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Bond Fukui Functions As Descriptor of the Electron Density Reorganization in π Conjugated Systems

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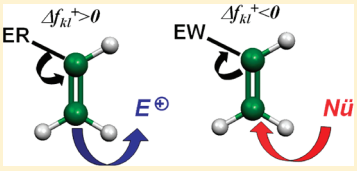
Supporting Information

ABSTRACT: The bond Fukui function is introduced and tested as a new reactivity index capable of predicting the evolution of bond breaking and formation processes during an organic reaction involving π conjugated systems. As an illustration, we examine many cases where substituted ethylenes and dienes may respond to different reagents to yield cycloaddition, Michael addition, and other reactions at double bonds.



INTRODUCTION

The atomic Fukui function (FF) obtained by integration of the local FF introduced in the density functional theory of Parr and Yang[1,2] has become a valuable tool to deal with site selectivity in a wide range of organic reactions.[3−6]

The working expression of the atomic FF is obtained as derivatives of the atomic charges with respect to the total number of electrons N as follows:[2,7]

$$f_k = \left[\frac{\partial q_k}{\partial N}\right]_{v(\mathbf{r})} \tag{1}$$

The derivative is taken at constant external potential $v(\mathbf{r})$ (i.e., at frozen molecular geometry).

Bond Fukui functions (BFF) may also be defined, either within semiempirical or all electron theories. For instance, within the Huckel molecular orbital (HMO) theory, the BFF is obtained as the derivative of bond orders with respect to the number of π electrons N_π, namely,[7]

$$f_{kl} = \left[\frac{\partial P_{kl}}{\partial N_\pi}\right]_{v(r)} \tag{2}$$

where P_{kl} is the bond order between atoms k and l. While the atomic FF[8,9] has been useful to describe regioselectivity in a number of cases, including Diels−Alder reactions,[10,11] electrophilic additions,[12] 1,3 dipolar cycloadditions,[13] and other reactions at double bonds,[14] the electrophilic and nucleophilic BFF have not been used or validated as descriptors of reactivity at bonds. We show herein that BFF are useful tools to describe electron density reorganization at bonds for an N electron system during a chemical reaction within an all electron theory. The working formula for the nucleophilic and electrophilic BFF is obtained as a generalization of the model presented by Balawender et al[15] for the derivatives of the element of the first-order density matrix with respect to the total number of electrons N. Within this approach, the nucleophilic and electrophilic BFF may be defined as:

$$f_{kl}^{-} = \sum_i c_{i,k}^{\mathrm{HOMO}} \sum_j c_{j,l}^{\mathrm{HOMO}} \tag{3}$$

$$f_{kl}^{+} = \sum_i c_{i,k}^{\mathrm{LUMO}} \sum_j c_{j,l}^{\mathrm{LUMO}} \tag{4}$$

respectively. The summation is made over the frontier molecular orbitals (i,j) associated with the atomic centers k and l within the molecule. A detailed derivation of eqs 3 and 4 is given in the section Summary of Approximations and Limitations of the Model (vide infra). The implementation is easy and requires simply the evaluation of the corresponding MO coefficients $c_{i,k}^{\alpha}$ and $c_{j,l}^{\alpha}$; α = HOMO, LUMO. Calculations at the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory were performed in order to test whether or not the calculation of nucleophilic and electrophilic BFF using eqs 3 and 4 are stable with respect to the computational method used. The calculations were performed using the Gaussian03[16] suite of programs. To illustrate the reliability and usefulness of the BFF model, the calculated electrophilic and nucleophilic BFF were used to rationalize the electron density reorganization that usually results in site electrophilic or nucleophilic activation/deactivation, for a series of organic reactions. The model was applied to a set of 26 compounds present in Diels−Alder reactions (DA), 1,3 dipolar cycloadditions, Michael additions, and other electrophilic and nucleophilic additions to double bond.

