

# Fukui and dual-descriptor matrices within the framework of spin-polarized density functional theory

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This work deals with the Fukui and dual reactivity descriptors within the framework of the spin-polarized density functional theory. The first and second derivatives of the electron density and the spin density with respect to the total number of electrons  $N = N_\alpha + N_\beta$  and with respect to the spin number  $N_S = N_\alpha - N_\beta$  have been formulated by means of reduced density matrices in the representation of the spin-orbitals of a given basis set, providing the matrix extension of those descriptors. The analysis of the eigenvalues and eigenvectors of the Fukui and dual-descriptor matrices yields information on the role played by the molecular orbitals in charge-transfer and spin-polarization processes. This matrix formulation enables determining similarity indices which allows one to evaluate quantitatively the quality of the simple frontier molecular orbital model in conceptual density functional theory. Selected closed- and open-shell systems in different spin symmetries have been studied with this matrix formalism at several levels of electronic correlation. The results confirm the suitability of this approach.

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## 1 Introduction

The reactivity of any chemical species, atoms, molecules, radicals, ions, *etc.*, is usually quantified by means of reactivity descriptors associated with chemical concepts, which have become very useful tools providing insights into reaction mechanisms. Most of these descriptors have been satisfactorily formulated within the density functional theory (DFT) framework,<sup>1–9</sup> leading to results which are in good agreement with the expected chemical behavior. These descriptors have proved to be very useful for characterizing thermodynamic, local selectivity and local activation/deactivation electronic proclivities of chemical species.<sup>7,10–12</sup> The spin-polarized versions of DFT (SP-DFT) have enabled an extended treatment of chemical reactivity,<sup>13–29</sup> allowing one to study electron transfer reactions as well as electron spin redistribution processes,<sup>30,31</sup> which are the consequences of the changes produced in the total number

of electrons  $N = N_\alpha + N_\beta$  and in the spin number  $N_S = N_\alpha - N_\beta$ , respectively.<sup>17,29,30,32–39</sup> The occurrence of both types of processes involves changes in the electron density and the spin density of a determined system and, consequently, the study of these quantities and their derivatives is of great interest within the goal of gaining a deeper understanding of reactivity in chemical processes, as exemplified in the recent literature.<sup>40–45</sup> As is well known, the first derivatives of the electron density and the spin density are the Fukui functions<sup>3,46,47</sup> while their second derivatives are the dual descriptors.<sup>36,39,48–52</sup> Within the DFT, both Fukui and dual descriptors are the main indicators of the chemical reactivity;<sup>48–50</sup> their spin-polarized versions<sup>30,36</sup> describe the tendency of a reagent to donate/accept electrons keeping constant the spin multiplicity as well as the proclivity of that system to decrease/increase spin multiplicity at a fixed electron number.

Although the Fukui and dual descriptors are usually formulated in terms of the variations in the electron and spin densities, recently several authors have proposed a matrix formalism for these quantities in which the associated matrix components are expressed by means of the elements of first-order reduced density matrices of  $N$ -electron systems.<sup>53–56</sup> However, this preliminary formalism is limited to the conventional approach of the DFT, in which the changes in the spin multiplicity are not taken into account. One of the purposes of this work is to extend the matrix treatment of the Fukui and dual descriptors to the more general SP-DFT framework and to study the capabilities of the matrix methodology in this scheme.

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The matrix algebra is very suitable for computational purposes. The diagonalization of the Fukui and dual-descriptor matrices allows one to know the nature and the sign of their eigenvalues as well as the dominant coefficients of their eigenvectors. This knowledge provides interesting information expressed in terms of molecular orbitals, which are those usually utilized for the qualitative analysis of reactivity trends within the framework of the so called conceptual DFT.<sup>1,2,7,30,57,58</sup> Another purpose of this work is to study quantitatively the well-known frozen core approximation (FCA), which accounts for the frontier molecular orbital model, taking advantage of the simplicity of the matrix algebra. The determination of indices of similarity between the matrices, which represent a reactivity descriptor at different levels of approximation allows one to compare and assess quantitatively the quality of that approach as well as to evaluate the influence of the orbital relaxation<sup>59,60</sup> and the electronic correlation on those descriptors.

The organization of this work is as follows. Section 2 describes a summary of the Fukui and dual-descriptor functions in the SP-DFT formulation, in which the first and second derivatives of the electron density and the spin density are calculated by means of the finite difference approach within the framework of the limitation that the FCA imposes. Section 3 reports the extension of these devices to the matrix formulation, indicating the relationships between their corresponding matrix elements. In Section 4 we present results obtained in selected systems by application of this methodology. Our treatment has been applied to closed- and open-shell systems with any spin symmetry and at several correlation levels. A discussion of these results is reported in that section in terms of the information drawn from the corresponding descriptor matrices. Finally, Section 5 has been dedicated to highlight the conclusions and remarks of this work.

## 2 Theoretical background

Let  $\rho(\mathbf{r})$  and  $\rho_S(\mathbf{r})$  be the electron and spin densities, respectively, corresponding to an  $N$ -electron system of spin  $S$ , at a point with spatial coordinates  $\mathbf{r}$ . We will consider all the first derivatives of these functions with respect to the number of electrons  $N$  and the spin number  $N_S$ , which are the spin-polarized (or generalized) Fukui functions. These first derivatives will be denoted by  $f_{NN}^\pm(\mathbf{r})$ ,  $f_{SN}^\pm(\mathbf{r})$ ,  $f_{NS}^\pm(\mathbf{r})$  and  $f_{SS}^\pm(\mathbf{r})$ , and defined as<sup>17,30,33,59,61</sup>

$$f_{NN}^\pm(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^\pm \quad (1)$$

$$f_{SN}^\pm(\mathbf{r}) = \left[ \frac{\partial \rho_S(\mathbf{r})}{\partial N} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^\pm \quad (2)$$

$$f_{NS}^\pm(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N_S} \right]_{N, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^\pm \quad (3)$$

$$f_{SS}^\pm(\mathbf{r}) = \left[ \frac{\partial \rho_S(\mathbf{r})}{\partial N_S} \right]_{N, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^\pm \quad (4)$$

in which the first subscript of these functions ( $N$  or  $S$ ) stands for the function ( $\rho$  or  $\rho_S$ , respectively) whose derivatives are being calculated, while the second subscript means that those derivatives are taken with respect to the variables  $N$  (subscript  $N$ ) or  $N_S$  (subscript  $S$ ). As in the case of the energy, one finds that the electron and spin densities have slope discontinuities at the integer numbers of electron and spin.<sup>61–64</sup> Therefore, the left-side and right-side derivatives are different and will be indicated by means of the superscripts  $+$  and  $-$ , respectively. In formulae (1)–(4),  $\nu(\mathbf{r})$  and  $\mathbf{B}(\mathbf{r})$  are the external potential and the external magnetic field which are kept constant along with  $N_S$  (for the derivatives with respect to  $N$ ) or  $N$  (for the derivatives with respect to  $N_S$ ). The descriptors expressed by formulae (1) and (2) give the response of the electron and spin densities to charge transfer processes while those expressed by formulae (3) and (4) are associated with spin polarization phenomena.<sup>17,33</sup>

