



## Ground and excited state similarity studies by means of Fukui and dual-descriptor matrices

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### ABSTRACT

This Letter reports a quantitative study of the similarity between the Fukui matrices corresponding to the ground state and those of the first excited state of a molecular system, as well as between the dual-descriptor matrices of those states. The formulation of the Fukui and dual-descriptor matrices in the basis set representation provides a simple evaluation of similarity indices, which show that the reactivity of the excited state is reversed from that of the ground state. The dependence of these indices on the electronic correlation is studied by means of numerical determinations performed in selected systems at different theoretical levels.

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### 1. Introduction

The Fukui functions have been widely utilized to describe the nucleophilic and electrophilic character of the different sites within a molecule. These tools constitute the main descriptors of the reactivity in the study of reactions that involve changes in the number of electrons of a determined system. The Fukui functions have been formulated as the right- and left-side derivatives of the electron density with respect to a change in the number of electrons, under constant external potential [1–3]. Similarly, the dual-descriptor function has been defined as the second derivative of the electron density function with respect to a change in the number of electrons, under identical constraint for the external potential [4–8]. The dual-descriptor function, which has also revealed as an important indicator of the molecular reactivity, provides simultaneously the nucleophilic and electrophilic character of the molecule at a determined point [9,10]. Recently, these three functions have been extended to their corresponding matrices [11,12]. The matrix formulation allows one to draw out an additional insight from the analysis of the eigenvalues and eigenvectors arising from the diagonalization of the matrices. Another advantage of the matrix representation is its suitability for computational purposes, due to the simplicity of its algebraic manipulations.

The above mentioned descriptors, formulated by means of their corresponding functions, have successfully been applied to implement studies on reactivity and other properties in the ground elec-

tronic states and in some excited ones as well as on the relationships between them [13–18]. In fact, Ref. [9] reports, for a simple uncorrelated molecular orbital model, relationships between the Fukui functions of the ground states and those of the excited states arising from the promotion of one electron, in terms of frontier molecular orbitals [2]. That reference also reports relationships between the dual-descriptor functions of both states, allowing one to compare the corresponding reactivities. Although those studies possess an approximate character, they enable one to draw out important and useful chemical conclusions. The aim of this Letter is to study and quantitatively assess these approximations by means of evaluations of similarity indices [19]. Another purpose of this Letter is to shed some light on the influence of the electronic correlation on this methodology. In order to get those goals we will use the matrix extension of these descriptors, that is more convenient for that purpose than the corresponding functions. In matrix terms, the calculation of similarity indices is a straightforward task. Moreover, the matrix eigenvalues and eigenvectors provide additional information that reinforce the conclusions.

The organization of this Letter is as follows. In the second section we describe the main concepts and equations which have been used in this Letter. The third section reports the computational details, the numerical determinations and the discussion of the results obtained in *N*-electron systems of several spin symmetries. We have also studied in this section the influence of the electronic correlation over our results, describing the systems at several levels of theory. Finally, the last section reports the conclusions of this Letter.

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## 2. Theoretical review

We will denote by  $\rho(\mathbf{r})$  the electronic density corresponding to an  $N$ -electron system at a point with coordinates  $\mathbf{r}$ . The Fukui functions  $f^+(\mathbf{r})$  and  $f^-(\mathbf{r})$  are the right- and left-side derivatives of the electron density with respect to a change in the number of electrons under constant external potential  $v$ , respectively, that is [1–3,20]

$$f^+(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_v^+ \quad (1)$$

and

$$f^-(\mathbf{r}) = \left[ \frac{\partial \rho(\mathbf{r})}{\partial N} \right]_v^- \quad (2)$$

$f^+(\mathbf{r})$  is big in places at which the molecule easily accepts electrons while  $f^-(\mathbf{r})$  is big in places at which easily donates electrons. An average of these two Fukui functions,  $f^0(\mathbf{r})$ , has also been proposed and used as a measure of reactivity toward an innocuous reagent [2,3,20]

$$f^0(\mathbf{r}) = \frac{1}{2} [f^+(\mathbf{r}) + f^-(\mathbf{r})] \quad (3)$$

Likewise, the dual-descriptor function,  $f^2(\mathbf{r})$ , has been defined as [4–6,9]

$$f^2(\mathbf{r}) = \left[ \frac{\partial^2 \rho(\mathbf{r})}{\partial N^2} \right]_v \quad (4)$$

whose positive or negative values point out molecular regions that tend to accept or donate electrons, respectively.

