

Symmetry Conservation in Fukui Functions

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Received May 18, 2009

Abstract: The problem of symmetry breaking in the evaluation of Fukui functions is addressed. It is also demonstrated that a reliable solution of the problem can be achieved using analytic methods. An automatic method that avoids occurrence of symmetry breaks has been implemented in a computer code and is described here. Negative regions of the Fukui function are shown to play a key role for the interpretation of reactivity. Example plots are presented for diatomic molecules, inorganic molecules, conjugated systems, and molecular cages. The potentiality of the Fukui functions as molecular scalar fields for prediction and analysis of regioselectivity is enhanced. Its advantages with respect to the use of condensed Fukui functions are discussed.

1. Introduction

Inspired by the pioneering works on molecular reactivity of Fukui,^{1–3} Parr and Yang^{4–6} have proposed an intrinsic local reactivity descriptor which they named the Fukui function⁴ and defined it as the derivative of the molecular density with respect to the total number of electrons for a given external potential. This descriptor can be used to predict regioselectivity. Both nucleophilic and electrophilic molecular regions can be predicted.^{7–10} It can also be used to do comparative studies of acidity or basicity.¹¹ Furthermore, the Fukui function plays a central role in the development and application of chemical reactivity theory.^{6,8,12–16}

There are two principal ways in which the Fukui function has been used to predict regioselectivity. One may use the Fukui function itself or find molecular regions with nucleophilic and electrophilic character with the condensed Fukui functions.¹⁷ The latter approach has the advantage of predicting reactive atomic centers. However, this coarse-grained approach also presents a number of disadvantages starting from the arbitrariness of the condensation procedures.¹⁸ In addition, it hides information related to off-atom regions.

The purpose of this contribution is to address a problem in the evaluation and interpretation of Fukui functions of symmetric molecules: the breaking of symmetry. Once this problem is solved, plotting the Fukui functions emerges as the method of choice for analysis of regioselectivity instead of calculation of condensed Fukui function values. In fact, the extensive use of the condensed values^{19–21} is one of the main reasons for the prevalence of the symmetry-breaking problem. Condensation hides this problem for many common systems.

This problem is very severe because it implies a violation of space symmetry. In the literature there are reports with erroneous Fukui function plots.^{22,23} Probably because this problem is only relevant to systems with degenerate frontier orbitals (vide infra), many researchers have not paid attention to its occurrence. However, the problem occurs in the very important family of aromatic hydrocarbons which, by satisfying Hückel's $4n + 2$ rule, have degeneracies in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Combination of efficient analytic methods with the results of the analysis presented here yield reliable molecular graphs of Fukui functions.

The paper is organized as follows. In section 2 the most widely used methods for the evaluation of Fukui functions are outlined and compared to the analytic formula. In section 3, the symmetry conservation problem is described

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and its solution is discussed. Application to a number of molecules is presented in section 4. Final remarks are given in section 5.

2. Methods for Evaluation of Fukui Functions

The following discussion is restricted to the Kohn–Sham approximation²⁴ of density functional theory (DFT),^{6,25} but many of the observations and conclusions are applicable to other methods. A nondegenerate state is assumed. For degenerate ground states, extra corrections are required.²⁶

The Fukui function, $f^\pm(\mathbf{r})$, is defined as the derivative of the density, $\rho(\mathbf{r})$, with respect to the total number of electrons, N , under a constant potential, $v(\mathbf{r})$:

$$f^\pm(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v^\pm \quad (1)$$

The superscript signs are used to label left, $-$, and right, $+$, side derivatives. There are alternative (but equivalent for nondegenerate states²⁶) definitions of the Fukui function.^{27,28} Within the Kohn–Sham approximation of DFT, the density is given by a fictitious noninteracting system

$$\rho(\mathbf{r}) = \sum_i n_i |\psi_i(\mathbf{r})|^2 \quad (2)$$

Here, $\psi_i(\mathbf{r})$ denotes the i th molecular orbital and n_i is its occupation number. Assuming that the electronic density is well-defined and its one-sided derivatives with respect to N exist, the Fukui function can be evaluated by^{5,29–31}

$$f^\pm(\mathbf{r}) = \sum_i \left(\frac{\partial n_i}{\partial N} \right)_v^\pm |\psi_i(\mathbf{r})|^2 + \sum_i n_i \left(\frac{\partial |\psi_i(\mathbf{r})|^2}{\partial N} \right)_v^\pm \quad (3)$$