Likewise, we will also consider the dual descriptor functions which are the second derivatives of the electron and spin densities.<sup>36</sup> Here, we will limit our analysis to the cases  $f_{NNN}^2(\mathbf{r})$ ,  $f_{SNN}^2(\mathbf{r})$ ,  $f_{NSS}^2(\mathbf{r})$ , and  $f_{SSS}^2(\mathbf{r})$ , defined as

$$f_{NNN}^2(\mathbf{r}) = \left[ \frac{\partial^2 \rho(\mathbf{r})}{\partial N^2} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})} \quad (5)$$

$$f_{SNN}^2(\mathbf{r}) = \left[ \frac{\partial^2 \rho_S(\mathbf{r})}{\partial N^2} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})} \quad (6)$$

$$f_{NSS}^2(\mathbf{r}) = \left[ \frac{\partial^2 \rho(\mathbf{r})}{\partial N_S^2} \right]_{N, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})} \quad (7)$$

$$f_{SSS}^2(\mathbf{r}) = \left[ \frac{\partial^2 \rho_S(\mathbf{r})}{\partial N_S^2} \right]_{N, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})} \quad (8)$$

where again the first subscript of these functions stands for the function whose derivatives are being determined ( $N$  for the function  $\rho$  and  $S$  for the function  $\rho_S$ ); the other subscripts mean that the derivative is calculated with respect to the second index and then with respect to the third one. We will refer to charge transfer processes, which produce changes in the functions  $\rho$  and  $\rho_S$  with  $N$ , imposing  $N_S$  to remain constant (descriptors  $f_{NNN}^2(\mathbf{r})$  and  $f_{SNN}^2(\mathbf{r})$ ), as well as to spin polarization processes, in which the changes in these functions are produced by changes in  $N_S$ , keeping constant  $N$  (descriptors  $f_{NSS}^2(\mathbf{r})$  and  $f_{SSS}^2(\mathbf{r})$ ). Hence, other second derivatives such as  $f_{NNS}^2(\mathbf{r})$ ,  $f_{NSN}^2(\mathbf{r})$ ,  $f_{SNS}^2(\mathbf{r})$  and  $f_{SSN}^2(\mathbf{r})$  will not be considered in this work because of their crossed character between the variables  $N$  and  $N_S$ .

Alternative representations of a SP-DFT formulation in terms of the number of electrons with each spin  $N_\alpha$  and  $N_\beta$ , and their associated external potentials, have also been reported.<sup>16,22,30</sup> In fact, it has been emphasized that the  $[N, N_S]$  and the  $[N_\alpha, N_\beta]$  representations are indeed linearly related.<sup>30,59</sup> When both electron and spin transfers can be considered as concerted processes, the  $[N_\alpha, N_\beta]$  representations will be the natural choice; but where the coupling between the

two processes can be neglected to the first order, the  $[N, N_S]$  representation seems to be an appropriate choice to deal with the problem of spin polarization.<sup>30</sup> A comprehensive derivation of the fundamental identities associated with the reactivity indicators in the spin-resolved conceptual DFT formulation is available through a versatile matrix–vector notation, enabling the formulation and study of quantities associated with electron-transfer and spin-polarization processes.<sup>30</sup> In the present contribution we focus on the formulation for the Fukui and dual descriptors using the  $[N, N_S]$  representation.

The Fukui functions are usually calculated using the finite difference approximation<sup>33,39,47</sup> in which those functions are evaluated by means of the relationships  $\frac{\Delta\rho}{\Delta N}$ ,  $\frac{\Delta\rho_S}{\Delta N}$ ,  $\frac{\Delta\rho}{\Delta N_S}$  and  $\frac{\Delta\rho_S}{\Delta N_S}$ . Similarly, the use of that approximation allows one to determine the dual descriptor functions<sup>33,39</sup> according to the relationships  $\frac{f^+ - f^-}{\Delta N}$  and  $\frac{f^+ - f^-}{\Delta N_S}$ , both applied to the functions  $\rho(\mathbf{r})$  and  $\rho_S(\mathbf{r})$ . Moreover, at the single determinant level of theory and in the simple frozen core approximation (FCA) where the orbital relaxation effects are neglected,<sup>8,17,32,59</sup> the functions of these descriptors can be formulated as

$$f_{NN^+}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 + |\phi_L^\beta(\mathbf{r})|^2 \quad f_{NN^-}(\mathbf{r}) \approx |\phi_H^\alpha(\mathbf{r})|^2 + |\phi_H^\beta(\mathbf{r})|^2 \quad (9)$$

$$f_{SN^+}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 - |\phi_L^\beta(\mathbf{r})|^2 \quad f_{SN^-}(\mathbf{r}) \approx |\phi_H^\alpha(\mathbf{r})|^2 - |\phi_H^\beta(\mathbf{r})|^2 \quad (10)$$

$$f_{NS^+}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 - |\phi_H^\beta(\mathbf{r})|^2 \quad f_{NS^-}(\mathbf{r}) \approx |\phi_H^\alpha(\mathbf{r})|^2 - |\phi_L^\beta(\mathbf{r})|^2 \quad (11)$$

$$f_{SS^+}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 + |\phi_H^\beta(\mathbf{r})|^2 \quad f_{SS^-}(\mathbf{r}) \approx |\phi_H^\alpha(\mathbf{r})|^2 + |\phi_L^\beta(\mathbf{r})|^2 \quad (12)$$

and

$$f_{N_{NN}^2}(\mathbf{r}) \approx f_{NN^+}(\mathbf{r}) - f_{NN^-}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 + |\phi_L^\beta(\mathbf{r})|^2 - |\phi_H^\alpha(\mathbf{r})|^2 - |\phi_H^\beta(\mathbf{r})|^2 \quad (13)$$

$$f_{S_{NN}^2}(\mathbf{r}) \approx f_{SN^+}(\mathbf{r}) - f_{SN^-}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 + |\phi_H^\beta(\mathbf{r})|^2 - |\phi_H^\alpha(\mathbf{r})|^2 - |\phi_L^\beta(\mathbf{r})|^2 \quad (14)$$

$$f_{N_{SS}^2}(\mathbf{r}) \approx f_{NS^+}(\mathbf{r}) - f_{NS^-}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 + |\phi_L^\beta(\mathbf{r})|^2 - |\phi_H^\alpha(\mathbf{r})|^2 - |\phi_H^\beta(\mathbf{r})|^2 \quad (15)$$