These derivatives are usually calculated by the finite difference approach. Then, in the simple molecular orbital approximation the functions of these four descriptors can be formulated for the ground state as [2,6,9,10,18]

$$f^+(\mathbf{r}) \approx |\phi_{\text{LUMO}}(\mathbf{r})|^2 \quad (5)$$

$$f^-(\mathbf{r}) \approx |\phi_{\text{HOMO}}(\mathbf{r})|^2 \quad (6)$$

$$f^0(\mathbf{r}) \approx \frac{1}{2} [|\phi_{\text{LUMO}}(\mathbf{r})|^2 + |\phi_{\text{HOMO}}(\mathbf{r})|^2] \quad (7)$$

$$f^2(\mathbf{r}) \approx |\phi_{\text{LUMO}}(\mathbf{r})|^2 - |\phi_{\text{HOMO}}(\mathbf{r})|^2 \quad (8)$$

where  $\phi_{\text{LUMO}}(\mathbf{r})$  and  $\phi_{\text{HOMO}}(\mathbf{r})$  stand for the lowest-unoccupied molecular orbital (LUMO) and the highest-occupied molecular orbital (HOMO), respectively.

The promotion of an electron from the  $\phi_{\text{HOMO}}(\mathbf{r})$  orbital to the  $\phi_{\text{LUMO}}(\mathbf{r})$  one leads to an excited configuration of the molecular system, with its corresponding descriptor functions  $f_{\text{ex}}^+(\mathbf{r})$ ,  $f_{\text{ex}}^-(\mathbf{r})$ ,  $f_{\text{ex}}^0(\mathbf{r})$  and  $f_{\text{ex}}^2(\mathbf{r})$ . Again, the application of the molecular orbital model to this excited configuration provides  $f_{\text{ex}}^+(\mathbf{r}) \approx |\phi_{\text{HOMO}}(\mathbf{r})|^2$  and  $f_{\text{ex}}^-(\mathbf{r}) \approx |\phi_{\text{LUMO}}(\mathbf{r})|^2$ , and the subsequent comparison with the descriptors of the ground configuration lead to [9]

$$f_{\text{ex}}^+(\mathbf{r}) \approx f^-(\mathbf{r}) \quad (9)$$

$$f_{\text{ex}}^-(\mathbf{r}) \approx f^+(\mathbf{r}) \quad (10)$$

$$f_{\text{ex}}^0(\mathbf{r}) = f^0(\mathbf{r}) \quad (11)$$

$$f_{\text{ex}}^2(\mathbf{r}) \approx -f^2(\mathbf{r}) \quad (12)$$

These equations predict for the excited state a reactivity reversed from that of the ground state; molecular regions with electrophilic character in the ground state become nucleophilic in the excited state and vice versa [9,16,18]. As has been mentioned in the Introduction, the main purpose of this Letter is to study quantitatively the approximations formulated by Eqs. (9)–(12), as well as to know the behavior of these approximations beyond single

determinant theories. This task can be performed more suitably if we express the reactivity descriptors by means of the corresponding matrices.

In the following we will denote by  $\phi_i^\sigma, \phi_j^\sigma, \dots$  the spin-orbitals of an orthonormal basis set, where  $\sigma$  is the spin coordinate ( $\alpha$  or  $\beta$ ). The first-order reduced density matrix is expressed by means of the matrix elements  $d_{ij}(\sigma)$  in that spin-orbital basis set as [2,21]

$$\rho(\mathbf{r}, \sigma; \mathbf{r}', \sigma) = \sum_{ij} d_{ij}(\sigma) \phi_i^{\sigma}(\mathbf{r}) \phi_j^{\sigma}(\mathbf{r}') \quad (13)$$