Equation 3 is the exact formula for the evaluation of the Fukui function. The first term on the right-hand side accounts for the location from which the electrons are removed. The second sum collects contributions from the relaxation of orbitals. Equation 3 can be evaluated using perturbation theory.^{32,33} In general it is assumed that electrons would leave from the HOMO and not from other orbitals. Justification for this assumption can be obtained by considering an ensemble of ionic states with different energies depending on whence electrons are removed or added in the neutral system. For the case where electrons are removed (left derivative), the highest population of these states in general corresponds to the state where electrons were removed from the HOMO because it is the orbital with the lowest energy. In an analogous way, occupation of the LUMO leads to an ensemble of anionic states. Population of other states is very low. For zero temperature, all other states with higher energy are empty. Therefore

$$\left(\frac{\partial n_i}{\partial N} \right)^- = \begin{cases} 1 & \text{if } i = \text{HOMO} \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

$$\left(\frac{\partial n_i}{\partial N} \right)^+ = \begin{cases} 1 & \text{if } i = \text{LUMO} \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

In the frontier approximation, the relaxation of orbitals is neglected. This is equivalent to assuming that second sum

in eq 3 vanishes. Thus, the left frontier Fukui function, $f_F^-(\mathbf{r})$, is given by³⁴

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

Another, frequently used method for the evaluation of Fukui functions evaluates densities of the system with N electrons and the system with $N - 1$ electrons and approximates the Fukui function by their difference, $f_D^-(\mathbf{r})$:

$$f^-(\mathbf{r}) \approx f_D^-(\mathbf{r}) \equiv \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \quad (7)$$

Equation 7 includes relaxation contributions in the evaluation of Fukui functions but also includes numerical errors and technical difficulties.³³ At 0 K, eq 7 is an exact formula²² for the evaluation of $f^-(\mathbf{r})$ if the exact density is used. Our analytical results³³ and numerical calculations with fractional charge^{21,33,35} yield different values because the exchange–correlation functional used in the calculations is not the exact one and, therefore, the density is not exact. Furthermore, incompleteness of the basis sets used leads to an unbalanced treatment of ionic species, especially anions. One feature of analytic methods is that they yield results consistent with the approximate nature of the functional employed. For the exact functional, the analytic result is also the exact one. Whereas for approximate functionals analytic results are consistent, eq 7 presents errors that disappear only with the exact functional. This motivates us to pursue the use of analytic methods.

3. Symmetry Conservation

There have been publications related to the interpretation and application of Fukui functions where the reported graphs present an artificial symmetry breaking.^{22,23} Those and our own previous results have motivated the following analysis. In this section, the particular cases of methane (CH_4), acetylene (HCCH), benzene (C_6H_6), and cubane (C_8H_8) are analyzed. This set includes linear, planar, and three-dimensional systems.

In many systems, HOMO and LUMO degeneracy appears as a consequence of symmetry. If only one of the frontier orbitals is considered for the removal or addition of electrons, then a symmetry break occurs in the corresponding Fukui function. Therefore, before discussing the Fukui function of the selected molecules, the HOMOs are presented in Figure 1. Note that lowercase letters are used to label different HOMOs in each molecule for further reference.

All the results presented in this contribution were obtained with a modified version of the deMon2k program.³⁶ The local density approximation with the VWN correlation functional was used.³⁷ The DZVP³⁸ basis and the GEN-A2^{39–42} auxiliary sets were employed. The molecular plots were obtained with Sinapsis 0.3.⁴³

3.1. Frontier Fukui Function. When only the HOMO a is used to evaluate $f_F^-(\mathbf{r})$, a symmetry break occurs. Figure 2 shows the results. For the evaluation of Fukui functions, all isosurfaces presented in this work were selected to satisfy $Nf(\mathbf{r}) = 0.1$, where N is the total number of electrons in the molecule. This choice is based on the fact that Fukui