Before proceeding with the analysis, we need a criterion to select the meaningful descriptors for bond donating charge (nucleophilic bond) and for bond accepting charge (electrophilic bonds). A nucleophilic bond is defined here as an internuclear region rich in electron density (in general a π bond), capable of releasing a fraction of electronic charge to

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another internuclear region (in general a σ bond) in the molecule. The following scenarios are possible:

$$f_{kl}^{-} = P_{kl}(N) - P_{kl}(N-1) > 0 \quad (5a)$$

or

$$f_{kl}^{-} = P_{kl}(N) - P_{kl}(N-1) < 0 \quad (5b)$$

An electrophilic bond is defined here as an internuclear region poor in electron density (in general a σ bond), capable of accepting a fraction of electronic charge from another internuclear region (in general a π bond) in the molecule. The following scenarios are possible:

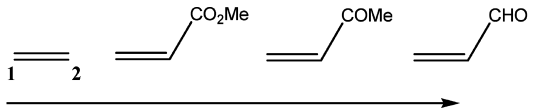
$$f_{kl}^{+} = P_{kl}(N+1) - P_{kl}(N) > 0 \quad (6a)$$

or

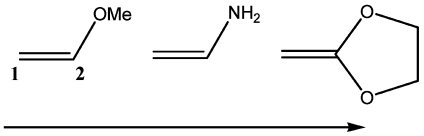
$$f_{kl}^{+} = P_{kl}(N+1) - P_{kl}(N) < 0 \quad (6b)$$

Situation 5a arises when in the process where the whole molecule releases an electron unit, the π bond (k,l) involved is weakened or, in the limit case, it may be stabilized as a σ bond at the end of the process. Situation 5b arises when in the process where the whole molecule release an electron unit, the π bond (k,l) involved may act as an electron density carrier toward another region in the molecule. Note that this situation does not entail that this π bond (k,l) is necessarily electronically enriched. For electrophilic BFF case 6a, the σ bond (k,l) stabilizes as a π bond after the molecule has accepted one electron unit. Case 6b describes a situation where the π bond involved is weakened by transferring electronic charge to one region k says, thereby creating a hole in the opposite site l. The net result is the electrophilic activation at site l. With these criteria at hand, we may analyze the reactivity of some organic processes. A quick reference about how the BFF indices may be used to analyze chemical reactivity is illustrated in Scheme 1 for some representative cases.

Scheme 1



Increase in electrophilic on the bond: For substituted ethylenes bearing electron withdrawing groups, the relevant information is contained in f_{1-2}^{+} *index.*



Increase in nucleophilic on the bond: For substituted ethylenes bearing electron releasing groups, the relevant information is contained in f_{1-2}^{-} *index.*

Note that the definitions of electrophilic and nucleophilic bonds are somehow arbitrary in the sense that the charge transfer patterns are restricted herein to $\sigma \rightarrow \pi$ and $\pi \rightarrow \sigma$ bonds. There may be some cases where charge transfer can take place between an electron rich π bond to another electron poor π bond and vice versa. These cases will not be discussed here.

RESULTS AND DISCUSSION

A first family including compounds **1**−**12** bearing electron withdrawing groups was selected for analysis. They are compiled in Table 1. Inspection of Table 1 reveals that the reference ethylene molecule shows the highest positive value of the nucleophilic BFF and the highest negative value of the electrophilic BFF. However, the main interest here is on the activated ethylene derivatives obtained by chemical substitution, and therefore these figures will be taken only as reference values. Compounds **2**−**12** correspond to ethylene derivatives bearing electron withdrawing (EW) substituents that usually entail electrophilic activation at the unsubstituted atomic center (i.e., Markovnikov rule, see last column in Table 1).[17] For this reason, the most useful index for these cases is the electrophilic BFF, f_{kl}^{+}. Note that within this series the electrophilic bond index at sites (1,2) is less negative than the reference value of ethylene (−1.408).

These cases (compounds **2**−**12**) can be described by situation 6b: the π bond is weakened by transferring electronic charge toward the substituent at position 2, thereby electrophilically activating site 1 for the general case of nucleophilic additions to the double bond, including cycloadditions, Michael additions, epoxidation, and other processes involving EW substituted ethylenes (see last column of Table 1). Note also that the electrophilic BFF at bond 2−3 are consistently positive, thereby showing that this bond can acquire a transient π character before the chemical process is finished. This situation corresponds to the case defined by criterion 6a (see fifth column in Table 1).

The analysis of the subseries of compounds **7**−**9** is also worth discussing. This series correspond to the CN-substituted ethylenes and criteria 6a and 6b may be applied to discuss the reactivity of these compounds toward cycloaddition reactions. For instance, the electrophilic BFF at bond (1,2) increases by increasing substitution and this result is consistent with enhanced reaction rates toward cyclopentadiene.[18,19] See Scheme 2.

