

Introducing “UCA-FUKUI” software: reactivity-index calculations

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Abstract A new software (UCA-FUKUI) has been developed to facilitate the theoretical study of chemical reactivity. This program can calculate global parameters like hardness, softness, philicities, and Fukui condensed functions, and also local parameters from the condensed functions. To facilitate access to the program we have developed a very easy-to-use interface. We have tested the performance of the software by calculating the global and local reactivity indexes of a group of representative molecules. Finite difference and frontier molecular orbital methods were compared and their correlation tested. Finally, we have extended the analysis to a set of ligands of importance in coordination chemistry, and the results are compared with the exact calculation. As a general trend, our study shows the existence of a high correlation between global parameters, but a weaker correlation between local parameters.

Keywords Fukui function · Hardness · Philicity · Softness · Electronic chemical potential

Introduction

The density functional theory (DFT) has proven to be very successful in understanding and developing the conceptual

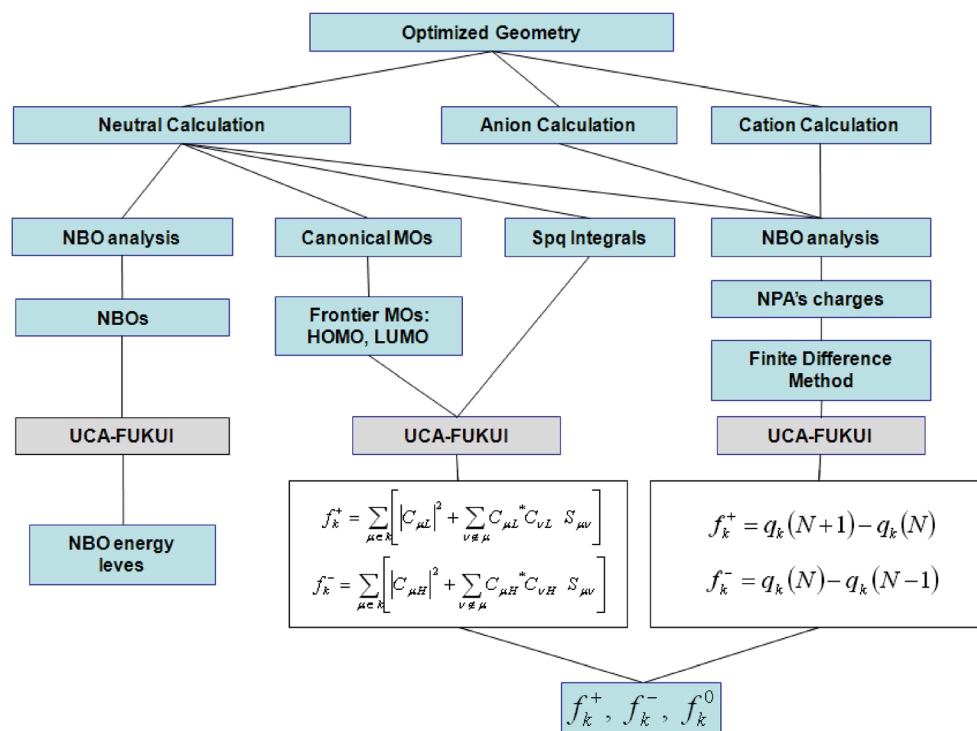
issues of chemical reactivity [1–6]. It gives the connection between the electronic chemical potential and Mulliken's electronegativity. Global hardness [7] has been identified as the derivative of the electronic chemical potential [8] with regard to the number of electrons. Local quantities like local softness and the Fukui function have also been developed. They have been very useful in the theoretical justification of the hard-soft acids-bases principle [9–14] and the principle of maximum hardness [15–23]. Global softness has been related to physically observable quantities such as dipole polarizability, as well as to other chemical concepts like molecular valency.

The interpretation and prediction of organic reactions are often complicated by the entanglement of electronic and steric effects amongst others. In 1963, Pearson [24] launched a unifying concept by which the chemical reactivities, selectivities, and stabilities of compounds could be readily rationalized. Chemical entities were categorized as "hard" and "soft" Lewis acids or bases. Complex stability, however, cannot be adequately estimated by considering only the hardness; additional parameters have to be introduced.

Condensed Fukui functions and the related local and global parameters are very useful to study chemical reactivity. Several reactivity studies [25–29] show the utility of this kind of theoretical descriptors. For this reason, we have developed a new software that can calculate this type of parameters of the reactive compounds in a chemical reaction. In turn, hardness, softness, philicities, electronic chemical potential, Fukui condensed functions and local parameters from the condensed functions can be obtained through the UCA-FUKUI software that we present in this study. The program has an easy-to-use interface. A graphical interface has been developed to facilitate program handling and to avoid errors. For example, starting the calculation is not permitted while any field in the window is empty (in this case a warning window will appear).

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Fig. 1 Scheme of the UCA-FUKUI code

Theoretical background

In 1999, the concept of the electrophilicity index (ω) was quantitatively introduced by Parr et al. [30–34] as the stabilization energy when atoms or molecules in their ground states acquire additional electronic charge from the environment.

At the second order, the energy change (ΔE) [35] due to the electron transfer (ΔN) satisfies Eq. 1:

$$\Delta E = \mu \Delta N + \frac{1}{2} \eta \Delta N^2, \quad (1)$$

where μ and η are the chemical potential (negative of the electronegativity) and chemical hardness, respectively defined by Eq. 2 and Eq. 3:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v \quad (2)$$

and

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_v, \quad (3)$$

with $v(r)$ as the external potential of the electrophile. Reference [36] shows how the H-K theorem is extended to fractional electron number (N) and in refs. [37, 38] the implications of derivative discontinuity for conceptual DFT are

explored. According to Mulliken [39–43], using a finite difference method, working equations for the calculation of μ and η may be given as:

$$\mu = -\frac{1}{2}(IP + EA) \quad (4)$$

and

$$\eta = (IP - EA), \quad (5)$$

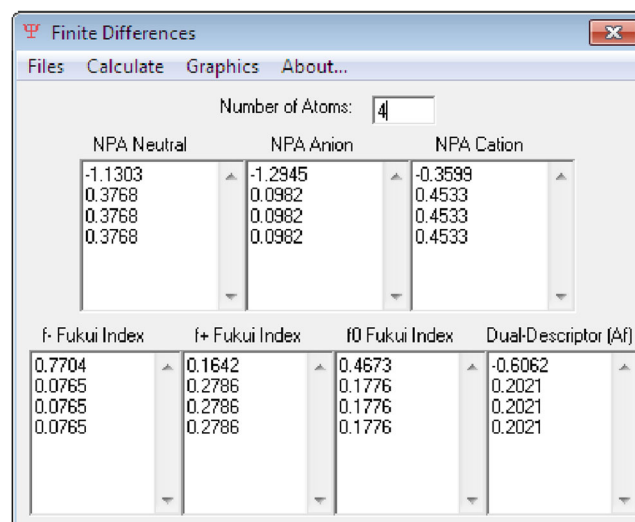
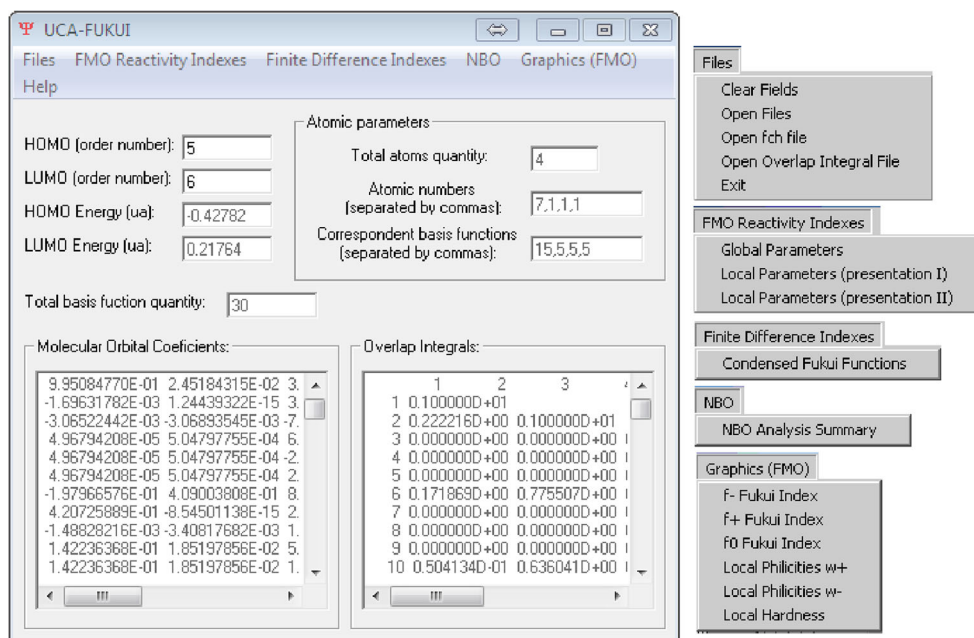
**Fig. 2** Finite difference window: NH₃ sample

Fig. 3 UCA-FUKUI main window, NH₃ sample

where IP and EA are the first ionization potential and electron affinity, respectively. According to, Janak's theorem [44] for DFT (and Koopmans' theorem [45] for Hartree-Fock), IP can be expressed in terms of the highest occupied molecular orbital (HOMO) energy, ϵ_H [46]. The HOMO-LUMO gap (E_g) is considered an excitation energy [47]. The fundamental band-gap for an N-electron system in an external potential $v(r)$, is given by: $E_g = (E_v(N-1) - E_v(N)) - (E_v(N) - E_v(N+1)) = IP - EA$ [48]. Thus,

$$\mu \approx \frac{1}{2}(\epsilon_L + \epsilon_H) \quad (6)$$

and

$$\eta \approx (\epsilon_L - \epsilon_H), \quad (7)$$

where ϵ_H and ϵ_L correspond to the Kohn-Sham [49] one-electron eigenvalues.

Table 1 NH₃ example to get the overlap integrals from Gaussian

#B3LYP/6-31G(d) iop(3/33=4) pop=full NH ₃ molecule example				
0	1			
N	0.000	0.000	0.130	
H	0.000	0.930	-0.290	
H	-0.810	-0.470	0.290	
H	0.810	-0.470	-0.290	

If the electrophile environment provides enough charge [36, 37], it will be become saturated with electrons according to Eq. 1:

$$\left(\frac{dE}{dN}\right) = 0, \quad (8)$$

leading to the maximum amount of electron charge

$$\Delta N_{\max} = -\frac{\mu}{\eta}, \quad (9)$$

and the total energy decrease

$$\Delta E_{\min} = -\frac{\mu^2}{2\eta}. \quad (10)$$

The new density functional theory (DFT) reactivity index, global electrophilicity index or electrophilicity index (ω) [50] is proposed as

$$\omega \equiv \frac{\mu^2}{2\eta}. \quad (11)$$

Table 2 Electronic potential, hardness, softness, and electrophilicity for the NH₃ example

Global parameters:	
Electronic potential (au):	-0.1051
Global hardness (au):	0.6455
Global softness (au):	1.5493
Electrophilicity (eV):	0.2328

Table 3 Condensed Fukui functions (electrophilic, nucleophilic, and radicalary attack), condensed dual-descriptor, local hardness, and local electrophilicities (electrophilic and nucleophilic attack) calculated for the NH₃ example

N	k	f ⁻	f ⁺	f ⁰	Dual-Descriptor	Hardness(au)	W ⁻ (eV)	W ⁺ (eV)
1	7	0.9559	0.5846	0.7703	-0.3713	0.5362	0.2225	0.1361
2	1	0.0147	0.1385	0.0766	0.1238	0.0364	0.0034	0.0322
3	1	0.0147	0.1385	0.0766	0.1238	0.0364	0.0034	0.0322
4	1	0.0147	0.1385	0.0766	0.1238	0.0364 </td <td>0.0034</td> <td>0.0322</td>	0.0034	0.0322

The electrophilicity index measures the stabilization energy when the system acquires an additional electronic charge $\Delta N_{max} = -\mu/\eta$ from the environment, in terms of the electronic chemical potential μ and the chemical hardness η .