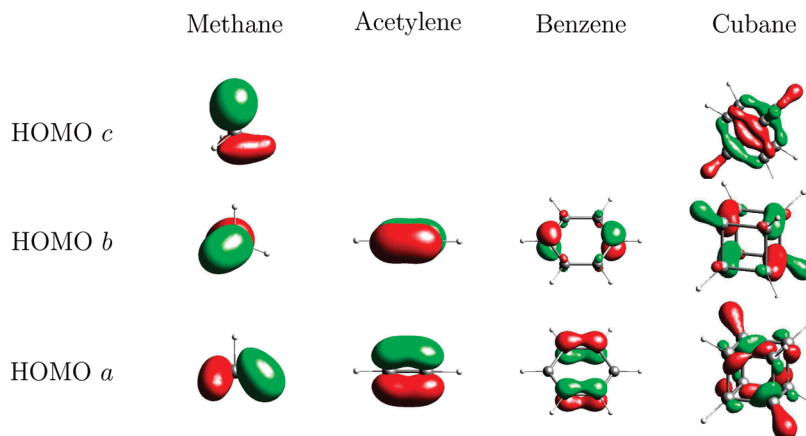


Figure 1. Isosurfaces taken at 0.1 au for HOMOs of the selected set of molecules.

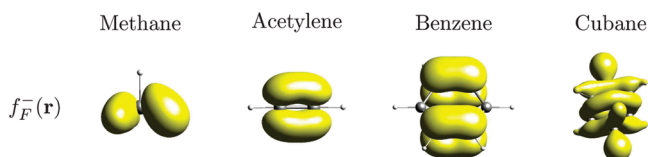


Figure 2. Symmetry break in frontier approximation to Fukui function evaluated as a^2 .

functions integrate to an absolute value of 1.0 and, therefore, for larger molecules smaller absolute values of Fukui functions are found. This also reflects the fact that larger molecules are more able to accommodate extra charge.

The Fukui functions resulting from this method have a shape that resembles very closely that of the last occupied MO. They are also, by construction, positive semidefinite, i.e., $f_F^-(\mathbf{r}) \geq 0$. If one would attempt to predict regioselectivity with these plots, one would arrive at the wrong conclusion that some atoms are more reactive than others that are equivalent to them by symmetry. In order to recover the correct symmetry when the HOMO is degenerate, eq 6 should be modified to allow the possibility for the electrons to leave evenly from all of the HOMOs. Meneses et al.⁴⁴ have applied averaging of frontier orbitals. Cedillo has employed a similar procedure.⁴⁵ Unfortunately, no justification has been given for the legitimacy of this action. This is properly justified by the ensemble of ionic systems proposed above. Equations 4 and 5 should be substituted for the following more general forms:

$$\left(\frac{\partial n_i}{\partial N}\right)^- = \begin{cases} 1/D_{\text{HOMO}} & \text{if } \varepsilon_i = \varepsilon_{\text{HOMO}} \\ 0 & \text{otherwise} \end{cases} \quad (8)$$

$$\left(\frac{\partial n_i}{\partial N}\right)^+ = \begin{cases} 1/D_{\text{LUMO}} & \text{if } \varepsilon_i = \varepsilon_{\text{LUMO}} \\ 0 & \text{otherwise} \end{cases} \quad (9)$$

Here, ε_i is the energy for the i th MO and D_{HOMO} and D_{LUMO} are the order of degeneracy of the HOMO and LUMO, respectively. The frontier Fukui function should be corrected accordingly. For $f_F^-(\mathbf{r})$, the corrected formula is

$$f_F^-(\mathbf{r}) = \frac{1}{D_{\text{HOMO}}} \sum_i^{D_{\text{HOMO}}} |\psi_i(\mathbf{r})|^2 \quad (10)$$

with the sum running over all degenerate HOMOs. The correction of symmetry as a result of the generalization described by eq 10 is a consequence of group theory. If the frontier orbital did not belong to a degenerate set, then its value squared would yield a frontier density belonging to the totally symmetric irreducible representation.⁴⁶ For degenerate frontier orbitals, no single one of them can produce a totally symmetric density, but the direct product of all of their irreducible representations is the totally symmetric one. (This statement is better appreciated using complex character tables that allow separate handling of degenerate orbitals.⁴⁶) This result is in accordance with the inclusion of all frontier orbitals in eq 10. The averaging preserves the normalization of the Fukui functions. In a recent paper⁴⁷ published while this work was in the reviewing process J. Martínez also points out the problem of symmetry breaking treated here. He reports some corrected plots with the frontier orbital approximation, including the one for HCCH presented here.⁴⁷

Note that we are assuming a closed-shell system in the discussion, but the results just obtained are also valid for half-filled, open shells of degenerate frontier orbitals. Actually, this is the molecular counterpart of Unsöld's theorem.^{48,49}

Figure 3 shows the results of this correction. Clearly, the resulting plots allow us to make reactivity predictions that do not violate molecular symmetry.