On the other hand, the electrophilic BFF at bonds (2,3) decreases by increasing CN substitution, a result that may be traced to symmetry arguments.[19] Note that for compounds **10**−**12** a similar pattern is observed.

Table 2 summarizes the BFF values for substituted ethylenes bearing electron releasing substituents (ER). Here the relevant information is mainly contained in the nucleophilic BFF, f_{kl}^{-}. For instance, for compounds **13** and **14**, the nucleophilic BFF at bond (1,2) increases in going from a single O-substitution compared to the double O-substitution in compound **14**. The corresponding nucleophilic BFF are positive, thereby indicating that this bond is acting as an electron releasing functionality and criterion 5a applies.

For compounds **15** and **16**, the BFF clearly diminishes according to criterion 5a. Note that in compounds **17** and **18** this behavior is consistent with the captodative character of these compounds that can act either as electrophiles or nucleophiles.[20]

Finally, we considered a series of substituted dienes displayed in Table 3, taking 1,3- butadiene as reference (compound **19**). We first discuss the subseries of compounds **20**−**23** that corresponds to butadiene derivatives bearing electron releasing substituents. The nucleophilic BFF at bonds (3,4) in compounds **20** and **21** significantly increases from 0.168 to 0.468 due to the marginal electron releasing CH_3 group and the

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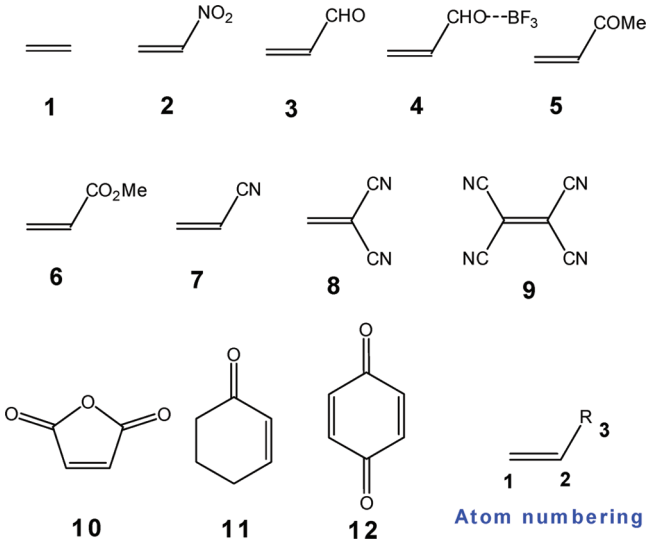
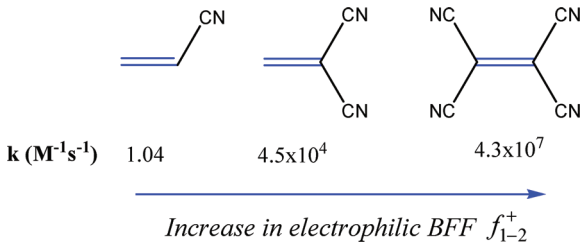
Table 1. Electrophilic and Nucleophilic BFF (f_{kl}^{+} and f_{kl}^{-}) and Local Electrophilic and Nucleophilic Fukui Functions (f_r^{+} and f_r^{-}) at Site r for Compounds Bearing an Electron Withdrawing Substituent at Different Positions[a]