As is well known, this matrix is composed of two spin blocks corresponding to the  $\alpha$ - and  $\beta$ -orbitals. The reactivity descriptors can be formulated by means of those matrix elements, resulting [11,12]

$$f_{ij}^+(\sigma) = \left[ \frac{\partial d_{ij}(\sigma)}{\partial N} \right]_v^+ = d_{ij}^{N+1}(\sigma) - d_{ij}^N(\sigma) \quad (14)$$

$$f_{ij}^-(\sigma) = \left[ \frac{\partial d_{ij}(\sigma)}{\partial N} \right]_v^- = d_{ij}^N(\sigma) - d_{ij}^{N-1}(\sigma) \quad (15)$$

$$f_{ij}^0(\sigma) = \frac{1}{2} [d_{ij}^{N+1}(\sigma) - d_{ij}^{N-1}(\sigma)] \quad (16)$$

$$f_{ij}^2(\sigma) = \left[ \frac{\partial^2 d_{ij}(\sigma)}{\partial N^2} \right]_v = f_{ij}^+(\sigma) - f_{ij}^-(\sigma) = d_{ij}^{N+1}(\sigma) - 2d_{ij}^N(\sigma) + d_{ij}^{N-1}(\sigma) \quad (17)$$

In these equations the derivatives have been calculated by the finite difference method and we have added the superscripts  $N-1$ ,  $N$  and  $N+1$  to indicate the number of electrons of the states of the chemical species that are described by the corresponding first-order reduced density matrices.

The matrix elements  $f_{ij}^+(\sigma)$ ,  $f_{ij}^-(\sigma)$ ,  $f_{ij}^0(\sigma)$  and  $f_{ij}^2(\sigma)$  constitute the matrix formulation of their corresponding reactivity descriptors. These elements can be calculated by means of those of the first-order reduced density matrix of the species of  $(N-1)$ ,  $N$ , and  $(N+1)$  electrons, which can be drawn out from most of the standard codes, and consequently their utilization is very accessible. In the next section we show the results arising from the diagonalization of these matrices in selected systems described at several levels of electronic correlation. Likewise, we study the quality of the approximations proposed in Eqs. (9)–(12) by measures of similarity between their corresponding matrices. To perform this task, we will use the similarity index reported in Ref. [19]

$$S(f^x, f^y) = 100 \frac{\sum_{ij} f_{ij}^x f_{ij}^y}{\sqrt{(\sum_{ij} f_{ij}^x f_{ij}^x) (\sum_{ij} f_{ij}^y f_{ij}^y)}} \quad (18)$$

## 3. Results and discussion

The matrix elements  $d_{ij}^{N-1}(\sigma)$ ,  $d_{ij}^N(\sigma)$  and  $d_{ij}^{N+1}(\sigma)$ , and the descriptor matrices defined by Eqs. (14)–(17), have been calculated with our own codes, using the information provided by the formatted checkpoint files arising from the execution of the GAUSSIAN 03 package [22]. In Tables 1–3 we have gathered the results referring to the simple molecules  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{O}$  and NOF, respectively. For each of these molecules the ground state is Singlet and the first excited state is Triplet, the lowest state of the Triplet series. These results have been obtained using the sequences of the spin states Doublet/Singlet/Doublet for the species of  $(N-1)/N/(N+1)$  electrons in the ground configuration of the  $N$ -electron system and Doublet/Triplet/Doublet for those species in the excited configuration arising from the promotion of one electron from the HOMO to LUMO orbital. In Table 4 we report results for the allyl radical  $\text{C}_3\text{H}_5$ , in which the ground state and the first excited one are Doublets, with sequences Singlet/Doublet/Triplet for both ground and excited configurations. Likewise, in Table 5 we describe results for the

**Table 1**

Highest (high) and lowest (low) eigenvalues of the descriptor matrices and similarity indices found in the C<sub>2</sub>H<sub>4</sub> molecule, 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).