$$f_{S_{SS}^2}(\mathbf{r}) \approx f_{SS^+}(\mathbf{r}) - f_{SS^-}(\mathbf{r}) \approx |\phi_L^\alpha(\mathbf{r})|^2 + |\phi_H^\beta(\mathbf{r})|^2 - |\phi_H^\alpha(\mathbf{r})|^2 - |\phi_L^\beta(\mathbf{r})|^2 \quad (16)$$

where  $\phi_X^\sigma(\mathbf{r})$  stands for the frontier molecular spin-orbitals ( $X = H$  for the highest-occupied molecular orbital (HOMO) and  $X = L$  for the lowest-unoccupied molecular orbital (LUMO)) and  $\sigma$  is the spin coordinate ( $\sigma = \alpha$  for spin up and  $\sigma = \beta$  for spin down). In order to get simpler expressions for formulae (9)–(16), the denominators  $\Delta N$  and  $\Delta N_S$  required in the application of the finite difference approximation have been omitted and are included within the normalization factors of these functions.

### 3 Matrix extension of spin-polarized Fukui and dual-descriptor functions

In this section we will work in a basis-set representation instead of the spatial representation. The first-order reduced density matrix is expressed by means of the matrix elements  $d_{ij}(\sigma)$  in an orthonormal spin-orbital basis set  $\phi_i^\sigma, \phi_j^\sigma, \dots$  as

$$\rho(\mathbf{r}, \sigma; \mathbf{r}', \sigma) = \sum_{i,j} d_{ij}(\sigma) \phi_i^{*\sigma}(\mathbf{r}) \phi_j^\sigma(\mathbf{r}') \quad (17)$$

in which  $\sigma$  is again the spin coordinate  $\alpha$  or  $\beta$ . As is well known, this matrix is composed of two spin blocks corresponding to the orbitals of the  $\alpha$  and  $\beta$  nature. The relationships between the Fukui matrices and the Fukui functions are similar to the relationships between the first-order reduced density matrix and the electron density function as it has been pointed out in ref. 53–56, 65 and 66. Hence, the reactivity descriptors can be represented by their matrix elements, which in the case of the electron-density-related Fukui descriptors are

$$(f_{NN^+})_{ij}(\sigma) = \left[ \frac{\partial d_{ij}(\sigma)}{\partial N} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^+ = d_{ij}^{(N_x+1, N_\beta+1)}(\sigma) - d_{ij}^{(N_x, N_\beta)}(\sigma) \quad (18)$$

$$(f_{NN^-})_{ij}(\sigma) = \left[ \frac{\partial d_{ij}(\sigma)}{\partial N} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^- = d_{ij}^{(N_x, N_\beta)}(\sigma) - d_{ij}^{(N_x-1, N_\beta-1)}(\sigma) \quad (19)$$

$$(f_{NS^+})_{ij}(\sigma) = \left[ \frac{\partial d_{ij}(\sigma)}{\partial N_S} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^+ = d_{ij}^{(N_x+1, N_\beta-1)}(\sigma) - d_{ij}^{(N_x, N_\beta)}(\sigma) \quad (20)$$

$$(f_{NS^-})_{ij}(\sigma) = \left[ \frac{\partial d_{ij}(\sigma)}{\partial N_S} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})}^- = d_{ij}^{(N_x, N_\beta)}(\sigma) - d_{ij}^{(N_x-1, N_\beta+1)}(\sigma) \quad (21)$$

where the superscripts  $N_x, N_\beta, \dots$  have been introduced into the elements of the first-order reduced density matrix to indicate the number of electrons  $\alpha$  and  $\beta$  of the states of the chemical species described by those matrix elements. Likewise, in formulae (18)–(21) we have omitted the increments  $\Delta N = 2$  and  $\Delta N_S = 2$  which appear in the implementation of the finite difference approximation since each spin block will be normalized to have a trace equal to  $|1|$ .

The matrix formulation allows one to express these descriptors by means of direct sums of their corresponding  $\alpha$  and  $\beta$  blocks

$$(f_{NN^+})_{ij} = (f_{NN^+})_{ij}(\alpha) \oplus (f_{NN^+})_{ij}(\beta) \quad (22)$$

$$(f_{NN^-})_{ij} = (f_{NN^-})_{ij}(\alpha) \oplus (f_{NN^-})_{ij}(\beta) \quad (23)$$

$$(f_{NS^+})_{ij} = (f_{NS^+})_{ij}(\alpha) \oplus (f_{NS^+})_{ij}(\beta) \quad (24)$$

$$(f_{NS^-})_{ij} = (f_{NS^-})_{ij}(\alpha) \oplus (f_{NS^-})_{ij}(\beta) \quad (25)$$

Because the spin density matrix is the difference between the  $\alpha$  and  $\beta$  blocks of the first-order reduced density matrix,

a similar treatment for the spin-density-related Fukui descriptors leads to the relationships

$$(f_{SN^+})_{ij} = (f_{NN^+})_{ij}(\alpha) \oplus (-f_{NN^+})_{ij}(\beta) \quad (26)$$

$$(f_{SN^-})_{ij} = (f_{NN^-})_{ij}(\alpha) \oplus (-f_{NN^-})_{ij}(\beta) \quad (27)$$

$$(f_{SS^+})_{ij} = (f_{NS^+})_{ij}(\alpha) \oplus (-f_{NS^+})_{ij}(\beta) \quad (28)$$

$$(f_{SS^-})_{ij} = (f_{NS^-})_{ij}(\alpha) \oplus (-f_{NS^-})_{ij}(\beta) \quad (29)$$

showing that the formulae which describe these Fukui matrices are identical to those related to the electron density matrix except for a change of sign in the  $\beta$  spin blocks.