	f_{1-2}^{-}	f_{1-2}^{+}	f_{2-3}^{-}	f_{2-3}^{+}	site	f_r^{-}	f_r^{+}
1	0.516 (0.470)	**−1.408 (−1.104)**			1	0.500 (0.500)	**0.500 (0.500)**
2	0.484 (0.015)	**−0.510 (−0.288)**	−0.063 (0.001)	0.402 (0.276)	1	0.422 (0.012)	**0.347 (0.278)**
3	0.463 (−0.024)	**−0.557 (−0.353)**	−0.042 (−0.009)	0.399 (0.296)	1	0.411 (0.011)	**0.387 (0.372)**
4	0.458 (0.365)	**−0.409 (−0.261)**	0.044 (0.018)	0.386 (0.263)	1	0.380 (0.366)	**0.381 (0.371)**
5	0.465 (−0.079)	**−0.653 (−0.443)**	−0.085 (0.017)	0.392 (0.332)	1	0.414 (0.010)	**0.394 (0.372)**
6	0.471 (0.035)	**−0.779 (−0.527)**	−0.059 (−0.032)	0.396 (0.332)	1	0.422 (0.004)	**0.437 (0.415)**
7	0.402 (0.325)	**−0.930 (−0.674)**	−0.179 (−0.147)	0.321 (0.266)	1	0.368 (0.267)	**0.437 (0.265)**
8	0.359 (0.285)	**−0.830 (−0.602)**	−0.148 (−0.121)	0.191 (0.117)	1	0.313 (0.197)	**0.510 (0.209)**
9	0.301 (0.220)	**−0.690 (−0.469)**	−0.120 (−0.095)	0.108 (0.057)	1	0.214 (0.176)	**0.292 (0.257)**
10	0.414 (0.113)	**−0.634 (−0.432)**	−0.018 (−0.006)	0.356 (0.264)	1	0.384 (0.040)	**0.275 (0.236)**
11	0.521 (−0.038)	**−0.785 (−0.496)**	−0.095 (0.016)	0.518 (0.401)	1	0.366 (0.011)	**0.363 (0.351)**
12	0.274 (−0.267)	**−0.200 (−0.060)**	0.016 (−0.152)	0.182 (0.146)	1	0.248 (0.053)	**0.114 (0.096)**

[a]In parentheses are shown values calculated at the B3LYP/6-31G(d) level of theory.

Scheme 2



stronger electron releasing OCH_3 group. Both indexes are positive, and therefore they are well described by criterion 5a: the final result is nucleophilic activation at position 4 (see ninth column in Table 3). On the other hand, when substitution is at position 2 of the diene (compound **22**, **23**), the nucleophilic activation is consistently shown at bond (1,2), in agreement with criterion 5a (see scheme in Table 3 for atom numbering). Note that in both cases at the end of the electron density reorganization, site 1 is nucleophilically activated.

Compounds **24**−**26** correspond to cyclic dienes, bearing carbon, oxygen, and nitrogen substitution at position 1. Compounds **24** and **25** show nucleophilic BFF activation at bond (3,4), compared to compound **26**, where the presence of a nitrogen atom deactivates this bond, probably due to the fact that in this compound the lone pair participates in the π system, thereby conferring an aromatic character to this molecule.

A final word is worth mentioning: the electrophilic BFF at sites (2,3) increases depending on the substitution pattern in complete agreement with criterion 6a. Note that for all cases presented in Tables 1−3, the definitions of electrophilic and nucleophilic BFF are consistently stable with respect to the computational methodology used.

A general scheme that summarizes the electron density reorganization for all cases considered here is depicted in Scheme 3. Note that the BFF formalism provides a quantitative justification to the curly arrow model to describe the reorganization of the electron density during the bond forming/bond breaking processes in an important set of reaction of π conjugated systems in organic chemistry.

SUMMARY OF APPROXIMATIONS AND LIMITATIONS OF THE MODEL

In this section, we derive our working equations 3 and 4 and present a summary of approximations made to define the electrophilic and nucleophilic BFF, emphasizing the limitations of the model.

First, let us point out that bond orders (BO) are not observable properties of the molecular systems. There exist several definitions for this quantity based on different schemes to perform the population analysis of a given system. Therefore,

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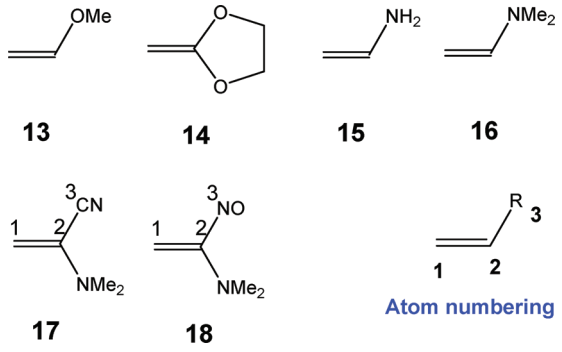
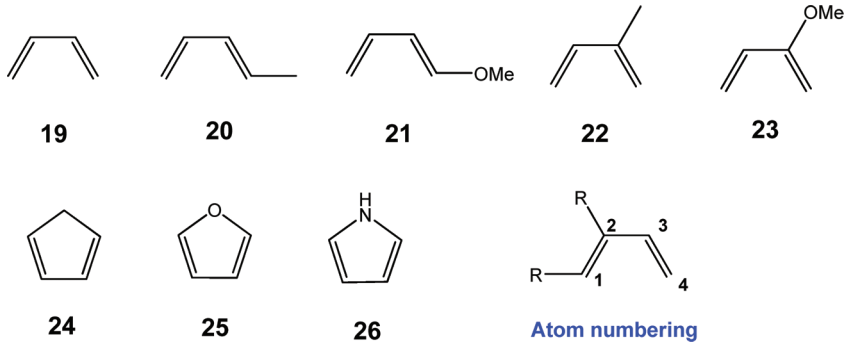
Table 2. Electrophilic and Nucleophilic BFF (f_{kl}^{+} and f_{kl}^{-}) and local Electrophilic and Nucleophilic Fukui Functions (f_r^{+} and f_r^{-}) at Site r for Compounds Bearing an Electron Releasing Substituent at Different Positions[a]



