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The Charge Transfer Fukui Function: Extension of the Finite-Difference Approach to Reactive Systems

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The Fukui function is one of the most important concepts in the theory of chemical reactivity. For the fixed positions of nuclei, it describes reorganization in electron density of a given molecule due to overall chemical oxidation/reduction. The concept of the Fukui function was extended to reactive systems, giving a real two-reactant description of the chemical reaction. In this paper, the finite-difference approach was adopted to derive formulas for diagonal and off-diagonal Fukui functions in local and in atoms-in-molecule resolutions. The obtained results generalize the approach of Parr and Yang or Yang and Mortier into reactive systems, e.g. interacting molecules. The self-consistent charge and configuration method for subsystems (SCCCMS) was applied to calculate these quantities. A combination of Becke's three-parameter hybrid functional and the Perdew/Wang 91 gradient-corrected functional with the 6-31G* basis set was used in Kohn−Sham calculations. Methyl radical addition to ethylene was taken as an illustrative example. Charge transfer from ethylene to the radical (forward donation), as well as that from the radical to ethylene (backward donation), was considered. We have shown that off-diagonal Fukui functions should be taken into account in realistic models of interacting molecules.

1. Introduction

The Fukui function (FF) of Parr and Yang[1,2]

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{\nu(\vec{r})} \tag{1}$$

describes the local changes in the electron density of the system, $\rho(\vec{r})$, due to the perturbation in the global number of electrons, N. The partial derivative in eq 1 is calculated under the constraint of constant external potential, $\nu(\vec{r})$; i.e., the positions of nuclei are fixed. One should notice that FF is normalized to unity ($\int f(\vec{r})\, d\vec{r} = (\partial/\partial N)(\int \rho(\vec{r})\, d\vec{r}) = \partial N/\partial N = 1$). FF reflects the open character of reactants which are able to accept (donate) electrons from (to) an external macroscopic reservoir and as such is very attractive for chemists as a reactivity criterion.

FF is modeled in local resolution (real three-dimensional Cartesian space) via the finite-difference method. Within this approximation, Parr and Yang derived the following expressions:[1,2]

$$f^{\mathrm{e}}(\vec{r}) = \rho_{N^0}(\vec{r}) - \rho_{N^0-1}(\vec{r}) \tag{2a}$$

$$f^{\mathrm{n}}(\vec{r}) = \rho_{N^0+1}(\vec{r}) - \rho_{N^0}(\vec{r}) \tag{2b}$$

$$f^{\mathrm{r}}(\vec{r}) = [f^{\mathrm{n}}(\vec{r}) + f^{\mathrm{e}}(\vec{r})]/2 = [\rho_{N^0+1}(\vec{r}) - \rho_{N^0-1}(\vec{r})]/2 \tag{2c}$$

Here, the superscripts of FF correspond to electrophilic (e), nucleophilic (n), and radical (r) reagent attacks, respectively. The subscripts of ρ specify the number of electrons in the system; N^0 denotes a neutral system. Equations 2a−c have been condensed to an atoms-in-molecule (AIM) resolution by Yang and Mortier:[3]

$$\boldsymbol{f}^{\mathrm{e}} = \boldsymbol{q}_{N^0-1} - \boldsymbol{q}_{N^0} \tag{3a}$$

$$\boldsymbol{f}^{\mathrm{n}} = \boldsymbol{q}_{N^0} - \boldsymbol{q}_{N^0+1} \tag{3b}$$

$$\boldsymbol{f}^{\mathrm{r}} = (\boldsymbol{f}^{\mathrm{n}} + \boldsymbol{f}^{\mathrm{e}})/2 = (\boldsymbol{q}_{N^0-1} - \boldsymbol{q}_{N^0+1})/2 \tag{3c}$$

where vector $\boldsymbol{q}$ groups AIM charges. Applicability of eqs 2 and 3 for diagnosing the preferred reaction sites for nucleophilic, electrophilic, and radical attacks has been reported in the literature.[4−8] Recently, Gazquez and Mendez[9] proposed that interaction between two chemical species should occur through those atoms possessing approximately equal values of FF's. This concept has been successfully applied to regioselectivity problems in "pseudo" two-reactant descriptions, i.e., by matching AIM FF's of isolated reactants.[7,8]

In the spin orbital [$\varphi_i(\vec{x})$] resolution, electron density is given as follows: $\rho(\vec{r}) = \sum_i \sum_\sigma n_i |\varphi_i(\vec{x})|^2$. Thus, one can obtain alternative expressions for electrophilic and nucleophilic FF's:

$$f^{\mathrm{e}}(\vec{r}) = |\varphi_{\mathrm{HOMO}}(\vec{r})|^2 + \sum_\sigma \sum_i n_i\, \partial |\varphi_i(\vec{x})|^2/\partial N \tag{4a}$$

$$f^{\mathrm{n}}(\vec{r}) = |\varphi_{\mathrm{LUMO}}(\vec{r})|^2 + \sum_\sigma \sum_i n_i\, \partial |\varphi_i(\vec{x})|^2/\partial N \tag{4b}$$