Unfortunately, the frontier approximation neglects relaxation contributions. Therefore, no attempt to interpret the resulting plots is made here. Nevertheless, this symmetric $f_F^-(\mathbf{r})$ serves as a starting point for evaluation of symmetrized analytic $f^-(\mathbf{r})$.

3.2. Finite Difference Method. In Figure 4, molecular densities for neutral and cationic systems are shown. Their difference is also evaluated to yield $f_D^-(\mathbf{r})$ as an approximation to the Fukui function. Positive values are in yellow and negative regions correspond to blue. Negative regions arise from relaxation contributions. Their existence has been pointed out.^{20,22,50,51} We believe this can be properly understood only by using Fukui function plots and not by the condensed forms.

In ref 22, the plot $f_D^-(\mathbf{r})$ for acetylene was reported. Likewise, in ref 23, a contour plot for benzene was reported. In these reports, as in our plots of $f_D^-(\mathbf{r})$, artificial symmetry breaks occur. These artifacts originate in the method and

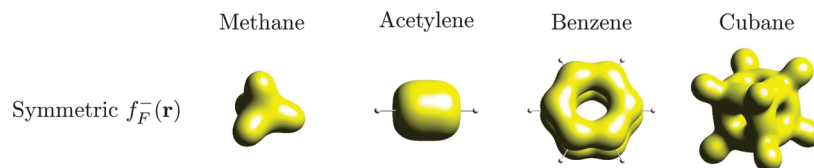


Figure 3. Symmetrized frontier approximation to Fukui function. Calculated using $(a^2 + b^2 + c^2)/3$ for methane and cubane and $(a^2 + b^2)/2$ for acetylene and benzene, according to eq 10.

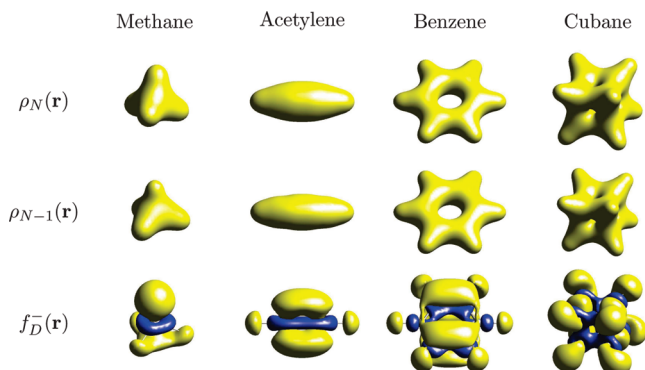


Figure 4. Density of systems with N and $N - 1$ electrons and the resulting approximated Fukui function obtained from their difference. Isosurfaces taken at 0.1 au for densities.

support our position that it is preferable to not involve calculations on the $(N - 1)$ -electron system in calculations on N -electron systems.³³

The analysis of Figure 4 reveals why symmetry breaking has not been an issue in calculations of Fukui functions. The density of the N -electron system adapts to the molecular symmetry. In Figure 4 it can be observed that the density of the $(N - 1)$ -electron system seems to follow the molecular symmetry. However, a careful analysis reveals that the density has a different symmetry. The deviations from symmetry are, for these molecules and others of similar size, about 1 order of magnitude smaller than the actual values of the density. Therefore, it is very hard to see the problem before actually evaluating the difference. On the other hand, people usually condense the difference instead of plotting it. Thus, hiding of the problem is very likely to occur.

Recovering adequate symmetry with the finite difference method is very difficult. More than one state of the $(N - 1)$ -electron system should be calculated. For many currently used methods, it would be very demanding to identify the correct states and recover the corresponding density as required, resulting in more computer and human work that is error-prone. Thus, $f_D^-(r)$ is able to recover relaxation and

allows for the appearance of negative regions. Unfortunately, symmetry breaking is hard to prevent.