The electrophilicity index encompasses both the propensity of the electrophile to acquire an additional electronic charge driven by μ^2 (the square of electronegativity) and the resistance of the system to exchange electronic charge with the environment described by η . A good electrophile is, in this sense, characterized by a high value of μ and a low value of η .

A previous study [51] presented a good linear correlation between the electrophilicity values obtained from the computed IPs and EAs of ethylene derivatives and those obtained from the HOMO and LUMO energies. The results from this study [51] allow us to confirm the use of accessible B3LYP/6-31G* HOMO and LUMO energies, ϵ_H and ϵ_L , to obtain reasonable values for the global electrophilicity index of organic molecules, and thus make valuable electrophilicity scales.

Local reactivity descriptors: local parameters

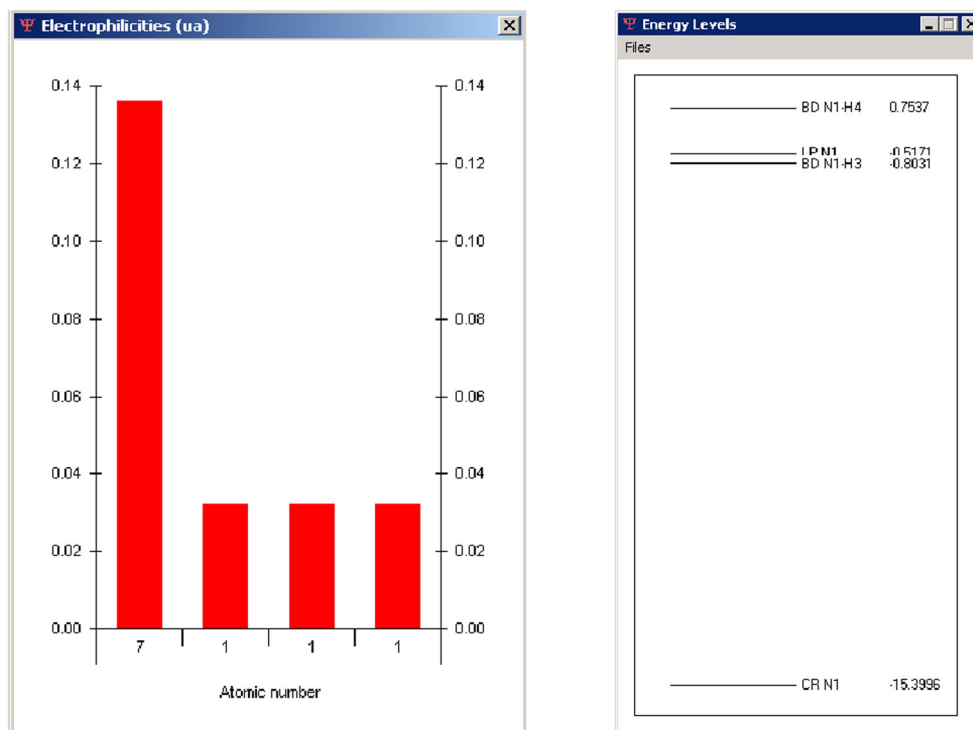
To understand detailed reaction mechanisms such as regioselectivity, apart from global properties, local reactivity parameters are necessary to differentiate the reactive behaviour of atoms forming a molecule. The Fukui function [52–54] ($f(r)$) and local softness [55, 56] ($s(r)$) are two of the most commonly used local reactivity parameters (Eq. 12).

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_\nu \quad (12)$$

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu} \right)_\nu = \left(\frac{\partial \rho(r)}{\partial N} \right)_\nu \cdot \left(\frac{\partial N}{\partial \mu} \right)_\nu = S \cdot f(r)$$

The Fukui function is primarily associated with the response of the density function of a system to a change in the number of electrons (N) under the constraint of a constant external potential [$v(r)$]. The Fukui function also represents

Fig. 4 (left) Local philicities (w^+) for the NH₃ molecule. (right) NBO energies for the NH₃ molecule



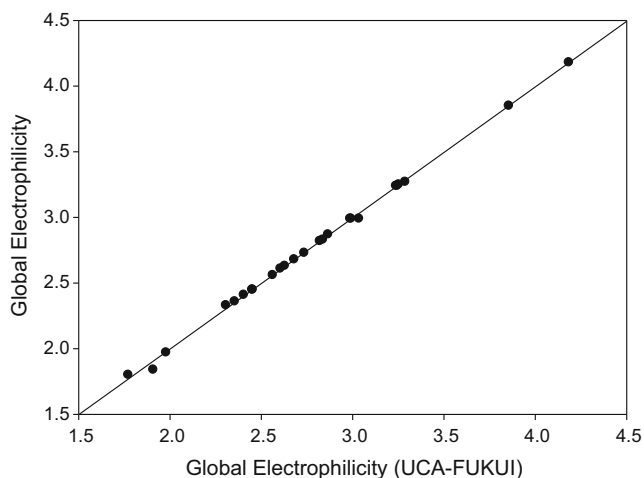


Fig. 5 Global electrophilicities vs the ones calculated by UCA-FUKUI

the response of the chemical potential of a system to a change in external potential. As the chemical potential is a measure of the intrinsic acidic or base strength [13], and local softness incorporates global reactivity, both parameters provide us a pair of indices to demonstrate, for example, the specific sites of interaction between two reagents.