	f_{1-2}^{-}	f_{1-2}^{+}	f_{2-3}^{-}	f_{2-3}^{+}	site	f_r^{-}	f_r^{+}
13	**0.404 (0.357)**	−1.108 (−1.149)	−0.342 (−0.660)	−0.309 (−0.440)	1	**0.500 (0.468)**	0.422 (0.436)
14	**0.302 (0.316)**	−0.060 (−0.978)	−0.115 (−0.206)	−0.182 (−0.389)	1	**0.571 (0.554)**	0.001 (0.391)
15	**0.364 (0.340)**	−1.181 (−1.119)	−0.159 (−0.292)	0.655 (0.238)	1	**0.425 (0.472)**	0.362 (0.407)
16	**0.273 (0.170)**	−0.102 (−1.086)	−0.244 (−0.139)	−0.259 (0.209)	1	**0.492 (0.410)**	0.372 (0.399)
17	**0.158 (0.001)**	−0.393 (−0.665)	−0.339 (−0026)	−0.140 (−0.042)	1	**0.369 (0.018)**	0.382 (0.452)
18	**0.102 (0.073)**	−0.030 (−0.019)	−0.221 (−0.133)	−0.020 (−0.012)	1	**0.361 (0.307)**	0.215 (0.184)

[a]In parentheses are shown values calculated at the B3LYP/6-31G(d) level of theory.

Table 3. Electrophilic and Nucleophilic BFFs (f_{kl}^{+} and f_{kl}^{-}) and Local Electrophilic and Nucleophilic Fukui Functions (f_r^{+} and f_r^{-}) at Site r for Substituted Dienes[a]



	f_{1-2}^{-}	f_{1-2}^{+}	f_{2-3}^{-}	f_{2-3}^{+}	f_{3-4}^{-}	f_{3-4}^{+}	site	f_r^{-}	f_r^{+}
19	**0.174 (0.240)**	−0.186 (−0.449)	−0.265 (−0.177)	0.657 (0.303)	**0.557 (0.264)**	−1.518 (−0.414)	1	**0.298 (0.337)**	0.307 (0.331)
							4	**0.298 (0.337)**	0.307 (0.331)
20	**0.623 (0.483)**	−1.278 (−0.853)	−0.280 (−0.198)	0.669 (0.442)	**0.168 (0.145)**	−0.245 (−0.261)	1	**0.280 (0.295)**	0.300 (0.301)
							4	**0.288 (0.309)**	0.276 (0.321)
21	**0.260 (0.295)**	−0.157 (−0.358)	−0.323 (−0.236)	0.722 (0.477)	**0.468 (0282)**	−1.887 (−1.033)	1	**0.217 (0.203)**	0.323 (0.298)
							4	**0.250 (0.259)**	0.262 (0.313)
22	**0.216 (0.188)**	−0.338 (−0.266)	−0.112 (−0.091)	0.150 (0.174)	**0.056 (0.084)**	−0.108 (−0.185)	1	**0.356 (0.377)**	0.309 (0.291)
							4	**0.254 (0.274)**	0.266 (0.329)
23	**0.268 (0.158)**	−0.205 (−0.126)	−0.127 (−0.090)	0.158 (0.105)	**0.072 (0.077)**	−0.171 (−0.175)	1	**0.456 (0.438)**	0.363 (0.236)
							4	**0.172 (0.146)**	0.197 (0.370)
24	**0.301 (0.250)**	−0.549 (−0.429)	−0.252 (−0.166)	0.361 (0.310)	**0.321 (0.266)**	−0.522 (−0.409)	1	**0.322 (0.340)**	0.283 (0.292)
							4	**0.322 (0.340)**	0.283 (0.292)
25	**0.328 (0.259)**	−0.509 (−0.409)	−0.228 (−0.144)	0.293 (0.246)	**0.307 (0.242)**	−0.530 (−0.421)	1	**0.339 (0.359)**	0.334 (0.325)
							4	**0.339 (0.359)**	0.334 (0.325)
26	**0.156 (0.247)**	−0.344 (−0.377)	−0.156 (−0.150)	0.284 (0.176)	**0.347 (0.264)**	−0.567 (0.362)	1	**0.353 (0.369)**	0.331 (0.322)
							4	**0.353 (0.369)**	0.331 (0.322)