3.3. Analytic Method. The analytic method is also able to recover relaxation by means of linear response.³³ In addition, the symmetry break is readily corrected. The symmetrized frontier Fukui function is used as the starting point. The relaxation adapts automatically to the same symmetry. The response to a symmetric change in the density, arising in the frontier, is also symmetric. The forces responsible for relaxation represent a symmetrized change in the density and will cause a symmetrized relaxation. In Figure 5, plots of analytic $f^-(r)$ are shown without and with symmetry correction. Note how once symmetry has been corrected, the analytic method presents both positive and negative regions, with adequate symmetry.

Fukui function plots are very rich in information. Once the symmetry has been corrected, the plots calculated are reliable for the interpretation of reactivity. Their full potentiality for description of chemical reactivity is revealed. First, they show how changes in density are frequently outside of atomic regions. Negative regions are clearly an important feature.

4. Applications

In this section, the analytic Fukui functions, $f^-(r)$ and $f^+(r)$, are evaluated for different sets of molecules of current interest to chemistry and technology. Many of the Fukui functions shown below have never been displayed previously with adequate symmetry or their novel negative domains. Molecules with degenerate frontier orbitals are treated to show the range of applications that benefit from the present approach.

Henceforth, all plots correspond to symmetry-corrected Fukui functions.

4.1. Diatomic Molecules. Diatomic molecules are very simple reactive systems, but the symmetry problem in Fukui functions affects them in such a way that equivalent spatial directions for approaching the molecule would result in

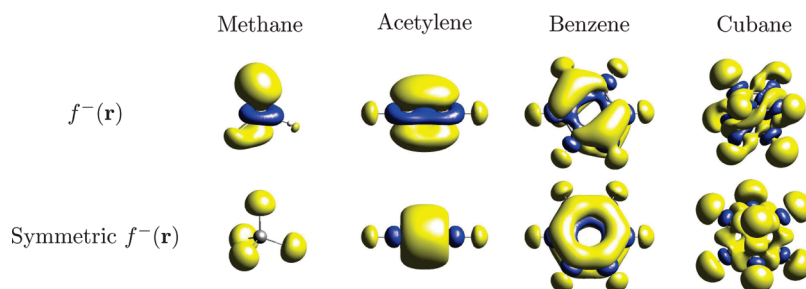


Figure 5. Analytic Fukui functions before and after symmetrization.

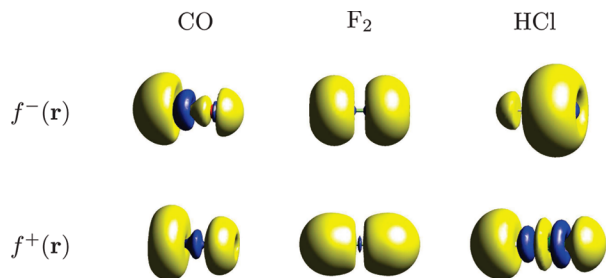


Figure 6. Fukui functions for diatomic molecules.

different reactivities. This violates space isotropy and should be corrected. In Figure 6, the symmetry-corrected analytic Fukui functions for CO, F₂, and HCl are shown. For the case of CO only the LUMO is degenerate. For F₂ and HCl, only the HOMOs are degenerate.

For F₂, the symmetry of the Fukui functions is $D_{\infty h}$, whereas before the correction the symmetry was D_{2h} . For CO and HCl, the correction goes from C_{2v} to $C_{\infty h}$. In addition to the symmetry correction in Figure 6, one can see how negative regions in Fukui functions are always present. This is not the first time that such regions are detected or reported. Nevertheless, one of the results of this work is that it reveals how the appearance of negative regions is the rule rather than the exception. This result contrasts with the long-standing debate on the appearance, meaning, and legitimacy of negative values in condensed Fukui functions.

In linear molecules, such as the diatomic molecules of Figure 6, the condensation of unsymmetrical Fukui functions leads to the same values as the condensation of the symmetry-corrected form. These results provide good examples of how condensation hides the symmetry-breaking problem. Fortunately, this conclusion also implies that published condensed values such as those of refs 22 and 33 are correct. For nonlinear molecules, this fortuitous correction does not occur at all. Probably this is the reason that symmetric molecules are not frequently reported with Fukui functions.