The matrix extensions of the dual functions  $f_{N\text{NN}}^2(\mathbf{r})$  and  $f_{N\text{SS}}^2(\mathbf{r})$  can be represented by their corresponding matrix elements as

$$(f_{N\text{NN}}^2)_{ij}(\sigma) = \left[ \frac{\partial^2 d_{ij}(\sigma)}{\partial N^2} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})} = (f_{NN^+} - f_{NN^-})_{ij}(\sigma) \quad (30)$$

and

$$(f_{N\text{SS}}^2)_{ij}(\sigma) = \left[ \frac{\partial^2 d_{ij}(\sigma)}{\partial N_S^2} \right]_{N_S, \nu(\mathbf{r}), \mathbf{B}(\mathbf{r})} = (f_{NS^+} - f_{NS^-})_{ij}(\sigma) \quad (31)$$

which by means of the direct sum approach can be expressed as

$$(f_{N\text{NN}}^2)_{ij} = (f_{NN^+} - f_{NN^-})_{ij}(\alpha) \oplus (f_{NN^+} - f_{NN^-})_{ij}(\beta) \quad (32)$$

$$(f_{N\text{SS}}^2)_{ij} = (f_{NS^+} - f_{NS^-})_{ij}(\alpha) \oplus (f_{NS^+} - f_{NS^-})_{ij}(\beta) \quad (33)$$

By an identical procedure one finds that the matrix extensions of the dual functions  $f_{S\text{NN}}^2(\mathbf{r})$  and  $f_{S\text{SS}}^2(\mathbf{r})$  are represented according to the equations

$$(f_{S\text{NN}}^2)_{ij} = (f_{NN^+} - f_{NN^-})_{ij}(\alpha) \oplus [-(f_{NN^+} - f_{NN^-})_{ij}(\beta)] \quad (34)$$

$$(f_{S\text{SS}}^2)_{ij} = (f_{NS^+} - f_{NS^-})_{ij}(\alpha) \oplus [-(f_{NS^+} - f_{NS^-})_{ij}(\beta)] \quad (35)$$

which present identical structure to the duals  $(f_{N\text{NN}}^2)_{ij}$  and  $(f_{N\text{SS}}^2)_{ij}$ , except for the sign of the  $\beta$  spin block.

The first-order reduced density matrices of the neutral, charged and excited chemical species can be drawn out from most of the standard codes, and consequently their utilization in the construction of the above mentioned matrices turns out to be very accessible. In the next section we show the results arising from the diagonalization of the descriptor matrices in selected systems in different spin symmetries, described at several levels of electronic correlation. Likewise, we study the quality of the matrix formulation of the approximations proposed in eqn (9)–(16) for a determined system by measures of similarity between the matrices representing the same descriptor at two levels of theory A and B. To perform this task, we will use the similarity index

$$S[f^x(\mathbf{A}), f^x(\mathbf{B})] = 100 \frac{\sum_{ij} f_{ij}^x(\mathbf{A}) f_{ji}^x(\mathbf{B})}{\sqrt{\left[ \sum_{ij} f_{ij}^x(\mathbf{A}) f_{ji}^x(\mathbf{A}) \right] \left[ \sum_{ij} f_{ij}^x(\mathbf{B}) f_{ji}^x(\mathbf{B}) \right]}} \quad (36)$$

which was reported in ref. 67–69. This index was used in ref. 55 and 56 to analyze the influence of the electron correlation on the conventional Fukui matrix and to compare reactivities

of the ground and first excited states of molecular systems respectively.

## 4 Results and discussion

The execution of the GAUSSIAN 03 package<sup>70</sup> has provided us with the numerical values of the first-order reduced density matrix elements of the neutral and ionic species. In subsequent steps and using our own codes we have calculated the descriptor matrices, according to eqn (18)–(25) (for the Fukui descriptors) and those (30)–(33) (for the dual descriptors). In all systems, our calculations have been performed with the experimental equilibrium geometries of the neutral species of  $N$  electrons in their ground states.<sup>71,72</sup> These geometries have also been kept for the corresponding ionic and excited species. Our treatment requires to calculate and to compare eigenvectors and indices of similarity between matrices; consequently all the numerical determinations of each system must be expressed in an identical basis set. Hence, we have constructed the Fukui and dual-descriptor matrices in the basis sets of the eigenvectors of the first-order reduced density matrices corresponding to the ground configuration of the neutral systems. Then, according to the proposal reported in ref. 53, we have transformed the matrix elements of the charged and excited species into these basis sets. Our results have been obtained using the basis sets 6-31G, at the levels unrestricted Hartree–Fock (UHF), unrestricted Becke-3-parameter-Lee-Yang-Parr (UB3LYP) functional and unrestricted configuration interaction with single and double excitations (UCISD). These levels of theory allow us to study the relaxation effects and those derived from the use of wave functions composed of unique or multiple Slater determinants. In order to cover the main spin symmetries, in Tables 1–10 we have gathered the results referring to the simple molecules  $\text{C}_2\text{H}_4$  and  $\text{CH}_2\text{O}$  as prototypes of singlet states, the doublet ground state species  $\text{NO}_2$  and  $\text{C}_3\text{H}_5$  and the radical  $\text{CH}_2$  whose ground state is a triplet. The maximum spin projection of the  $S_z$  quantum number has been used for these states.

Tables 1–5 show results arising from the diagonalization of the  $\alpha$  and  $\beta$  blocks of the matrices associated with variations in the electron density matrix; the Fukui descriptor matrices  $f_{NN^+}$ ,  $f_{NN^-}$ ,  $f_{NS^+}$  and  $f_{NS^-}$  as well as the dual matrices  $f_{N\text{NN}}^2$  and  $f_{N\text{SS}}^2$ . The traces of these spin blocks are given by eqn (18)–(21) for the Fukui matrices and by eqn (30)–(31) for the dual ones. Obviously, according to eqn (26)–(29), (34) and (35) the same  $\alpha$  and  $\beta$  blocks (the last ones with opposite sign) describe the counterpart descriptors related to the spin density,  $f_{SN^+}$ ,  $f_{SN^-}$ ,  $f_{SS^+}$ ,  $f_{SS^-}$ ,  $f_{S\text{NN}}^2$  and  $f_{S\text{SS}}^2$ . As can be seen from these tables, when the wave function is a Slater determinant (as in the UHF and UB3LYP approximations) all systems described present a highest eigenvalue equal to 1 in both  $\alpha$  and  $\beta$  spin blocks of the Fukui descriptors  $f_{NN^+}$  and  $f_{NN^-}$ , while the descriptors  $f_{NS^+}$  and  $f_{NS^-}$  exhibit an eigenvalue equal to 1 for the  $\alpha$  block and  $-1$  for the  $\beta$  one, in agreement with the matrix extension of eqn (9)–(12). The other eigenvalues of these descriptors turn out to be much smaller in absolute values in most cases, and are grouped in pairs of identical values but opposite sign. However, these behaviors

**Table 1** Highest (high) and lowest (low) eigenvalues of the electron descriptor matrices found in the  $C_2H_4$ , using 6-31G basis sets at the UHF, UB3LYP and UCISD levels. C–H/C–L mean the dominant coefficients in the eigenvectors of the descriptor matrices with eigenvalues close to  $1/(-1)$ . Frontier occupied/unoccupied orbitals:  $8\alpha$ ,  $8\beta/9\alpha$ ,  $9\beta$  (UHF, UB3LYP, UCISD)

