begin{pmatrix} N \\ N_S \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} N \\ N_S \end{pmatrix}. \tag{66}$$

Up to second order, the energy change takes the form

$$\begin{aligned} dE &= \begin{pmatrix} \mu_\alpha \\ \mu_\beta \end{pmatrix} \cdot \begin{pmatrix} dN_\alpha \\ dN_\beta \end{pmatrix} + \frac{1}{2}\begin{pmatrix} dN_\alpha \\ dN_\beta \end{pmatrix} \cdot \begin{pmatrix} \eta_{\alpha\alpha} & \eta_{\alpha\beta} \\ \eta_{\beta\alpha} & \eta_{\beta\beta} \end{pmatrix}\begin{pmatrix} dN_\alpha \\ dN_\beta \end{pmatrix} \\ &= \begin{pmatrix} \mu_N \\ \mu_S \end{pmatrix} \cdot \begin{pmatrix} dN \\ dN_S \end{pmatrix} + \frac{1}{2}\begin{pmatrix} dN \\ dN_S \end{pmatrix} \cdot \begin{pmatrix} \eta_{NN} & \eta_{NS} \\ \eta_{SN} & \eta_{SS} \end{pmatrix}\begin{pmatrix} dN \\ dN_S \end{pmatrix}. \end{aligned}$$

Using the linear transformation and equating the coefficients one gets the relationship between the generalized chemical potentials and hardnesses,

$$\begin{pmatrix} \mu_N \\ \mu_S \end{pmatrix} = \frac{1}{2}\mathbf{P}\begin{pmatrix} \mu_\alpha \\ \mu_\beta \end{pmatrix} = \frac{1}{2}\begin{pmatrix} \mu_\alpha + \mu_\beta \\ \mu_\alpha - \mu_\beta \end{pmatrix},$$

$$\begin{aligned} \begin{pmatrix} \eta_{NN} & \eta_{NS} \\ \eta_{SN} & \eta_{SS} \end{pmatrix} &= \frac{1}{4}\mathbf{P}\begin{pmatrix} \eta_{\alpha\alpha} & \eta_{\alpha\beta} \\ \eta_{\beta\alpha} & \eta_{\beta\beta} \end{pmatrix}\mathbf{P} \\ &= \frac{1}{4}\begin{pmatrix} \eta_{\alpha\alpha} + 2\eta_{\alpha\beta} + \eta_{\beta\beta} & \eta_{\alpha\alpha} - \eta_{\alpha\beta} \\ \eta_{\alpha\alpha} - \eta_{\alpha\beta} & \eta_{\alpha\alpha} - 2\eta_{\alpha\beta} + \eta_{\beta\beta} \end{pmatrix}. \end{aligned}$$

The derivatives transform in a similar way,

$$\begin{pmatrix} \frac{\partial}{\partial N_\alpha} \\ \frac{\partial}{\partial N_\beta} \end{pmatrix} = \begin{pmatrix} \frac{\partial N}{\partial N_\alpha} & \frac{\partial N_S}{\partial N_\alpha} \\ \frac{\partial N}{\partial N_\beta} & \frac{\partial N_S}{\partial N_\beta} \end{pmatrix}\begin{pmatrix} \frac{\partial}{\partial N} \\ \frac{\partial}{\partial N_S} \end{pmatrix} = \mathbf{P}^T\begin{pmatrix} \frac{\partial}{\partial N} \\ \frac{\partial}{\partial N_S} \end{pmatrix} = \mathbf{P}\begin{pmatrix} \frac{\partial}{\partial N} \\ \frac{\partial}{\partial N_S} \end{pmatrix}.$$

Therefore, the generalized Fukui functions come from the derivatives of the density and spin density, respectively

$$\begin{aligned} \begin{pmatrix} f_{NN} \\ f_{NS} \end{pmatrix} &= \begin{pmatrix} \frac{\partial \rho}{\partial N} \\ \frac{\partial \rho}{\partial N_S} \end{pmatrix} = \frac{1}{2}\mathbf{P}\begin{pmatrix} \frac{\partial \rho}{\partial N_\alpha} \\ \frac{\partial \rho}{\partial N_\beta} \end{pmatrix} \\ &= \frac{1}{2}\begin{pmatrix} f_{\alpha\alpha} + f_{\beta\alpha} + f_{\alpha\beta} + f_{\beta\beta} \\ f_{\alpha\alpha} + f_{\beta\alpha} - f_{\alpha\beta} - f_{\beta\beta} \end{pmatrix}, \end{aligned}$$

and

$$\begin{pmatrix} f_{SN} \\ f_{SS} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} f_{\alpha\alpha} - f_{\beta\alpha} + f_{\alpha\beta} - f_{\beta\beta} \\ f_{\alpha\alpha} - f_{\beta\alpha} - f_{\alpha\beta} + f_{\beta\beta} \end{pmatrix}.$$

Acknowledgements Financial support for R V, A C and M G was provided by CONACYT, México, with the projects C01-39621, 39622-F and 36482-E, respectively. We thank the Laboratorio de Visualización y Cómputo Paralelo at UAM — Iztapalapa for providing access to its computer facilities and Mr. Utpal Sarkar for the manuscript preparation.

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