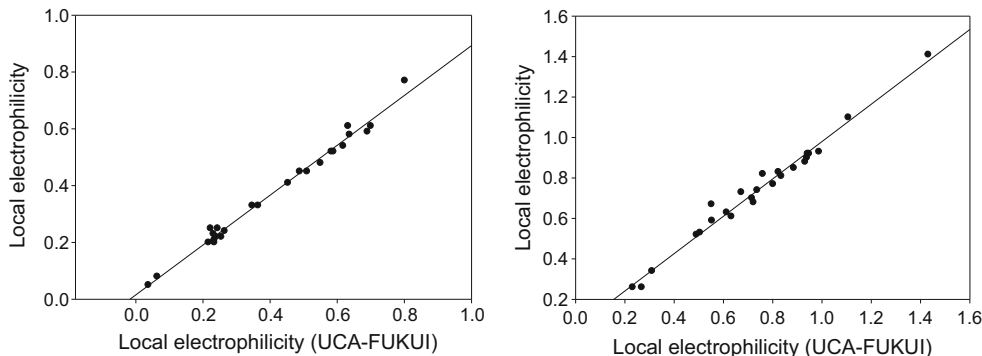
Due to the discontinuity of the electron density with respect to N , finite difference approximation leads to three types of Fukui function for a system, namely $f^+(r)$ (Eq. 13), $f^-(r)$ (Eq. 14) and $f^0(r)$ (Eq. 15) for nucleophilic, electrophilic and radical attack, respectively. $f^+(r)$ is measured by the electron density change following addition of an electron, and $f^-(r)$ by the electron density change upon removal of an electron. $f^0(r)$ is approximated as the average of both previous terms. They are defined as follows:

$$f^+(r) = \rho_{N_0+1}(r) - \rho_{N_0}(r), \text{ for nucleophilic attack, } (13)$$

$$f^-(r) = \rho_{N_0}(r) - \rho_{N_0-1}(r), \text{ for electrophilic attack, } (14)$$

$$f^0(r) = \frac{1}{2}(\rho_{N_0+1}(r) - \rho_{N_0-1}(r)), \text{ for neutral (or radical) attack. } (15)$$

Fig. 6 Local electrophilicities for the alpha (left) and beta (right) carbons vs. the one calculated by UCA-FUKUI



In references [57] and [58] is proposed a new index (Dual Descriptor) of selectivity toward nucleophilic attack, but it can also be used to characterize an electrophilic attack. It is defined as

$$\Delta f(r) = [f^+(r) - f^-(r)] (16)$$

If $\Delta f(r) > 0$, then the site is favored for a nucleophilic attack, whereas if $\Delta f(r) < 0$, then the site could hardly be susceptible to undertake a nucleophilic attack but it may be favored for an electrophilic attack.

Because Fukui functions are positive ($0 \leq f(r) \leq 1$), $-1 \leq \Delta f(r) \leq 1$ and the normalization condition for $\Delta f(r)$ is

$$\int \Delta f(r) dr = 0 (17)$$

On the basis of these results, it is clear that numerical values of $\Delta f(r)$ are defined within the range $\{-1; 1\}$. This is an advantage with respect to other reactivity indexes that may present large values, thus leading to hard-to-interpret results. Reference [59] shows a complete comparison between two local-evaluation common methods (finite difference linearization and Koopmans approximation) and also studies two atomic condensations schemes (Hirshfeld's and Bader's partitions)

A common simplification of the Fukui function [60] is to condense its values to individual atoms in the molecule. That is, through the use of a particular population analysis, one can determine the number of electrons associated with every atom in the molecule. The condensed Fukui function is then determined through a finite differences approach, so that for the k th atom in the molecule one has that

$$f_k^- = q_k(N_0) - q_k(N_0 - 1), \text{ for electrophilic attack, } (18)$$

$$f_k^+ = q_k(N_0 + 1) - q_k(N_0), \text{ for nucleophilic attack, } (19)$$

$$f_k^0 = \frac{1}{2}(f_k^+ + f_k^-), \text{ for neutral (or radical) attack. } (20)$$

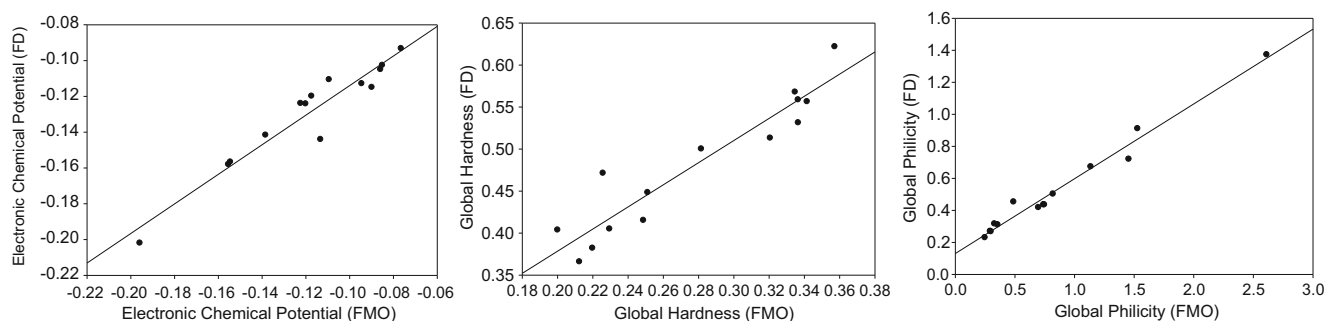


Fig. 7 a Global electronic chemical potential (ua) b global hardness (ua) c global philicity (eV), calculated with FD method vs. calculated with FMO

In these relationships, $q_k(N_0-1)$, $q_k(N_0)$, and $q_k(N_0+1)$ are the number of electrons associated with the k^{th} atom in the molecule, when the total number of electrons in the molecule is N_0-1 , N_0 , and N_0+1 electrons, respectively. The calculation of the N_0-1 and N_0+1 electron systems is done at the ground-state geometry of the N_0 electron system.