		Ground			Excited			Similarity index
		UHF	UB3LYP	UCISD	UHF	UB3LYP	UCISD	
$f^+$	High	1.000	1.000	0.963	1.000	1.000	0.977	$S_{\text{UHF}}(f^+, f_{\text{ex}}) = 99.1$
	Low	-0.080	-0.073	-0.071	-0.077	-0.079	-0.075	$S_{\text{UB3LYP}}(f^+, f_{\text{ex}}) = 99.1$
	C-H	0.998	1.000	-0.955	0.999	-0.999	-0.998	$S_{\text{UCISD}}(f^+, f_{\text{ex}}) = 98.9$
$f^-$	High	1.000	1.000	0.964	1.000	1.000	0.976	$S_{\text{UHF}}(f^-, f_{\text{ex}}) = 99.1$
	Low	-0.079	-0.078	-0.077	-0.083	-0.075	-0.074	$S_{\text{UB3LYP}}(f^-, f_{\text{ex}}) = 99.1$
	C-H	1.000	-1.000	-1.000	0.990	0.999	0.976	$S_{\text{UCISD}}(f^-, f_{\text{ex}}) = 99.0$
$f^0$	High (1)	0.500	0.500	0.490	0.500	0.500	0.490	$S_{\text{UHF}}(f^0, f_{\text{ex}}^0) = 100$
	High (2)	0.500	0.500	0.489	0.500	0.500	0.489	$S_{\text{UB3LYP}}(f^0, f_{\text{ex}}^0) = 100$
	C-H (1)	-0.999	0.999	0.998	0.999	0.999	-0.998	$S_{\text{UCISD}}(f^0, f_{\text{ex}}^0) = 100$
	C-H (2)	0.998	1.000	0.956	-0.998	1.000	0.956	
$f^2$	High	1.000	1.000	0.947	1.000	1.000	0.975	$S_{\text{UHF}}(f^2, -f_{\text{ex}}^2) = 98.2$
	Low	-1.006	-1.005	-0.954	-1.011	-1.012	-0.985	$S_{\text{UB3LYP}}(f^2, -f_{\text{ex}}^2) = 98.1$
	C-H	0.998	1.000	0.954	0.999	-0.999	-0.998	$S_{\text{UCISD}}(f^2, -f_{\text{ex}}^2) = 97.8$
	C-L	-0.999	0.999	-0.998	0.977	0.991	-0.990	

**Table 2**

Highest (High) and lowest (Low) eigenvalues of the descriptor matrices and similarity indices found in the CH<sub>2</sub>O molecule, 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).

		Ground			Excited			Similarity index
		UHF	UB3LYP	UCISD	UHF	UB3LYP	UCISD	
$f^+$	High	1.000	1.000	0.964	1.000	1.000	0.980	$S_{\text{UHF}}(f^+, f_{\text{ex}}) = 90.4$
	Low	-0.121	-0.112	-0.109	-0.208	-0.132	-0.150	$S_{\text{UB3LYP}}(f^+, f_{\text{ex}}) = 96.3$
	C-H	-0.998	-1.000	0.949	0.951	0.995	0.772	$S_{\text{UCISD}}(f^+, f_{\text{ex}}) = 95.3$
$f^-$	High	1.000	1.000	0.978	1.000	1.000	0.973	$S_{\text{UHF}}(f^-, f_{\text{ex}}) = 91.3$
	Low	-0.262	-0.142	-0.163	-0.146	-0.086	-0.094	$S_{\text{UB3LYP}}(f^-, f_{\text{ex}}) = 96.4$
	C-H	-0.964	1.000	-0.806	0.959	0.990	0.951	$S_{\text{UCISD}}(f^-, f_{\text{ex}}) = 95.6$
$f^0$	High (1)	0.500	0.500	0.488	0.500	0.500	0.488	$S_{\text{UHF}}(f^0, f_{\text{ex}}^0) = 100$
	High (2)	0.500	0.500	0.487	0.500	0.500	0.487	$S_{\text{UB3LYP}}(f^0, f_{\text{ex}}^0) = 100$
	C-H (1)	0.962	-0.995	-0.807	0.962	0.995	-0.807	$S_{\text{UCISD}}(f^0, f_{\text{ex}}^0) = 100$
	C-H (2)	0.965	0.990	-0.936	0.965	0.990	0.936	
$f^2$	High	1.115	1.035	1.004	1.003	1.004	0.989	$S_{\text{UHF}}(f^2, -f_{\text{ex}}^2) = 81.9$
	Low	-1.017	-1.020	-0.997	-1.007	-1.007	-0.979	$S_{\text{UB3LYP}}(f^2, -f_{\text{ex}}^2) = 92.6$
	C-H	0.975	0.992	0.941	0.939	0.992	0.736	$S_{\text{UCISD}}(f^2, -f_{\text{ex}}^2) = 90.8$
	C-L	0.961	0.995	-0.804	0.951	0.987	-0.963	

**Table 3**

Highest (High) and lowest (Low) eigenvalues of the descriptor matrices and similarity indices found in the NOF molecule, 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).