[a]In parentheses are shown values calculated at the B3LYP/6-31G(d) level of theory.

the BFF analysis will fail wherever the population analysis fails. In the present case, we have used a Mulliken-like population analysis and the results are qualitatively sound. A benchmark study including different levels of theory and a reasonable number of population analyses could probably help to establish some criteria about the most adequate method for calculating BO and the corresponding BFF. This aspect is however beyond the objectives defined for the present work.

Another potentially problematic aspect of the model is related to the discontinuity nature of the differentiated BO leading to the BFFs. We rely on the work reported by Balawender et al.[15] that provides a framework where the

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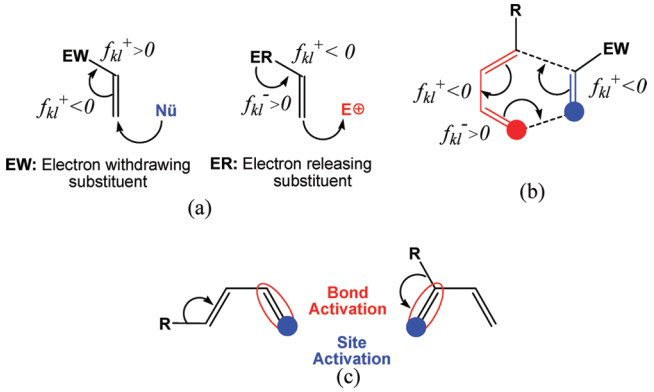
Scheme 3. Electron Density Reorganization for: Ethylene Derivatives (a), Cycloaddition Processes (b), and Butadiene Derivatives (c)



derivatives of the first-order density matrix can be obtained. It is based on a finite difference approach for the energy with respect to the number of electrons. Therein, the discontinuity of the derivatives of the functional $E_v[N]$, i.e., the derivatives of energy of the ground state system of a N electron system at constant external potential is transferred to the derivatives of the first-order density matrix as follows: write the total electronic energy of a N electron system as

$$E = \frac{1}{2}\sum_k \sum_l P_{kl}(H_{kl} + F_{kl}) \tag{7}$$

H_{kl} are matrix elements of the one electron operator representing the contributions of kinetic energy and electron−nuclei attractions. F_{kl} are the matrix elements including the classic electronic repulsion plus exchange contributions. P_{kl} are elements of the first-order reduced density matrix. Under the Hartree−Fock Roothan scheme, the problem of discontinuity of $E(N)$ function can be shifted to somewhat deeper level:[15]

$$\left(\frac{\partial E}{\partial N}\right)_v = \sum_{kl} \frac{\partial E}{\partial P_{kl}}\frac{\partial P_{kl}}{\partial N} = \sum_{kl} F_{kl}\left(\frac{\partial P_{kl}}{\partial N}\right)_v \tag{8}$$

Following this scheme, the right- and left-side derivatives of P_{kl} are obtained under Koopmans restriction as:[15]

$$\left(\frac{\partial P_{kl}}{\partial N}\right)_v^{+} = P_{kl}^{+} - P_{kl} = c_k^{\mathrm{LUMO}} c_l^{\mathrm{LUMO}} \tag{9}$$

$$\left(\frac{\partial P_{kl}}{\partial N}\right)_v^{-} = P_{kl}^{-} - P_{kl} = c_k^{\mathrm{HOMO}} c_l^{\mathrm{HOMO}} \tag{10}$$

respectively.