		UHF		UB3LYP		UCISD	
		$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block
$f_{NN}^+$	High	1.000	1.000	1.000	1.000	0.960	0.960
	Low	-0.132	-0.132	-0.133	-0.133	-0.124	-0.124
	C–H	1.000 (9 $\alpha$ )	1.000 (9 $\beta$ )	0.996 (9 $\alpha$ )	0.996 (9 $\beta$ )	0.936 (9 $\alpha$ )	0.936 (9 $\beta$ )
	C–L	—	—	—	—	—	—
$f_{NN}^-$	High	1.000	1.000	1.000	1.000	0.962	0.962
	Low	-0.139	-0.139	-0.144	-0.144	-0.138	-0.138
	C–H	1.000 (8 $\alpha$ )	1.000 (8 $\beta$ )	1.000 (8 $\alpha$ )	1.000 (8 $\beta$ )	1.000 (8 $\alpha$ )	1.000 (8 $\beta$ )
	C–L	—	—	—	—	—	—
$f_{NNN}^2$	High	1.000	1.000	1.000	1.000	0.938	0.938
	Low	-1.002	-1.002	-1.007	-1.007	-0.945	-0.945
	C–H	1.000 (9 $\alpha$ )	1.000 (9 $\beta$ )	0.996 (9 $\alpha$ )	0.996 (9 $\beta$ )	0.933 (9 $\alpha$ )	0.933 (9 $\beta$ )
	C–L	0.999 (8 $\alpha$ )	0.999 (8 $\beta$ )	0.998 (8 $\alpha$ )	0.998 (8 $\beta$ )	0.998 (8 $\alpha$ )	0.998 (8 $\beta$ )
$f_{NS}^+$	High	1.000	0.046	1.000	0.027	0.960	0.034
	Low	-0.061	-1.000	-0.030	-1.000	-0.040	-0.962
	C–H	0.990 (9 $\alpha$ )	—	0.999 (9 $\alpha$ )	—	0.976 (9 $\alpha$ )	—
	C–L	—	1.000 (8 $\beta$ )	—	1.000 (8 $\beta$ )	—	1.000 (8 $\beta$ )
$f_{NS}^-$	High	1.000	0.061	1.000	0.030	0.962	0.040
	Low	-0.046	-1.000	-0.027	-1.000	-0.034	-0.960
	C–H	1.000 (8 $\alpha$ )	—	1.000 (8 $\alpha$ )	—	1.000 (8 $\alpha$ )	—
	C–L	—	0.990 (9 $\beta$ )	—	0.999 (9 $\beta$ )	—	0.976 (9 $\beta$ )
$f_{NSS}^2$	High	1.000	1.000	1.000	1.000	0.936	0.936
	Low	-1.007	-1.007	-1.002	-1.002	-0.939	-0.939
	C–H	0.990 (9 $\alpha$ )	0.990 (9 $\beta$ )	0.999 (9 $\alpha$ )	0.999 (9 $\beta$ )	0.974 (9 $\alpha$ )	0.974 (9 $\beta$ )
	C–L	0.998 (8 $\alpha$ )	0.998 (8 $\beta$ )	1.000 (8 $\alpha$ )	1.000 (8 $\beta$ )	0.999 (8 $\alpha$ )	0.999 (8 $\beta$ )

**Table 2** Highest (high) and lowest (low) eigenvalues of the electron descriptor matrices found in the  $H_2CO$ , using 6-31G basis sets at the UHF, UB3LYP and UCISD levels. C–H/C–L mean the dominant coefficients in the eigenvectors of the descriptor matrices with eigenvalues close to  $1/(-1)$ . Frontier occupied/unoccupied orbitals:  $8\alpha, 8\beta/9\alpha, 9\beta$  (UHF, UB3LYP),  $7\alpha, 7\beta/9\alpha, 9\beta$  (UCISD)

		UHF		UB3LYP		UCISD	
		$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block
$f_{NN}^+$	High	1.000	1.000	1.000	1.000	0.962	0.962
	Low	-0.196	-0.196	-0.203	-0.203	-0.187	-0.187
	C–H	1.000 (9 $\alpha$ )	1.000 (9 $\beta$ )	0.995 (9 $\alpha$ )	0.995 (9 $\beta$ )	0.927 (9 $\alpha$ )	0.927 (9 $\beta$ )
	C–L	—	—	—	—	—	—
$f_{NN}^-$	High	1.000	1.000	1.000	1.000	0.957	0.957
	Low	-0.279	-0.279	-0.170	-0.170	-0.176	-0.176
	C–H	0.996 (8 $\alpha$ )	0.996 (8 $\beta$ )	0.987 (8 $\alpha$ )	0.987 (8 $\beta$ )	0.911 (7 $\alpha$ )	0.911 (7 $\beta$ )
	C–L	—	—	—	—	—	—
$f_{NNN}^2$	High	1.119	1.119	1.043	1.043	1.005	1.005
	Low	-1.056	-1.056	-1.072	-1.072	-1.016	-1.016
	C–H	0.978 (9 $\alpha$ )	0.978 (9 $\beta$ )	0.986 (9 $\alpha$ )	0.986 (9 $\beta$ )	0.922 (9 $\alpha$ )	0.922 (9 $\beta$ )
	C–L	0.985 (8 $\alpha$ )	0.985 (8 $\beta$ )	0.971 (8 $\alpha$ )	0.971 (8 $\beta$ )	0.904 (7 $\alpha$ )	0.904 (7 $\beta$ )
$f_{NS}^+$	High	1.000	0.191	1.000	0.110	0.964	0.152
	Low	-0.068	-1.000	-0.060	-1.000	-0.060	-0.981
	C–H	0.992 (9 $\alpha$ )	—	1.000 (9 $\alpha$ )	—	0.965 (9 $\alpha$ )	—
	C–L	—	0.954 (8 $\beta$ )	—	0.999 (8 $\beta$ )	—	0.775 (7 $\beta$ )
$f_{NS}^-$	High	1.000	0.068	1.000	0.060	0.981	0.060
	Low	-0.191	-1.000	-0.110	-1.000	-0.152	-0.964
	C–H	0.954 (8 $\alpha$ )	—	0.999 (8 $\alpha$ )	—	0.775 (7 $\alpha$ )	—
	C–L	—	0.992 (9 $\beta$ )	—	1.000 (9 $\beta$ )	—	0.965 (9 $\beta$ )
$f_{NSS}^2$	High	1.068	1.068	1.023	1.023	0.996	0.996
	Low	-1.009	-1.009	-1.005	-1.005	-0.987	-0.987
	C–H	0.977 (9 $\alpha$ )	0.977 (9 $\beta$ )	0.994 (9 $\alpha$ )	0.994 (9 $\beta$ )	0.955 (9 $\alpha$ )	0.955 (9 $\beta$ )
	C–L	0.952 (8 $\alpha$ )	0.952 (8 $\beta$ )	0.998 (8 $\alpha$ )	0.998 (8 $\beta$ )	0.773 (7 $\alpha$ )	0.773 (7 $\beta$ )