		Ground			Excited			Similarity index
		UHF	UB3LYP	UCISD	UHF	UB3LYP	UCISD	
$f^+$	High	1.000	1.000	0.966	1.000	1.000	0.980	$S_{\text{UHF}}(f^+, f_{\text{ex}}) = 84.5$
	Low	-0.131	-0.086	-0.104	-0.250	-0.067	-0.110	$S_{\text{UB3LYP}}(f^+, f_{\text{ex}}) = 97.4$
	C-H	0.998	1.000	-0.964	-0.980	0.992	-0.852	$S_{\text{UCISD}}(f^+, f_{\text{ex}}) = 95.8$
$f^-$	High	1.000	1.000	0.969	1.000	1.000	1.002	$S_{\text{UHF}}(f^-, f_{\text{ex}}) = 86.7$
	Low	-0.302	-0.081	-0.146	-0.290	-0.154	-0.182	$S_{\text{UB3LYP}}(f^-, f_{\text{ex}}) = 97.3$
	C-H	-0.983	1.000	-0.898	0.955	-0.999	0.973	$S_{\text{UCISD}}(f^-, f_{\text{ex}}) = 95.6$
$f^0$	High (1)	0.500	0.500	0.501	0.500	0.500	0.501	$S_{\text{UHF}}(f^0, f_{\text{ex}}^0) = 100$
	High (2)	0.500	0.500	0.487	0.500	0.500	0.487	$S_{\text{UB3LYP}}(f^0, f_{\text{ex}}^0) = 100$
	C-H (1)	0.978	0.997	0.964	0.978	0.997	-0.964	$S_{\text{UCISD}}(f^0, f_{\text{ex}}^0) = 100$
	C-H (2)	-0.958	0.999	-0.900	0.958	-0.999	0.900	
$f^2$	High	1.136	1.001	0.938	1.040	1.035	1.033	$S_{\text{UHF}}(f^2, -f_{\text{ex}}^2) = 71.1$
	Low	-1.025	-1.010	-0.981	-1.003	-1.004	-1.006	$S_{\text{UB3LYP}}(f^2, -f_{\text{ex}}^2) = 94.6$
	C-H	0.973	-0.999	-0.961	0.964	-0.971	0.793	$S_{\text{UCISD}}(f^2, -f_{\text{ex}}^2) = 91.1$
	C-L	-0.976	0.997	0.891	0.951	-0.997	-0.981	

methylene radical CH<sub>2</sub>, in which the ground state is Triplet and the first excited one is Singlet, with the sequences Doublet/Triplet/Doublet for the ground configuration and that Doublet/Singlet/Doublet

for the excited one. The maximum spin projection for the S<sub>z</sub> quantum number has been utilized in all our numerical determinations. The excited electronic configurations have been chosen so that

**Table 4**  
Highest (High) and lowest (Low) eigenvalues of the descriptor matrices and similarity indices found in the  $C_3H_5$  radical, 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  $1/(-1)$ .

		Ground			Excited			Similarity index
		UHF	UB3LYP	UCISD	UHF	UB3LYP	UCISD	
$f^+$	High	1.000	1.000	0.975	1.000	1.000	0.872	$S_{UHF}(f^+, f_{ex}^-) = 90.1$
	Low	-0.236	-0.146	-0.158	-0.109	-0.084	-0.130	$S_{UB3LYP}(f^+, f_{ex}^-) = 99.1$
	C-H	-0.995	-1.000	0.908	-1.000	1.000	1.000	$S_{UCISD}(f^+, f_{ex}^-) = 96.6$
$f^-$	High	1.000	1.000	0.965	1.000	1.000	0.895	$S_{UHF}(f^-, f_{ex}^+) = 91.3$
	Low	-0.305	-0.114	-0.148	-0.121	-0.114	-0.228	$S_{UB3LYP}(f^-, f_{ex}^+) = 99.1$
	C-H	-1.000	-1.000	1.000	-0.946	-0.997	0.912	$S_{UCISD}(f^-, f_{ex}^+) = 96.4$
$f^0$	High (1)	0.500	0.500	0.490	0.500	0.500	0.490	$S_{UHF}(f^0, f_{ex}^0) = 100$
	High (2)	0.500	0.500	0.487	0.500	0.500	0.487	$S_{UB3LYP}(f^0, f_{ex}^0) = 100$
	C-H (1)	-1.000	1.000	0.896	-1.000	1.000	0.896	$S_{UCISD}(f^0, f_{ex}^0) = 100$
	C-H (2)	0.949	-0.997	-1.000	-0.949	-0.997	1.000	
$f^2$	High	1.158	1.012	1.019	1.000	1.000	0.770	$S_{UHF}(f^2, -f_{ex}^2) = 82.8$
	Low	-1.000	-1.001	-0.956	-1.005	-1.002	-0.821	$S_{UB3LYP}(f^2, -f_{ex}^2) = 98.2$
	C-H	0.967	0.997	0.900	1.000	-1.000	-0.999	$S_{UCISD}(f^2, -f_{ex}^2) = 93.1$
	C-L	-1.000	1.000	-1.000	-0.939	-0.996	-0.927	

**Table 5**  
Highest (High) and lowest (Low) eigenvalues of the descriptor matrices and similarity indices found in the  $CH_2$  radical, 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  $1/(-1)$ .