The last approximation is related to the fact that bond orders do not map directly into ground state energy. However, within the frozen core approximation used to derive the BFF using Balawender et al.[15] model, the finite difference involves the ground state of the systems with N, $(N + 1)$, and $(N - 1)$ electrons. The method used in this work is equivalent to the finite difference formula even though the calculations are performed as a single point calculation for the system with N electrons. The justification is as follows: the Fukui function can be obtained by differentiating $\rho(\mathbf{r}) = \mathrm{Tr}\mathbf{PS}$ with respect to the number of electrons N as follows:

$$f(r) = \left.\frac{\partial \rho(r)}{\partial N}\right|_{v(r)} = \sum_{\mu} \frac{\partial P_{\mu\mu}}{\partial N} + \sum_{\mu<\nu} \frac{\partial P_{\mu\nu}}{\partial N} \tag{11}$$

where $\mathbf{S}$ and $\mathbf{P}$ are the overlap and the first-order density matrix, respectively. In deriving the above equation, we have used that $[\partial S_{\mu\nu}/\partial N] = 0$ at constant external potential. Within Mülliken population analysis,[21] the bond order can be defined as

$$P_{kl} = \sum_{i}^{occ} c_{k,i} c_{l,i} \tag{12}$$

Taken a finite difference between $P_{kl}(N)$ and $P_{kl}(N - 1)$, we obtain the nucleophilic BFF as follows:

$$f_{kl}^{-} = P_{kl}(N) - P_{kl}(N-1) \tag{13}$$

$$\begin{aligned} f_{kl}^{-} &= \sum_{i}^{occ-1} c_{i,k} c_{l,j} + c_k^{\mathrm{HOMO}} c_l^{\mathrm{HOMO}} - \sum_{i}^{occ-1} c_{k,i} c_{l,i} \\ &= c_k^{\mathrm{HOMO}} c_l^{\mathrm{HOMO}} \end{aligned} \tag{14}$$

and for the electrophilic BFF, we use a finite difference between $P_{kl}(N + 1)$ and $P_{kl}(N)$

$$f_{kl}^{+} = P_{kl}(N+1) - P_{kl}(N) \tag{15}$$

$$\begin{aligned} f_{kl}^{+} &= \sum_{i}^{occ} c_{i,k} c_{l,j} + c_k^{\mathrm{LUMO}} c_l^{\mathrm{HOMO}} - \sum_{i}^{occ} c_{k,i} c_{l,i} \\ &= c_k^{\mathrm{LUMO}} c_l^{\mathrm{LUMO}} \end{aligned} \tag{16}$$

In eqs 14 and 16, k and l represents quantities condensed to atomic centers.[8]

By considering all the contributions of the atomic orbitals to each atomic center, we obtain for the electrophilic and nucleophilic BFF:

$$f_{kl}^{-} = \sum_{i} c_{i,k}^{\mathrm{HOMO}} \sum_{j} c_{j,l}^{\mathrm{HOMO}}$$

$$f_{kl}^{+} = \sum_{i} c_{i,k}^{\mathrm{LUMO}} \sum_{j} c_{j,l}^{\mathrm{LUMO}}$$

respectively, which are the working eqs 3 and 4 defined in the text. The above equations provide a simple scheme of calculation for the BFF, from a single-point calculation of the electronic structure, without resorting to additional calculations involving ionic species of different spin multiplicity.

The method described above can not completely raise the problem of the mapping of bond orders with ground states, and in this sense it has to be understood as an empirical approach that connects the GS of the system with N electrons with the corresponding GS of cation and anion.

■ CONCLUDING REMARKS

The bond Fukui function is introduced and tested as a new reactivity index capable of predicting the evolution of bond breaking and formation processes during a set of organic reactions. The model initially proposed to deal with the

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chemical reactivity and selectivity of conjugated π systems using semi-empirical methods is herein extended to an all electron model. As an illustration, we examine many cases where substituted ethylene and dienes may respond to different reagents to yield cycloaddition, Michael additions, and other additions to double bonds reaction. In general, the electron density reorganization scheme is described as charge transfer between bonds that ends in electrophilic or nucleophilic activation at an atomic site. The main result is that the BFF formalism gives a quantitative justification to the curly arrow model to describe the reorganization of the electron density during the bond forming/bond breaking processes in an important set of reaction of π conjugated systems in organic chemistry.

■ ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates, total energies, and number of imaginary frequencies NIMAG for the 26 optimized molecules in their ground state. Complete reference 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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