A rationalization of negative regions of Fukui functions is possible with the analysis of the plots shown in this work. When a molecule loses electrons, there is a charge compensation that migrates toward the positive nuclear frame. Valence electrons will be attracted more strongly since the shielding has been lowered. This causes a net increase of core density. In the opposite case, if the molecule gains electrons, the charge compensation goes in favor of the electrons. The shielding increases in this case and core electrons can expand away from the nuclear framework, generating a depletion in core density. This is in agreement with the previous observations and analysis of Ayers et al.^{22,50,51} This also explains why negative regions were not found close to hydrogens in the systems treated here.

4.2. Inorganic Systems. Generally, the Fukui function is used in the analysis of reactivity of organic molecules. There is no fundamental reason to restrict attention to those systems. On the other hand, calculation of charged systems happens to be more difficult in inorganic molecules, making application of the numeric difference method more difficult. With

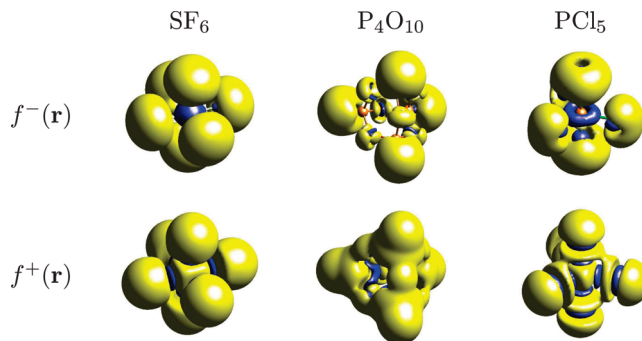


Figure 7. Fukui functions for inorganic molecules.

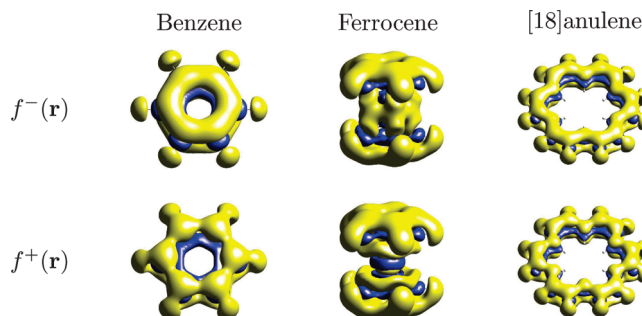


Figure 8. Fukui functions for conjugated molecules.

the analytic method, charged systems are not calculated; only the neutral system is of interest. Therefore, we can proceed without worry to the treatment of inorganic molecules.

Examples of inorganic molecules are SF₆, P₄O₁₀, and PCl₅. P₄O₁₀ and PCl₅ offer an opportunity for testing regioselectivity in a case where atoms of the same type appear in different conditions. Only the HOMO is degenerate for these systems. In Figure 7, one can observe how axial Cl atoms of PCl₅ are affected more upon removal of electrons. For the case of P₄O₁₀, oxygen atoms linked to a single P atom are the first source of electrons.

4.3. Conjugated Systems. Conjugated systems are very important in synthesis, in polymers and biological chemistry. Many of them have degenerate frontier orbitals. In particular the aromatic systems, by obeying Hückel's $4n + 2$ rule, present doubly degenerate frontier orbitals. In this section, benzene, ferrocene, and [18]anulene are treated as examples of conjugated molecules. While benzene is the prototype of all aromatic systems, ferrocene is the prototype of organo-metallic sandwich systems. [18]Anulene offers the possibility of testing atoms of the same type in different conditions. In Figure 8 the plots can be observed. For these three molecules both the HOMO and LUMO are doubly degenerate. It is interesting to note that $f^-(\mathbf{r})$ of ferrocene predicts that removal of electrons affects mostly the metal atom. This is in agreement with the experimental observation where it was found that Fe²⁺ oxidizes to Fe³⁺.⁵² In the cases of benzene and [18]anulene, the missing electrons come from the aromatic π -system. For addition of electron, $f^+(\mathbf{r})$ shows a clear tendency to localize. For [18]anulene, one can also conclude in electron transfer reactions that the external hydrogens are more likely to react than the internal hydrogens of the [18]anulene ring.