		Ground			Excited			Similarity index
		UHF	UB3LYP	UCISD	UHF	UB3LYP	UCISD	
$f^+$	High	1.000	1.000	0.984	1.000	1.000	0.954	$S_{UHF}(f^+, f_{ex}^-) = 98.0$
	Low	-0.117	-0.115	-0.114	-0.118	-0.105	-0.097	$S_{UB3LYP}(f^+, f_{ex}^-) = 98.2$
	C-H	-0.995	-1.000	0.899	0.996	0.996	-0.996	$S_{UCISD}(f^+, f_{ex}^-) = 98.1$
$f^-$	High	1.000	1.000	0.984	1.000	1.000	0.955	$S_{UHF}(f^-, f_{ex}^+) = 98.0$
	Low	-0.112	-0.104	-0.103	-0.132	-0.127	-0.143	$S_{UB3LYP}(f^-, f_{ex}^+) = 98.2$
	C-H	1.000	1.000	1.000	-0.979	0.997	0.932	$S_{UCISD}(f^-, f_{ex}^+) = 98.1$
$f^0$	High (1)	0.500	0.500	0.492	0.500	0.500	0.492	$S_{UHF}(f^0, f_{ex}^0) = 100$
	High (2)	0.500	0.500	0.492	0.500	0.500	0.492	$S_{UB3LYP}(f^0, f_{ex}^0) = 100$
	C-H (1)	0.996	-0.996	-0.996	-0.996	-0.996	0.996	$S_{UCISD}(f^0, f_{ex}^0) = 100$
	C-H (2)	-0.994	0.999	0.898	-0.994	0.999	0.898	
$f^2$	High	1.003	1.001	0.987	1.000	1.000	0.925	$S_{UHF}(f^2, -f_{ex}^2) = 95.7$
	Low	-1.015	-1.014	-0.999	-1.020	-1.018	-0.943	$S_{UB3LYP}(f^2, -f_{ex}^2) = 96.1$
	C-H	0.994	-0.999	0.898	0.996	0.996	0.996	$S_{UCISD}(f^2, -f_{ex}^2) = 95.9$
	C-L	0.996	-0.997	0.997	0.955	0.985	0.959	

they have the lowest energy for a particular symmetry. In all the systems, we have used the ground state experimental equilibrium geometries of the neutral species with  $N$  electrons [23,24] for both configurations (ground and excited). These geometries have also been kept for the corresponding ionic species of  $N - 1$  and  $N + 1$  electrons for these two configurations. In order to compare matrix eigenvectors and to calculate similarity indices, the numerical determinations must be expressed in identical basis sets for each system. Consequently, we have constructed the Fukui and dual-descriptor matrices in the basis sets of the eigenvectors of the matrices  $d_{ij}^N(\sigma)$  corresponding to the ground configuration; we have transformed the matrix elements of the ionic species  $d_{ij}^{N-1}(\sigma)$  and  $d_{ij}^{N+1}(\sigma)$  and those of the elements  $d_{ij}^N(\sigma)$  of the excited configuration into these basis sets. The calculations have been performed, 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 allows us to study the correlation effects and those derived from the use of wave functions composed of a unique or multiple Slater determinants.