Local parameters: frontier molecular orbital method

Equation 12 was used to develop another condensed form of the Fukui function that can be approximately defined as:

$$f^-(r) = \rho_{HOMO}(r), \text{ for electrophilic attack,} \quad (21)$$

$$f^+(r) = \rho_{LUMO}(r), \text{ for nucleophilic attack,} \quad (22)$$

$$f^0(r) = \frac{1}{2}(\rho_{LUMO}(r) - \rho_{HOMO}(r)), \text{ for neutral (or radical) attack.} \quad (23)$$

Under frozen orbital approximation (FOA) of Fukui and neglecting the second-order variations in the electron density, the Fukui function can be approximated as:

$$f^\alpha(r) \approx |\phi^\alpha(r)|^2, \quad (24)$$

where $\phi^\alpha(r)$ is a particular frontier molecular orbital (FMO) chosen depending upon the value of $\alpha=+$ or $\alpha=-$. Expanding the FMO in terms of the atomic basis functions, the condensed Fukui function at the atom k is:

$$f_k^\alpha = \sum_{\nu \in k} \left[|C_{\nu\alpha}|^2 + \sum_{\chi \notin \mu} C_{\chi\alpha}^* C_{\nu\alpha} S_{\chi\nu} \right] \quad (25)$$

$$f_k^- = \sum_{\nu \in k} \left[|C_{\nu H}|^2 + \sum_{\chi \notin \nu} C_{\chi H}^* C_{\nu H} S_{\chi\nu} \right] \text{ (electrophilic attack)} \quad (26)$$

Fig. 8 Condensed Fukui function (f^-) calculated with FD method vs. calculated with FMO method

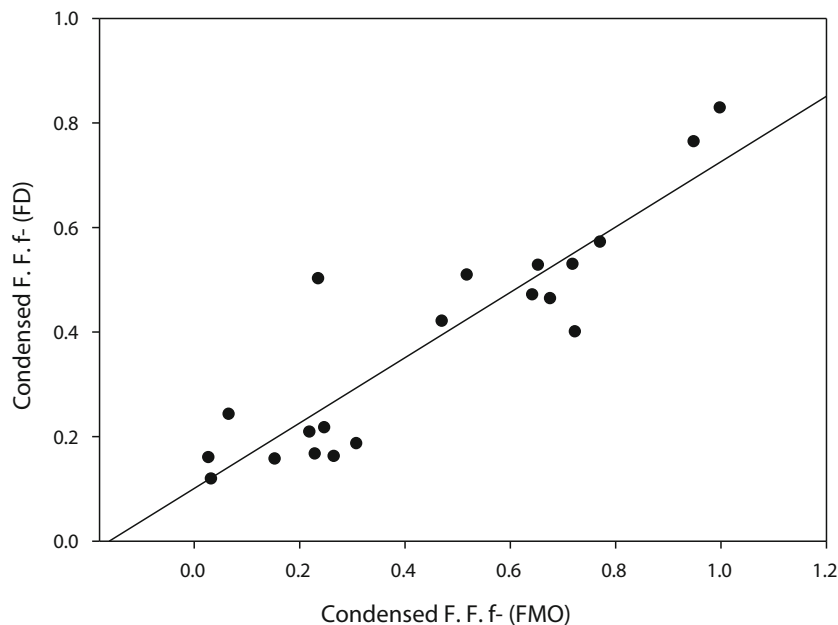
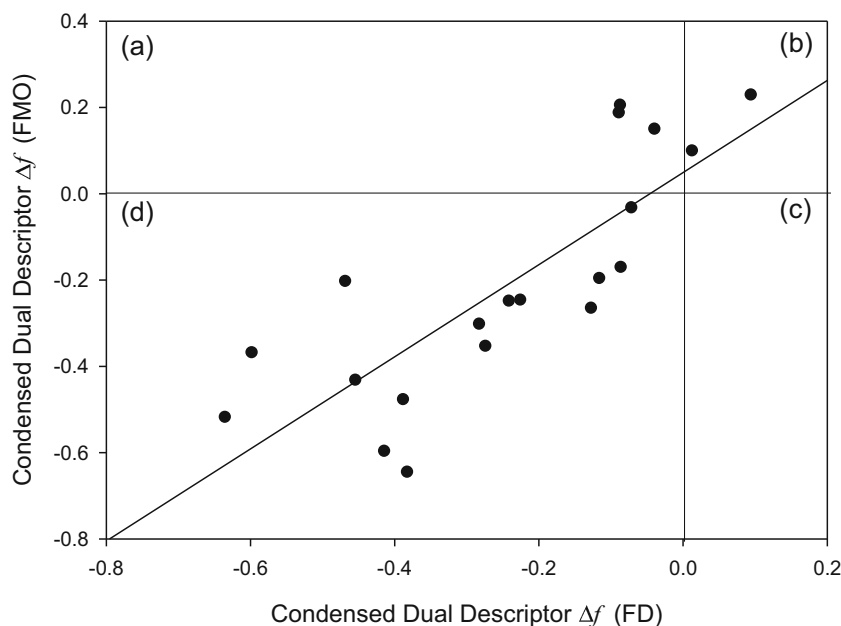


Fig. 9 Condensed dual descriptor (Δf^-) calculated with FMO method vs. calculated with FD method



$$f_k^+ = \sum_{\nu \in k} \left[|C_{\nu L}|^2 + \sum_{\chi \in \nu} C_{\chi L}^* C_{\nu L} S_{\chi \nu} \right] \text{ (nucleophilic attack)} \quad (27)$$

$$f_k^0 = \frac{1}{2} (f_k^+ + f_k^-) \text{ (radicalary attack)}, \quad (28)$$

where $C_{\nu\alpha}$ are the molecular frontier orbital coefficients, and $S_{\chi\nu}$ are the atomic orbital overlap matrix elements. The sub-indexes “H” and “L” are referenced to the HOMO and LUMO orbitals. This definition of the condensed Fukui function (Eqs. 25–28) has been used in a variety of studies yielding reliable results [61–63] but it has been severely criticized by Joubert [59].