**Table 3** Highest (high) and lowest (low) eigenvalues of the electron descriptor matrices found in the NO<sub>2</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels. C-H/C-L mean the dominant coefficients in the eigenvectors of the descriptor matrices with eigenvalues close to 1/(-1). Frontier occupied/unoccupied orbitals: 12 $\alpha$ ,11 $\beta$ /13 $\alpha$ ,12 $\beta$  (UHF, UB3LYP), 9 $\alpha$ ,10 $\beta$ /13 $\alpha$ ,13 $\beta$  (UCISD)

		UHF		UB3LYP		UCISD	
		$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block
$f_{NN}^+$	High	1.000	1.000	1.000	1.000	0.959	0.967
	Low	-0.133	-0.139	-0.114	-0.121	-0.113	-0.136
	C-H	1.000 (13 $\alpha$ )	1.000 (12 $\beta$ )	0.998 (13 $\alpha$ )	0.997 (12 $\beta$ )	0.951 (13 $\alpha$ )	0.888 (13 $\beta$ )
	C-L	—	—	—	—	—	—
$f_{NN}^-$	High	1.000	1.000	1.000	1.000	0.973	0.965
	Low	-0.202	-0.493	-0.089	-0.183	-0.110	-0.295
	C-H	0.896 (12 $\alpha$ )	0.999 (11 $\beta$ )	0.985 (12 $\alpha$ )	0.999 (11 $\beta$ )	0.801 (9 $\alpha$ )	0.864 (10 $\beta$ )
	C-L	—	—	—	—	—	—
$f_{NN}^2$	High	1.065	1.320	1.006	1.046	0.964	1.093
	Low	-1.033	-1.011	-1.023	-1.006	-0.997	-0.961
	C-H	0.987 (13 $\alpha$ )	0.964 (12 $\beta$ )	0.996 (13 $\alpha$ )	0.988 (12 $\beta$ )	0.949 (13 $\alpha$ )	0.877 (13 $\beta$ )
	C-L	0.885 (12 $\alpha$ )	0.997 (11 $\beta$ )	0.978 (12 $\alpha$ )	0.998 (11 $\beta$ )	0.797 (9 $\alpha$ )	0.861 (10 $\beta$ )
$f_{NS}^+$	High	1.000	0.217	1.000	0.099	0.958	0.119
	Low	-0.076	-1.000	-0.040	-1.000	-0.049	-0.966
	C-H	0.996 (13 $\alpha$ )	—	1.000 (13 $\alpha$ )	—	0.973 (13 $\alpha$ )	—
	C-L	—	1.000 (11 $\beta$ )	—	1.000 (11 $\beta$ )	—	0.873 (10 $\beta$ )
$f_{NS}^-$	High	1.000	0.107	1.000	0.041	0.968	0.058
	Low	-0.107	-1.000	-0.041	-1.000	-0.058	-0.968
	C-H	0.987 (12 $\alpha$ )	—	0.998 (12 $\alpha$ )	—	0.781 (9 $\alpha$ )	—
	C-L	—	0.993 (12 $\beta$ )	—	0.999 (12 $\beta$ )	—	0.920 (13 $\beta$ )
$f_{NSS}^2$	High	1.002	1.078	1.000	1.006	0.955	0.966
	Low	-1.006	-1.021	-1.001	-1.003	-0.970	-0.964
	C-H	0.996 (13 $\alpha$ )	0.977 (12 $\beta$ )	1.000 (13 $\alpha$ )	0.998 (12 $\beta$ )	0.972 (13 $\alpha$ )	0.915 (13 $\beta$ )
	C-L	0.984 (12 $\alpha$ )	0.995 (11 $\beta$ )	0.998 (12 $\alpha$ )	0.999 (11 $\beta$ )	0.781 (9 $\alpha$ )	0.870 (10 $\beta$ )

**Table 4** Highest (high) and lowest (low) eigenvalues of the electron descriptor matrices found in the C<sub>3</sub>H<sub>5</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels. C-H/C-L mean the dominant coefficients in the eigenvectors of the descriptor matrices with eigenvalues close to 1/(-1). Frontier occupied/unoccupied orbitals: 12 $\alpha$ ,11 $\beta$ /13 $\alpha$ ,12 $\beta$  (UHF, UB3LYP, UCISD)

		UHF		UB3LYP		UCISD	
		$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block
$f_{NN}^+$	High	1.000	1.000	1.000	1.000	0.976	0.974
	Low	-0.123	-0.435	-0.115	-0.188	-0.113	-0.284
	C-H	0.993 (13 $\alpha$ )	0.999 (12 $\beta$ )	0.997 (13 $\alpha$ )	0.999 (12 $\beta$ )	0.887 (13 $\alpha$ )	0.965 (12 $\beta$ )
	C-L	—	—	—	—	—	—
$f_{NN}^-$	High	1.000	1.000	1.000	1.000	0.973	0.977
	Low	-0.440	-0.127	-0.183	-0.115	-0.282	-0.115
	C-H	1.000 (12 $\alpha$ )	1.000 (11 $\beta$ )	1.000 (12 $\alpha$ )	1.000 (11 $\beta$ )	1.000 (12 $\alpha$ )	1.000 (11 $\beta$ )
	C-L	—	—	—	—	—	—
$f_{NN}^2$	High	1.294	1.000	1.057	1.000	1.114	0.964
	Low	-1.012	-1.292	-1.011	-1.066	-0.975	-1.119
	C-H	0.956 (13 $\alpha$ )	0.999 (12 $\beta$ )	0.986 (13 $\alpha$ )	0.999 (12 $\beta$ )	0.875 (13 $\alpha$ )	0.964 (12 $\beta$ )
	C-L	0.997 (12 $\alpha$ )	0.967 (11 $\beta$ )	0.997 (12 $\alpha$ )	0.986 (11 $\beta$ )	0.998 (12 $\alpha$ )	0.975 (11 $\beta$ )
$f_{NS}^+$	High	1.000	0.062	1.000	0.029	0.973	0.040
	Low	-0.064	-1.000	-0.027	-1.000	-0.041	-0.975
	C-H	0.987 (13 $\alpha$ )	—	0.999 (13 $\alpha$ )	—	0.927 (13 $\alpha$ )	—
	C-L	—	1.000 (11 $\beta$ )	—	1.000 (11 $\beta$ )	—	1.000 (11 $\beta$ )
$f_{NS}^-$	High	1.000	0.506	1.000	0.188	0.969	0.295
	Low	-0.506	-1.000	-0.188	-1.000	-0.295	-0.969
	C-H	1.000 (12 $\alpha$ )	—	1.000 (12 $\alpha$ )	—	1.000 (12 $\alpha$ )	—
	C-L	—	0.988 (12 $\beta$ )	—	0.999 (12 $\beta$ )	—	0.984 (12 $\beta$ )
$f_{NSS}^2$	High	1.370	1.000	1.065	1.000	1.126	0.960
	Low	-1.000	-1.373	-1.000	-1.066	-0.961	-1.128
	C-H	0.950 (13 $\alpha$ )	0.988 (12 $\beta$ )	0.985 (13 $\alpha$ )	0.999 (12 $\beta$ )	0.907 (13 $\alpha$ )	0.984 (12 $\beta$ )
	C-L	1.000 (12 $\alpha$ )	0.966 (11 $\beta$ )	1.000 (12 $\alpha$ )	0.986 (11 $\beta$ )	1.000 (12 $\alpha$ )	0.973 (11 $\beta$ )