Here, n_i is an occupation number, σ is a spin coordinate, and $\vec{x} = \{\vec{r}, \sigma\}$. Neglecting the orbital relaxation due to addition or removal of an electron (the second components in eqs 4a and 4b), one can relate FF's[1,2] to frontier orbital densities:[10] $f^{\mathrm{e}}(\vec{r}) \approx \rho_{\mathrm{HOMO}}(\vec{r}) = |\varphi_{\mathrm{HOMO}}(\vec{r})|^2$, $f^{\mathrm{n}}(\vec{r}) \approx \rho_{\mathrm{LUMO}}(\vec{r}) = |\varphi_{\mathrm{LUMO}}(\vec{r})|^2$. This indicates that frontier orbital [HOMO (highest occupied mo-

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lecular orbital), LUMO (lowest unoccupied molecular orbital)] channels play important roles in charge transfer (CT) reactions.

The concept of FF was later extended into reactive systems.[11−17] For interacting (mutually closed) species, one can define not only diagonal but also off-diagonal responses in FF. These responses can be combined into the so-called CT FF,[11,12] which predicts reorganization in electron density during CT.

In this paper, we focus our attention on real two-reactant description of chemical reactions. We derive two independent expressions for CT FF in local resolution using the finite-difference approach. These expressions confirm adequacy of the computational scheme used to describe polarized reactants (before CT). All formulas in local resolution have been condensed to the AIM resolution. CT FF in local resolution, as well as its components, is illustrated for the first time. We also show that off-diagonal FF's are especially important in π-electron systems. Addition of a methyl radical to ethylene is chosen as a typical example in order to illustrate the FF concept.

Our recent study has shown[18] that Becke's three-parameter hybrid functional[19] with the Perdew/Wang 91 correlation functional[20] using the 6-31G* basis set (B3PW91/6-31G*) adequately describes the activation energies for addition of fluoromethyl radicals to fluoroethylenes. The mechanism of the addition reactions was investigated using the energy-partitioning scheme, based upon the self-consistent charge and configuration method for subsystems (SCCCMS)[21] and charge sensitivity concepts.[11−13] It has been shown that CT energy significantly stabilizes the transition states. In the systems of fluoromethyl radicals and fluoroethylenes, including nonfluorinated parent system (methyl radical/ethylene), radicals accept electrons and ethylenes donate electrons. Thus, CT from ethylene to the radical can be considered as forward donation and that from the radical to ethylene as backward donation.

2. Finite-Difference Expressions for the Charge Transfer Fukui Function

Let us consider a molecular system M composed of two subsystems A and B. Our starting point is a hypothetical stage in which subsystems are mutually closed but polarized M = (A|B). Thus, CT between A and B is not allowed. Let us suppose that subsystems are now open to each other M = (A⋮B) and that electrons flow from B (a base) to A (an acid), B → A. Obviously, the change in the number of electrons in subsystem A is equal to the negative of that change in B

$$\mathrm{d}N_A = -\mathrm{d}N_B = \mathrm{d}N_{CT} > 0 \tag{5}$$

The amount of CT is denoted by $\mathrm{d}N_{CT}$.

The partial derivative of ρ with respect to N_{CT} defines the CT FF:[11,12]

$$f^{CT}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N_{CT}}\right) = \left(\frac{\partial\rho_A(\vec{r})}{\partial N_{CT}}\right) + \left(\frac{\partial\rho_B(\vec{r})}{\partial N_{CT}}\right) \equiv f_A^{CT}(\vec{r}) + f_B^{CT}(\vec{r}) \tag{6a}$$

$$f^{CT}(\vec{r}) = \left\{\left(\frac{\partial\rho_A(\vec{r})}{\partial N_A}\right)\left(\frac{\partial N_A}{\partial N_{CT}}\right) + \left(\frac{\partial\rho_A(\vec{r})}{\partial N_B}\right)\left(\frac{\partial N_B}{\partial N_{CT}}\right)\right\} + \left\{\left(\frac{\partial\rho_B(\vec{r})}{\partial N_A}\right)\left(\frac{\partial N_A}{\partial N_{CT}}\right) + \left(\frac{\partial\rho_B(\vec{r})}{\partial N_B}\right)\left(\frac{\partial N_B}{\partial N_{CT}}\right)\right\} \equiv \{f_{AA}^M(\vec{r}) - f_{BA}^M(\vec{r})\} + \{f_{AB}^M(\vec{r}) - f_{BB}^M(\vec{r})\} \tag{6b}$$