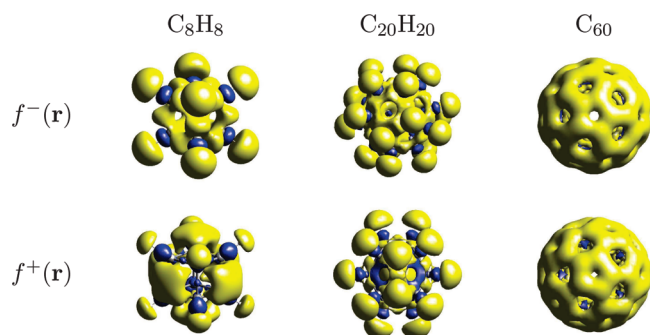


Figure 9. Fukui functions for carbon molecular cages.

4.4. Molecular Cages. Molecular cages are very important in nanotechnology, in trapping of atoms and smaller molecules, and for the study of confinement effects.⁵³ They are also suitable for analyzing off-atom regions of Fukui functions.

Molecular cages C_8H_8 , $C_{20}H_{20}$, and C_{60} are considered. Because of the number of degenerate frontier orbitals, the size of the systems, and the very small values of the calculated Fukui functions in these molecules, the calculation of symmetry-corrected functions by the finite difference method appears very hard to realize. This is a challenge for those who might be reluctant to employ analytic methods for the calculation of Fukui functions.

Figure 9 shows the analytic Fukui functions evaluated for these molecular cages. One can observe that removal of electrons from cubane affects mostly C–C bonds and the zones of hydrogen atoms. The addition of electrons to the same molecule would increase density in off-atom regions. In particular, there are zones out of the cubane box that increase density. In the opposite case, $C_{20}H_{20}$ shows that extra electrons would be better accepted inside the box.

In C_{60} , there is only one type of C atom, but there are two types of C–C bonds. If the symmetrized Fukui functions calculated here were condensed, then all atoms would show the same reactivity as expected. However, no information about the reactivity of bonds would be recovered. The direct analysis of these functions allows one to conclude that removal of electrons affects C–C bonds that are not part of the pentagons and addition of electrons would go to bonds on the C_5 motifs.

Note that the size of the systems that are being treated here is not small. For the case of C_{60} , about 900 basis functions and 2040 auxiliary functions are employed. Consider also that the calculations here shown do not exploit symmetry for efficiency. In an Intel Xeon 2.40 GHz CPU, the calculation of both Fukui functions took 7 h 41 min using a RAM under 512 MB. About 1 h of this time was consumed by the SCF calculation. This performance is to be expected from deMon2k,³⁶ which takes advantage of the variational fitting of the Coulomb potential^{54,55} and other developments of auxiliary density functional theory.^{56,57} It demonstrates that evaluation of analytic Fukui functions with linear response as described in ref 33 is very efficient and can be realized routinely for many chemically interesting systems. This method can help to extend the horizon of applications of Fukui functions in chemical reactivity theory.

5. Conclusions

Treating degenerate frontier orbitals on an equal footing, as dictated by 0 K statistical mechanics and molecular group theory,⁴⁶ corrects symmetry breaking in frontier Fukui functions and analytic Fukui functions for nondegenerate states. A number of symmetry-corrected Fukui function plots were evaluated to demonstrate the range of areas that can benefit from this development. The analysis of the plots presented here encourages the use of direct analysis of Fukui functions instead of the condensed forms.

The results of this work complement our recent effort to develop an efficient analytic method for reliable and reproducible calculation of Fukui functions.

Negative regions of Fukui functions appear in most graphs and can be rationalized on the basis of charge compensation. This is in agreement with previously published results.^{22,50,51}

Acknowledgment. Funding from Conacyt under the project 60117-F is gratefully acknowledged. The support of Prof. Dr. Andreas M. Köster is greatly appreciated. I also would like to thank Prof. J. V. Ortiz, V. D. Domínguez, and R. Grande for careful reading of the manuscript and for their suggestions. Many valuable suggestions from the reviewers are also acknowledged.

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CT9002527