**Table 5** Highest (high) and lowest (low) eigenvalues of the electron descriptor matrices found in the CH<sub>2</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels. C-H/C-L mean the dominant coefficients in the eigenvectors of the descriptor matrices with eigenvalues close to 1/(-1). Frontier occupied/unoccupied orbitals: 5 $\alpha$ ,3 $\beta$ /6 $\alpha$ ,4 $\beta$  (UHF, UB3LYP), 3 $\alpha$ ,3 $\beta$ /6 $\alpha$ ,7 $\beta$  (UCISD)

		UHF		UB3LYP		UCISD	
		$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block	$\alpha$ -Block	$\beta$ -Block
$f_{NN}^+$	High	1.000	1.000	1.000	1.000	0.979	0.982
	Low	-0.211	-0.062	-0.150	-0.089	-0.173	-0.075
	C-H	0.999 (6 $\alpha$ )	0.998 (4 $\beta$ )	0.995 (6 $\alpha$ )	0.998 (4 $\beta$ )	0.795 (6 $\alpha$ )	0.883 (7 $\beta$ )
	C-L	—	—	—	—	—	—
$f_{NN}^-$	High	1.000	1.000	1.000	1.000	0.982	0.978
	Low	-0.185	-0.192	-0.190	-0.151	-0.180	-0.162
	C-H	1.000 (5 $\alpha$ )	1.000 (3 $\beta$ )	1.000 (5 $\alpha$ )	1.000 (3 $\beta$ )	1.000 (3 $\alpha$ )	1.000 (3 $\beta$ )
	C-L	—	—	—	—	—	—
$f_{NNN}^2$	High	1.008	1.001	1.015	1.000	0.985	0.982
	Low	-1.026	-1.008	-1.028	-1.016	-1.006	-0.991
	C-H	0.997 (6 $\alpha$ )	0.998 (4 $\beta$ )	0.992 (6 $\alpha$ )	0.998 (4 $\beta$ )	0.793 (6 $\alpha$ )	0.881 (7 $\beta$ )
	C-L	0.994 (5 $\alpha$ )	0.998 (3 $\beta$ )	0.994 (5 $\alpha$ )	0.996 (3 $\beta$ )	0.994 (3 $\alpha$ )	0.997 (3 $\beta$ )
$f_{NS}^+$	High	1.000	0.114	1.000	0.058	0.943	0.048
	Low	-0.056	-1.000	-0.047	-1.000	-0.047	-0.935
	C-H	0.991 (6 $\alpha$ )	—	0.998 (6 $\alpha$ )	—	0.884 (6 $\alpha$ )	—
	C-L	—	1.000 (3 $\beta$ )	—	1.000 (3 $\beta$ )	—	1.000 (3 $\beta$ )
$f_{NS}^-$	High	1.000	0.071	1.000	0.049	0.955	0.061
	Low	-0.056	-1.000	-0.040	-1.000	-0.037	-0.955
	C-H	1.000 (5 $\alpha$ )	—	1.000 (5 $\alpha$ )	—	1.000 (3 $\alpha$ )	—
	C-L	—	0.980 (4 $\beta$ )	—	0.997 (4 $\beta$ )	—	0.933 (7 $\beta$ )
$f_{NSS}^2$	High	1.003	1.007	1.001	1.003	0.941	0.958
	Low	-1.005	-1.003	-1.003	-1.001	-0.955	-0.934
	C-H	0.990 (6 $\alpha$ )	0.979 (4 $\beta$ )	0.997 (6 $\alpha$ )	0.996 (4 $\beta$ )	0.884 (6 $\alpha$ )	0.930 (7 $\beta$ )
	C-L	0.999 (5 $\alpha$ )	0.999 (3 $\beta$ )	0.999 (5 $\alpha$ )	1.000 (3 $\beta$ )	0.999 (3 $\alpha$ )	1.000 (3 $\beta$ )

**Table 6** Similarity indices found in the C<sub>2</sub>H<sub>4</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels

A		B		
		UHF	UB3LYP	UCISD
FCA (UHF)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	94.9	94.7	94.8
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	94.5	94.2	94.1
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	98.3	98.6	98.6
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	98.3	98.6	98.6
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	99.5	99.1	99.2
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	98.7	98.8	99.1
FCA (UB3LYP)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	94.1	94.0	93.8
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	94.4	94.3	94.1
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	99.1	99.6	99.4
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	99.1	99.6	99.4
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	99.1	99.0	98.8
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	99.3	99.7	99.7

are not longer fulfilled when the wave function is of multi-determinantal nature (as in the UCISD approximation). These results can be explained in terms of the idempotency of the first-order reduced density matrices derived from a single Slater determinant wave function and the lack of this property when those reduced matrices arise from wave functions composed of multiple Slater determinants. As it has been shown in ref. 73 a matrix only presents grouping of the eigenvalues in pairs of values of opposite sign (excluding the value |1|) when that matrix can be expressed as a difference of two idempotent matrices.