Once the Fukui function is evaluated following a particular scheme, condensed-to-atom softness can easily be evaluated from Eq. 12 as Eq. 29,

$$s_k^\alpha = S f_k^\alpha (\alpha = +, - \text{ or } 0), \quad (29)$$

the corresponding condensed-to-atom philicity index [64] can be expressed as Eq. 30:

$$w_k^\alpha = w f_k^\alpha (\alpha = +, - \text{ or } 0), \quad (30)$$

and finally, local hardness [65–67] has been defined as Eq. 31. This definition is less conventional than the Berkowitz concept [68] but it is very useful.

$$\eta_k = \epsilon_L f_k^+ - \epsilon_H f_k^- \quad (31)$$

UCA-FUKUI package. Programming details

Figure 1 shows the scheme of the UCA-FUKUI code. It can calculate many parameters like hardness, softness and philicities. It can also calculate the Fukui condensed functions and estimate the local parameters obtained with them. Moreover, the program can read natural bond orbitals from a Gaussian analysis (Gaussian03 [69] or 09 [70]) and can display the NBOs energy levels in a graphical interface as a helpful tool in a reactivity study.

For UCA-FUKUI (http://www2.uca.es/dept/quimica_fisica/software/UCA-FUKUI.zip), the electronic charges ($q_k(i)$) from Eqs. 18 and 19 are the natural population atomic (NPA) charges obtained from a natural bond orbital (NBO) analysis [71]. It is necessary to select "finite difference

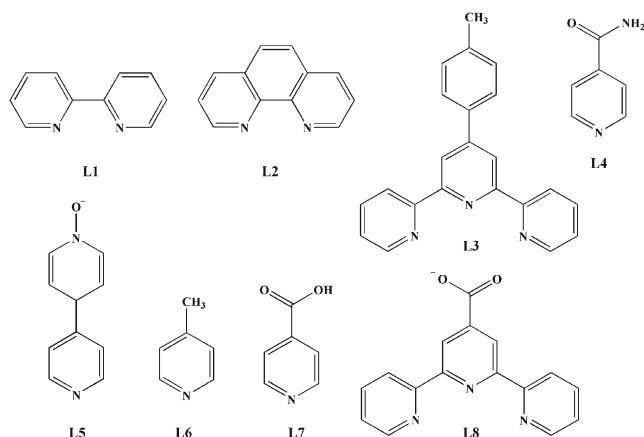
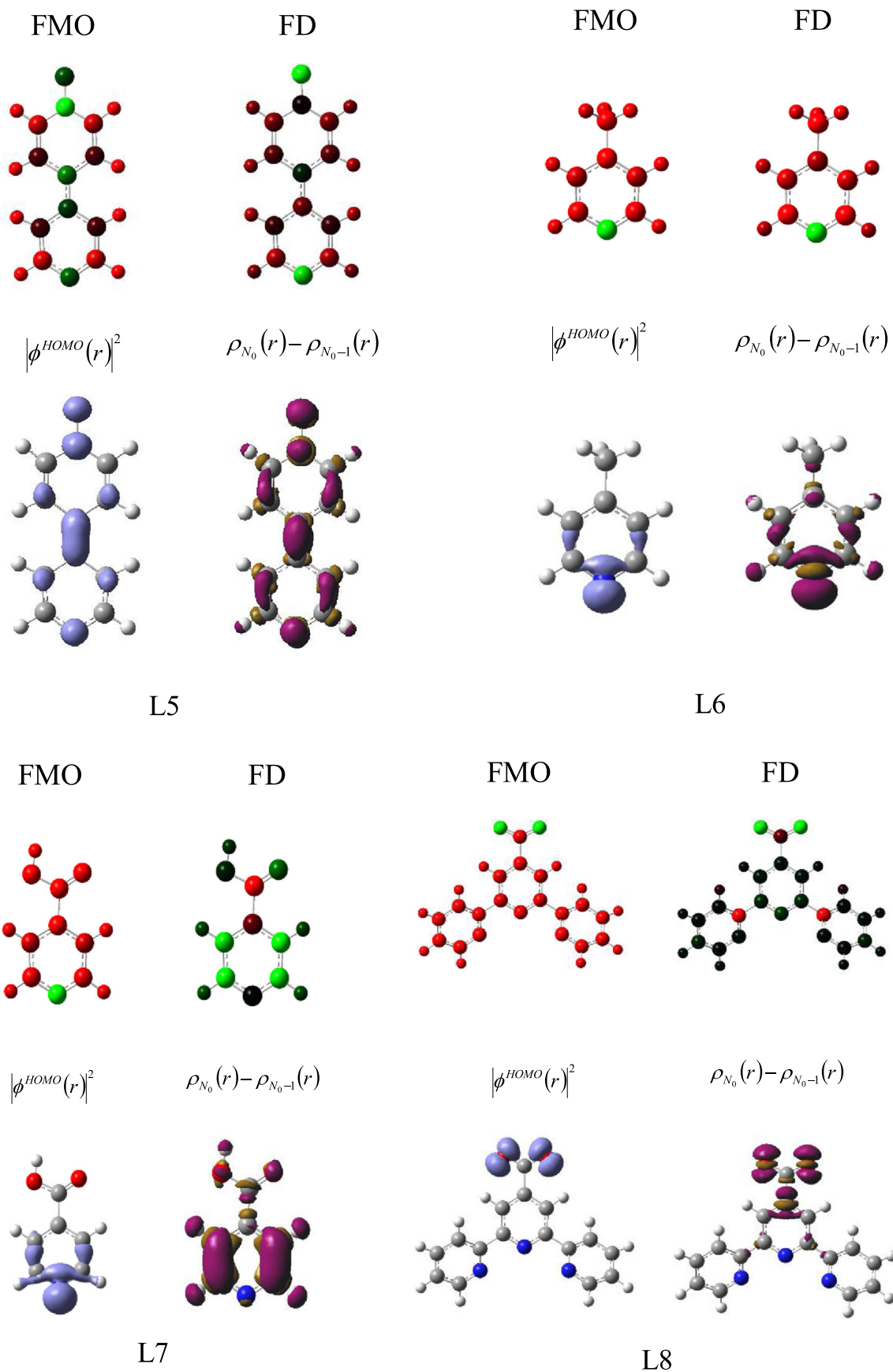


Fig. 10 Dyes type ligands. L1–4 and L6–7 are neutral, L5 and L8 have charge –1



◀ **Fig. 11** Local Fukui function f^- calculated for the L1, L4, L5, and L7 ligands with the methods: frontier molecular orbital (FMO) method (Eq. 24), finite difference (FD) (Eq. 16), frozen orbital approximation of Fukui (Eq. 22), and exactly calculated (Eq. 13)

indexes/condensed Fukui functions" in the main menu to obtain a window (Fig. 2) that allows us to calculate the Fukui functions. This window can read the NPA charges from a Gaussian file (*.log or *.out). When the "calculate/all indexes" option is selected, the program calculates the condensed Fukui functions (f^- , f^+ and f^0), and displays a result window like in Fig. 2; as an example, we show the results for NH_3 .