In Tables 1–5 we report indices of similarity between the Fukui matrices  $f^-$  and  $f_{ex}^+$  and between their counterparts  $f^+$  and  $f_{ex}^-$ , in order to evaluate quantitatively the quality of the approximations

proposed in formulas (9) and (10), respectively. The high values found for the percentages of similarity between these matrices mean the suitability of the molecular orbital model used in the derivations of Eqs. (5) and (6) and the relationships (9) and (10). In the ethylene molecule (Table 1) and the methylene radical (Table 5), the treatments UHF, UB3LYP and UCISD lead to very close values of the similarity indices for the Fukui matrices in the ground and excited states. However, the results for the other systems, which are shown in Tables 2–4, indicate that the higher similarity indices correspond to the descriptions arising from the UB3LYP functional and the UCISD treatment, highlighting the influence of the electronic correlation on these values. As expected, the indices of similarity between the matrices  $f^0$  and  $f_{ex}^0$  show that both matrices are identical; the changes of  $f^+$  and  $f^-$  of the excited state with respect to those corresponding of the ground state are exactly identical but of opposite sign. The results arising from the comparison of the dual-descriptor matrices  $f^2$  and  $f_{ex}^2$  present similar qualitative features to those found in the case of the Fukui matrices, which justify again the approximations formulated in Eqs. (8) and (12). However, as can be seen in these Tables the numerical values of the similarity indices between the dual-descriptor matrices are slightly lower than in the Fukui counterparts. Moreover, the differences between the values obtained at different levels of correlation are higher in the case of dual descriptors. Hence, the similarity indices

turns out to be more stringent when are described in terms of the dual descriptors than in terms of Fukui ones. The influence of the electronic correlation on the values of the similarity indices in the dual-descriptor matrices follows the same tendency than in the Fukui descriptors; the highest values are obtained with the UB3LYP functional and the lowest ones with the UHF procedure. All these results justify and evaluate quantitatively the approximations reported in Ref. [9] in terms of descriptor functions, which predict that the excited state possesses a reactivity reversed from the ground state, interchanging the nucleophilic/electrophilic character. Furthermore, our results show that those approximations are fulfilled beyond the simple uncorrelated molecular orbital model scheme invoked in that reference; in fact, the similarity between the corresponding reactivity indicators of both states becomes still higher in that case.

All the above mentioned matrices have been diagonalized and their highest and lowest eigenvalues have been included in Tables 1–5. These Tables also contain the dominant coefficients of the eigenvectors associated to those eigenvalues. An analysis of the eigenvalues of the Fukui matrices ( $f^+$  and  $f^-$ ) shows that these matrices possess an eigenvalue equal to 1 and the others can be grouped in pairs with identical value and opposite sign in all the studied systems, as for the ground as for the excited states, when they are described by a wave function constituted by a single Slater determinant (UHF and UB3LYP). However, the highest eigenvalue slightly decreases from 1 and the grouping in pairs is broken when the wave functions are composed of more than one Slater determinant (UCISD). These features have previously been pointed out in Refs. [11,12,25] in relation with the ground states. Our results indicate that the same behavior is fulfilled for the systems in the excited state described by unrestricted orbitals. These results also reinforce the explanation of the break of the pairing property, which has been attributed to the loss of idempotency of the first-order reduced density matrices in the case of multideterminantal wave functions respect to the monodeterminantal case [26]. The survey of  $f^0$  and  $f^2$  matrices indicates that these two descriptors retain the information contained in the  $f^+$  and  $f^-$  Fukui matrices, in agreement with the relationships  $f^0 = (f^+ + f^-)/2$  and  $f^2 = f^+ - f^-$ . As can be observed, a high dominant coefficient appears in each of the reported eigenvectors of the Fukui and dual-descriptor matrices although its value decreases in the UCISD treatment due to the influence of the electronic correlation. These dominant coefficients correspond to the same orbital in the eigenvector with highest eigenvalue of  $f^+$  and  $f_{ex}^-$  and the same feature is found for the pairs of matrices  $(f^-, f_{ex}^+)$ ,  $(f^0, f_{ex}^0)$  and  $(f^2, -f_{ex}^2)$ , which explain the above reported similarity indices between the ground and excited reactivity descriptors and the reversed reactivity of both states.

#### 4. Concluding remarks

In this Letter we have dealt with devices which describe the molecular reactivity (Fukui and dual descriptors) in a matrix formulation. This approach has allowed us to compare quantitatively reactivities of the ground and first excited states, within and beyond the model of molecular orbitals, by means of indices of similarity between two matrices. The values of the indices determined confirm the suitability of the approximation which considers that

the ground and excited states have reversed reactivities and this conclusion is reinforced by the analysis of the eigenvalues and eigenvectors of the corresponding descriptor matrices. These studies, which have been performed at several levels of theory, point out that there is not significant influence of the electronic correlation on this reported behavior. We are currently working on the local evaluation of these matrix devices to study molecular regions according to their electrophilic and nucleophilic character [27].

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