In the above equation, derivatives $(\partial N_A/\partial N_{CT})$ and $(\partial N_B/\partial N_{CT})$ are equal to 1 and −1 (see eq 5), respectively. Diagonal FF's (f_{AA}^M, f_{BB}^M) are normalized to unity ($\int f_{AA}^M\,\mathrm{d}\vec{r} = \int f_{BB}^M\,\mathrm{d}\vec{r} = 1$), while off-diagonal FF's (f_{AB}^M, f_{BA}^M) are normalized to zero ($\int f_{AB}^M\,\mathrm{d}\vec{r} = \int f_{BA}^M\,\mathrm{d}\vec{r} = 0$). Consequently, the CT FF of A(f_A^{CT}) is normalized to unity ($\int f_A^{CT}\,\mathrm{d}\vec{r} = 1$) and the CT FF of B ($f_B^{CT}$) to minus one ($\int f_B^{CT}\,\mathrm{d}\vec{r} = -1$). Thus, the CT FF of the whole system (f^{CT}) is normalized to zero ($\int f^{CT}\,\mathrm{d}\vec{r} = 0$). All the derivatives in eq 6 are calculated under an additional constraint, i.e., constant external potential. We wish to remark that the excitation function of Tachibana[16,17] is just half of the CT FF. This author has rotated the (N_A, N_B)-coordinate system into (N, Γ)-coordinate system; N represents external CT ($N = N_A + N_B$) and Γ represents internal CT ($\Gamma = N_A - N_B$). The excitation function has been defined as the derivative of the electron density with respect to Γ. Thus, the excitation function can be considered as the earliest definition of the CT FF.

Diagonal (f_{AA}^M, f_{BB}^M) and off-diagonal (f_{AB}^M, f_{BA}^M) components of the CT FF can be approximated by the finite-difference method as follows:

$$\begin{aligned} f_{AA}^M &= \rho_A(N_A^0 + 1, N_B^0) - \rho_A(N_A^0, N_B^0) \\ f_{BA}^M &= \rho_A(N_A^0, N_B^0) - \rho_A(N_A^0, N_B^0 - 1) \\ f_{AB}^M &= \rho_B(N_A^0 + 1, N_B^0) - \rho_B(N_A^0, N_B^0) \\ f_{BB}^M &= \rho_B(N_A^0, N_B^0) - \rho_B(N_A^0, N_B^0 - 1) \end{aligned} \tag{7}$$

The electron densities appearing in eq 7 correspond to an intrareactant equilibrium.[11,12] Here, we have omitted the position vector. The numbers of electrons in both subsystems are specified in the parentheses.

By analogy to eq 4, one can also express the components of CT FF as follows:

$$f_{AA}^M(\vec{r}) = |\varphi_{LUMO}^A(\vec{r})|^2 + \sum_\sigma\sum_i n_i^A\ \partial|\varphi_i^A(\vec{x})|^2/\partial N_A \tag{8a}$$

$$f_{BA}^M(\vec{r}) = \sum_\sigma\sum_i n_i^A\ \partial|\varphi_i^A(\vec{x})|^2/\partial N_B \tag{8b}$$

$$f_{AB}^M(\vec{r}) = \sum_\sigma\sum_i n_i^B\ \partial|\varphi_i^B(\vec{x})|^2/\partial N_A \tag{8c}$$

$$f_{BB}^M(\vec{r}) = |\varphi_{LUMO}^B(\vec{r})|^2 + \sum_\sigma\sum_i n_i^B\ \partial|\varphi_i^B(\vec{x})|^2/\partial N_B \tag{8d}$$

Here, $\{\varphi_i^A\}$, $\{\varphi_i^B\}$ and $\{n_i^A\}$, $\{n_i^B\}$ are the spin orbitals of A and B in M and their occupation numbers, respectively. If the distance between the reactants goes to infinity, then off-diagonal (f_{BA}^M, f_{AB}^M) responses disappear. In such a case, diagonal (f_{AA}^M, f_{BB}^M) responses can be identified as the nucleophilic and electrophilic FF of A and B (eqs 4a and 4b), respectively.