Program handling

The software needs two Gaussian files to run. Figure 3 depicts the window where the files must be loaded ("files/open fch file" and "files/open overlap integral file"). One is a "*.fch" (formatted chk) single point calculation file and the other one is a "*.out" or "*.log" result file with all the overlap integrals. The file order is not important. Also, the program has been developed to work with Linux or Windows *.fch and *.out (*.log) Gaussian files.

The keywords to get Gaussian overlap integrals are shown in Table 1 for the NH_3 molecule.

The program generates three types of result files. The "calculate" menu shows the type of results that can be obtained.

In Table 2 we can see the global parameters: electronic potential, hardness, softness, and electrophilicity calculated with UCA-FUKUI for the previous example (NH_3).

In Table 3 we can see the local parameters: condensed Fukui functions (electrophilic, nucleophilic, and radicalary attack), local hardness, and local electrophilicities (electrophilic and nucleophilic attack) calculated for the NH_3 molecule.

The program can draw graphical representations of the calculated parameters by selecting "graphics" in the main window and then choosing the graph type. For example, Fig. 4 (left) shows a graphical representation of local philicity (w^+) for the four atoms of the NH_3 molecule. Also, the results of an NBO analysis (obtained with Gaussian) can be used to generate another graph type. Figure 4 (right) shows an NBO energy diagram corresponding to the NH_3 molecule.

Computational details

All the structures included in this study were optimized at the B3LYP/6-31G(d) level of theory using the Gaussian09 package [70]. The UCA-FUKUI software needs the MO

coefficients and the overlap integrals that are calculated by the Gaussian program. The electrophilic Fukui function is evaluated from a single point calculation in terms of the molecular orbital coefficients and the overlap matrix. Local electrophilicity values are obtained from the global electrophilicity index (Eq. 11) and the electrophilic Fukui function (Eq. 25).

Results and discussion

To test the correct performance of the software, we have repeated the calculations of the global electrophilicities (Eq. 11) and local electrophilicities (Eq. 25) for the first 25 molecules from the work of Domingo et al. on the reactivity of the carbon-carbon double bond toward nucleophilic additions [72].

Figure 5 shows a good correlation between the two sets of global electrophilicities. The correlation coefficient (R^2) is 0.999. We have chosen this parameter because it depends on the electronic chemical potential μ and the chemical hardness η as we can see in Eq. 11, and in this way we get a very significant test.

Figure 6 shows the local electrophilicities of the alpha and beta carbons from reference [72] vs. the one calculated by the UCA-FUKUI program. The alpha carbon linear regression has a correlation coefficient (R^2) of 0.988, while for the beta carbon it is 0.980. The results of the UCA-FUKUI are completely satisfactory, and the minor difference between the two sets may be due to the fact that the original results were obtained by using Gaussian 98 [73] and the new results with Gaussian 09.

Finite differences and frontier molecular orbital: comparison in a set of representative molecules

The molecule set used to compare the finite differences with the frontier molecular orbital methods is: H_2O , NH_3 , CH_2O , CH_3OH , $\text{C}_5\text{H}_5\text{N}$, $\text{C}_6\text{H}_5\text{OH}$, $\text{C}_6\text{H}_5\text{COOH}$, CH_2CHF , CH_3NHOH , CH_2CHNO_2 , $\text{NH}_2\text{CH}_2\text{COOH}$, NH_2OCH_3 and NH_2OH .

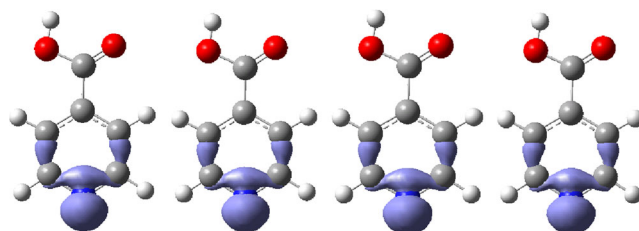


Fig. 12 $|\phi^{HOMO}(r)|^2$ with the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), cc-pVDZ basis sets.

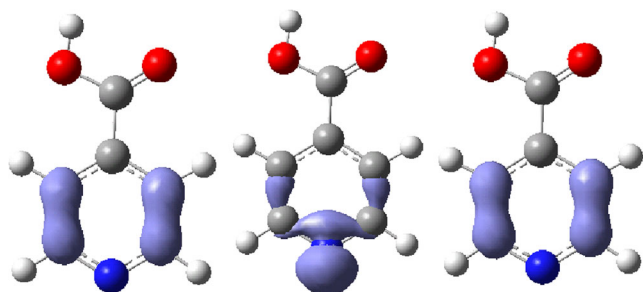


Fig. 13 $|\phi^{HOMO}(r)|^2$ with the HF, B3LYP, CAM-B3LYP methods

Finite differences and frontier molecular orbital: global parameters comparison

Figure 7 shows a good correlation between the global parameters calculated by the finite difference and frontier molecular orbital methods. In the case of the philicity, the correlation coefficient (R^2) is 0.977.