These features have been reported in ref. 53–55 for the conventional Fukui matrices (out of the spin-polarized framework). The results found now in the spin-polarized approach show that these characteristics are also fulfilled by the  $f_{NN}^+$ ,  $f_{NN}^-$ ,  $f_{NS}^+$  and  $f_{NS}^-$  spin-polarized descriptors. Moreover, as in the non-spin-polarized case,<sup>53,74</sup> the negative eigenvalues found in these matrices justify the possible occurrence of negative values for the corresponding spin-polarized Fukui functions. The dual descriptor matrices  $f_{NNN}^2$  and  $f_{NSS}^2$  present one eigenvector with eigenvalue close to 1 and another one with eigenvalue

**Table 7** Similarity indices found in the H<sub>2</sub>CO, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels

A		B		
		UHF	UB3LYP	UCISD
FCA (UHF)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	94.1	93.7	94.0
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	89.7	94.8	94.3
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	92.2	97.1	95.2
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	92.2	97.1	95.2
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	94.9	96.9	96.9
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	92.3	96.6	94.9
FCA (UB3LYP)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	92.9	92.7	92.7
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	90.2	92.7	92.5
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	95.3	98.8	97.5
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	95.3	98.8	97.5
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	94.5	95.0	95.0
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	95.9	98.7	97.6

**Table 8** Similarity indices found in the NO<sub>2</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels

A		B		
		UHF	UB3LYP	UCISD
FCA (UHF)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	95.6	95.7	95.7
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	77.3	92.7	88.0
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	95.2	98.2	97.6
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	96.2	98.1	97.6
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	89.2	97.1	94.7
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	96.0	98.2	98.0
FCA (UB3LYP)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	94.6	95.7	95.1
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	78.4	94.0	89.2
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	95.2	98.9	98.0
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	96.8	99.4	98.6
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	88.5	97.4	94.3
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	95.5	99.3	98.4

**Table 9** Similarity indices found in the C<sub>3</sub>H<sub>5</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels

A		B		
		UHF	UB3LYP	UCISD
FCA (UHF)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	86.8	91.6	90.4
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	87.7	92.8	91.4
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	98.0	95.5	97.3
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	79.3	95.0	89.7
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	91.2	98.5	96.9
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	89.4	98.2	96.3
FCA (UB3LYP)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	85.9	93.4	90.9
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	86.4	94.2	91.7
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	96.3	99.7	99.1
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	80.2	96.2	90.6
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	84.5	97.7	93.2
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	82.9	98.0	93.1

close to  $-1$  in both  $\alpha$  and  $\beta$  blocks, in all the reported approximation levels, which is in agreement with the matrix extension of eqn (13)–(16). However, the grouping of the small eigenvalues in pairs exhibited by the Fukui matrices has not been found for the dual descriptor matrices; in fact, according to eqn (30) and (31) these matrices are not a difference of idempotent matrices in any of the used approximations. The results reported in Tables 1–5 also show the dominant coefficients of the eigenvectors with the highest/lowest eigenvalues of

these descriptor matrices. In all cases these coefficients correspond to frontier orbitals. This is another important aspect which immediately reveals the quality of the well-known frontier molecular orbital model also in the spin-polarized approach. As can be observed in these tables, in the UHF and UB3LYP approximations these coefficients are above 0.9 in most situations, meaning that those Fukui and dual-descriptor orbitals nearly behave like HOMO and LUMO ones. However, the values of the dominant coefficients decrease in the eigenvectors



**Table 10** Similarity indices found in the CH<sub>2</sub>, using 6-31G basis sets at the UHF, UB3LYP and UCISD levels

A		B		
		UHF	UB3LYP	UCISD
FCA (UHF)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	95.7	96.3	96.1
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	95.0	95.3	95.2
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	98.0	98.5	97.3
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	97.4	97.5	89.7
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	98.0	98.2	98.2
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	97.3	98.1	96.3
FCA (UB3LYP)	$S[f_{NN}^+(A), f_{NN}^+(B)] = S[f_{SN}^+(A), f_{SN}^+(B)]$	95.3	96.1	90.9
	$S[f_{NN}^-(A), f_{NN}^-(B)] = S[f_{SN}^-(A), f_{SN}^-(B)]$	95.0	95.4	91.7
	$S[f_{NS}^+(A), f_{NS}^+(B)] = S[f_{SS}^+(A), f_{SS}^+(B)]$	98.6	99.2	99.1
	$S[f_{NS}^-(A), f_{NS}^-(B)] = S[f_{SS}^-(A), f_{SS}^-(B)]$	99.0	99.4	90.6
	$S[f_{NNN}^2(A), f_{NNN}^2(B)] = S[f_{SNN}^2(A), f_{SNN}^2(B)]$	97.9	98.3	93.2
	$S[f_{NSS}^2(A), f_{NSS}^2(B)] = S[f_{SSS}^2(A), f_{SSS}^2(B)]$	98.3	99.3	93.1

arising from the UCISD approximation, what must be interpreted in terms of the influence of the electronic correlation contained in those wave functions.

As it has been mentioned in the Introduction, one of the purposes of this work is to provide a quantitative measure allowing one to analyze the quality of the FCA.<sup>59</sup> In Tables 6–10 we report results of similarity indices, according to formula (36), between matrices which represent the identical descriptor but obtained by means of two different procedures A and B. The procedure A utilized in these tables is the FCA one, which consists of determining the reactivity descriptors by means of formulae (9)–(16); the matrix elements of these descriptors are formulated only in terms of the molecular orbitals HOMO and LUMO arising from the approximations UHF and UB3LYP. Alternatively, the descriptors in the procedure B have been obtained from formulae (18)–(35); the matrix elements of these descriptors are expressed by those of the first-order reduced density matrices resulting from the execution of the codes at the theory levels UHF, UB3LYP and UCISD. A survey of the values reported in Tables 6–10 shows the suitability of the FCA approach which leads to high values of indices of similarity with descriptor matrices formulated from finite difference approximations, without significant influence of electron correlation on this behavior. The lower values of these similarity indices have been found for the descriptors  $f_{NN}^-$ , in the NO<sub>2</sub> molecule, and for that  $f_{NS}^-$ , in the C<sub>3</sub>H<sub>5</sub> radical, when the procedures FCA(UHF) and UHF are compared. These situations are corroborated by the high absolute values found for the “much less than |1|” eigenvalues of these descriptor matrices and disappear when the wave function UHF is substituted by the UB3LYP and UCISD ones (Tables 3 and 4). The high spin-contamination of the UHF wave functions in these systems is probably the cause of this effect.

## 5 Concluding remarks

In this work we have extended the matrix formulation of the conventional Fukui and dual reactivity descriptors to the SP-DFT. This extension provides suitable tools to get information concerning chemical reactivity in a more general spin-polarized framework. Our algorithms have been applied to closed- and

open-shell systems, in any spin symmetry at uncorrelated and correlated levels. The use of wave functions composed of unique or multiple Slater determinants causes remarkable changes in the spectrum of the Fukui matrices. Similarly, the effect of electron correlation lies in the value of the dominant coefficient of the Fukui and dual matrix eigenvectors. The analysis of the eigenvalues and eigenvectors of the obtained descriptor matrices sheds light on some features found in the functional formulation of these descriptors. The matrix formalism turns out to be particularly useful to evaluate quantitatively the frozen core approximation by means of measures of indices of similarity between matrices. The numerical results of these determinations are in agreement with the information obtained from the study of the eigenvalues and eigenvectors of these matrices. We are currently working on studies of several charge transfer and spin polarization processes within the proposed matrix approach.

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