Finite differences and frontier molecular orbital: local parameters comparison

Figure 8 shows the condensed Fukui function (f^-) calculated with the finite difference method and the frontier molecular orbital (FMO) method. In this case, the correlation between the two methods is smaller than in the global parameters case, the correlation coefficient being 0.811. As noted by Bultick [74] different approaches to atom condensed Fukui functions can provide too different values. Concerning the dual descriptor (Fig. 9), correlation coefficient between FD and FMO drop to 0.16 and FMO values are greater than FD ones. Figure 9 also shows chemical content while considering the quadrants formed by the axes. Since both 'a' and 'c' quadrants correspond to dual descriptor values of opposite signs, the points lying in these zones correspond to cases where the two approximations predict contradictory chemical reactive tendency ($\Delta f > 0$ predominantly electrophilic, $\Delta f < 0$ predominantly nucleophilic). Of the considered atomic sites 15 % are located

within those quadrants, thus supporting the claim that FMO approximation deviates significantly from FD ones.

Comparison between the finite differences and frontier molecular orbital methods in a ligand set

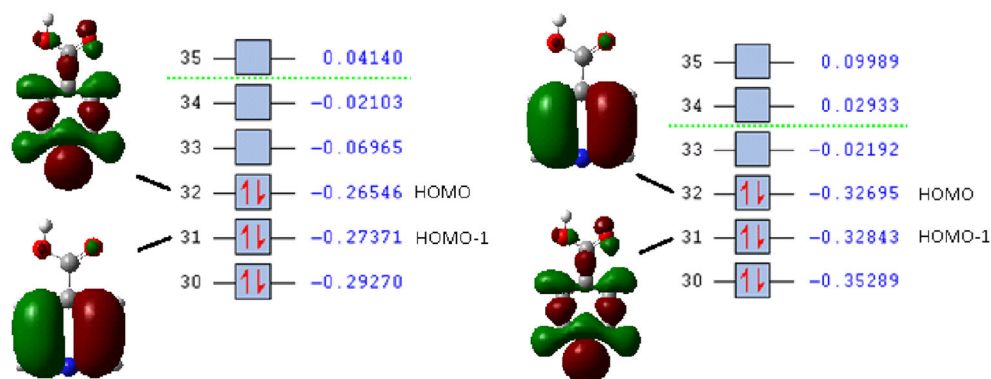
We studied nucleophilicity, by means of the condensed Fukui function (electrophilic attack, f^-), in a ligand set (Fig. 10). We performed this analysis to check the previously obtained results, but in a more complex molecule sample. The exact condensed Fukui function (Eq. 13) was also calculated (with the same method and base), as a reference.

The selected ligands belong to dye sensitized solar cell coordination complexes and they are molecules with a great nucleophilic character. The L1 ligand belongs to the ACIDIA [75], ACAYUZ [76], ACAYOT [76], ABUWID [77], ABUWAD [78], HUWLUH [79], and PEKSAA [80] complexes; the L2 to ACODEB [81]; the L3 to ACIDIA [75]; the L4 to GOKMOI [82]; the L5 to AFARAB [83] and AFAREF [83]; the L6 to GAGMOS [84]; the L7 to GAGMOS [85]; and L8 to EFEKIK [85] and XIMWUM [86]. The nomenclature of the complexes was taken from the Cambridge Crystallographic Data Centre (CCPC) (<http://www.ccdc.cam.ac.uk/pages/Home.aspx>).

Figure 11 shows representations of the condensed Fukui function (f^-) for L1, L4, L5, and L7 (Fig. S1 shows representations for all the ligands). The f^- values are represented by colors. The smaller values are colored in red, the intermediate ones in black, and the high ones in green. In Fig. 11 four representations of f^- can be compared:

- (I) Calculated with the frontier molecular orbital method (Eq. 26). Figure S2 shows a complementary representation of these values,
- (II) Finite difference method (Eq. 18),
- (III) Frozen orbital approximation (FOA) of Fukui (Eq. 24),
- (IV) Exactly calculated (Eq. 14). The electronic densities were normalized to the appropriate number of electrons

Fig. 14 Energy levels with B3LYP (left) and CAM-B3LYP (right)



before their subtraction. The brown color represents negative values for f^- [87].

The topological analysis of the Fukui function (III and IV) presents an alternative to the analysis of the Fukui function [88]. The four kinds of representations (Fig. 11) have been plotted by using the GaussView program [89].

In most of the cases the tendencies are similar (Fig. 11), but there are important exceptions (L7) that we will discuss in the next section. The interpretation of the exact condensed Fukui function is very complicated, but the other representation of f^- (FD) helps in the interpretation. It is important to have all the graphics, as this makes the information easier to understand.

Method and basis set dependence

Next, regarding the reactivity index calculation, several combinations of methods and basis sets were studied. We used the L7 ligand to carry out this study because it was the only one where we found significant differences between the frontier molecular orbital and finite difference methods.

The “methods/basis sets” used in this study were B3LYP with the basis sets 6-31G(d) [90, 91], 6-31G(d,p) [92], 6-31+G(d,p) [93], and cc-pVDZ [94]. Otherwise we have compared the methods HF [95], B3LYP [96], CAM-B3LYP [97] using the 6-31G(d) basis set. For all the calculations we used the B3LYP/6-31G(d) optimized geometry.

Figure 12 shows that the change of basis set did not significantly affect the results. With regard to the method, Fig. 13 shows that the B3LYP results are clearly different to the other two methods; in this case, we find a strong dependence on the method. Figure 14 shows the orbital energy levels calculated with B3LYP and with CAM-B3LYP; in the right figure (CAM-B3LYP) the HOMO and HOMO-1 orbitals have similar energy (-0.32695 and -0.32843), which leads us to believe that small changes in the functional could lead to exchanges in the energy levels, which is an important matter to bear in mind when we calculate the reactivity indexes.

Conclusions

The UCA-FUKUI software, which calculates the most standard chemical reactivity parameters, was developed. It can calculate global hardness, softness, philicity, condensed Fukui functions and their related parameters (local hardness and local philicities). The program results were tested on a reasonable number of molecules and its correct behavior was proven.

To show the usefulness of the software, it was applied to compare the finite difference and frontier molecular orbital methods for a molecule sample. The study shows a high correlation between global parameters and a weaker

correlation between local parameters. The nucleophilicity in a ligand set was also studied to check previously obtained results and we found that the results were similar.

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