In addition, we wish to mention that finite-difference expressions for the CT FF can be derived directly from the definition (eq 6a):

$$\begin{aligned} f_A^{CT}(\vec{r}) &\equiv \left(\frac{\partial\rho_A}{\partial N_{CT}}\right) = \rho_A(N_A^0 + 1, N_B^0 - 1) - \rho_A(N_A^0, N_B^0) \\ f_B^{CT}(\vec{r}) &\equiv \left(\frac{\partial\rho_B}{\partial N_{CT}}\right) = \rho_B(N_A^0 + 1, N_B^0 - 1) - \rho_B(N_A^0, N_B^0) \end{aligned} \tag{9}$$

Here, we assume that electron flows from reactant B to reactant A. In contrast to eq 9, eq 6b describes CT from B to A as a two-step process; i.e., CT occurs indirectly via external electron reservoirs (B → reservoir and reservoir → A). These equations (6b and 9) can be used to test the adequacy of our computational scheme, since both should give the same results (linear response approximation).

Transformation from local to AIM resolution is straightforward. Substitution of local quantities (densities) in eq 6 by vectors (AIM populations) leads to the AIM CT FF

$$\boldsymbol{f}^{\mathrm{CT}} = \frac{\partial \boldsymbol{N}}{\partial N_{\mathrm{CT}}} = \left(\frac{\partial \boldsymbol{N}_{\mathrm{A}}}{\partial N_{\mathrm{CT}}}, \frac{\partial \boldsymbol{N}_{\mathrm{B}}}{\partial N_{\mathrm{CT}}}\right) \equiv (\boldsymbol{f}_{\mathrm{A}}^{\mathrm{CT}}, \boldsymbol{f}_{\mathrm{B}}^{\mathrm{CT}}) \equiv (\boldsymbol{f}_{\mathrm{AA}}^{\mathrm{M}} - \boldsymbol{f}_{\mathrm{BA}}^{\mathrm{M}}, \boldsymbol{f}_{\mathrm{AB}}^{\mathrm{M}} - \boldsymbol{f}_{\mathrm{BB}}^{\mathrm{M}}) \quad (10)$$

Here, vector $\boldsymbol{N} = (\boldsymbol{N}_{\mathrm{A}}, \boldsymbol{N}_{\mathrm{B}})$ collects electron populations in both subsystems. In the same way, the components of the CT FF in local resolution (eq 7) can be condensed to the AIM picture:

$$\begin{aligned}
\boldsymbol{f}_{\mathrm{AA}}^{\mathrm{M}} &= \boldsymbol{N}_{\mathrm{A}}(N_{\mathrm{A}}^{0} + 1, N_{\mathrm{B}}^{0}) - \boldsymbol{N}_{\mathrm{A}}(N_{\mathrm{A}}^{0}, N_{\mathrm{B}}^{0}) \\
\boldsymbol{f}_{\mathrm{BA}}^{\mathrm{M}} &= \boldsymbol{N}_{\mathrm{A}}(N_{\mathrm{A}}^{0}, N_{\mathrm{B}}^{0}) - \boldsymbol{N}_{\mathrm{A}}(N_{\mathrm{A}}^{0}, N_{\mathrm{B}}^{0} - 1) \\
\boldsymbol{f}_{\mathrm{AB}}^{\mathrm{M}} &= \boldsymbol{N}_{\mathrm{B}}(N_{\mathrm{A}}^{0} + 1, N_{\mathrm{B}}^{0}) - \boldsymbol{N}_{\mathrm{B}}(N_{\mathrm{A}}^{0}, N_{\mathrm{B}}^{0}) \\
\boldsymbol{f}_{\mathrm{BB}}^{\mathrm{M}} &= \boldsymbol{N}_{\mathrm{B}}(N_{\mathrm{A}}^{0}, N_{\mathrm{B}}^{0}) - \boldsymbol{N}_{\mathrm{B}}(N_{\mathrm{A}}^{0}, N_{\mathrm{B}}^{0} - 1)
\end{aligned} \quad (11)$$

Instead of $\boldsymbol{N}_{\mathrm{A}}$ and $\boldsymbol{N}_{\mathrm{B}}$, one can also introduce vectors $\boldsymbol{q}_{\mathrm{A}}$ and $\boldsymbol{q}_{\mathrm{B}}$, grouping atomic charges. Thus, eqs 11 can be rewritten as follows

$$\begin{aligned}
\boldsymbol{f}_{\mathrm{AA}}^{\mathrm{M}} &= \boldsymbol{q}_{\mathrm{A}}(0, 0) - \boldsymbol{q}_{\mathrm{A}}(-1, 0) \\
\boldsymbol{f}_{\mathrm{BA}}^{\mathrm{M}} &= \boldsymbol{q}_{\mathrm{A}}(0, 1) - \boldsymbol{q}_{\mathrm{A}}(0, 0) \\
\boldsymbol{f}_{\mathrm{AB}}^{\mathrm{M}} &= \boldsymbol{q}_{\mathrm{B}}(0, 0) - \boldsymbol{q}_{\mathrm{B}}(-1, 0) \\
\boldsymbol{f}_{\mathrm{BB}}^{\mathrm{M}} &= \boldsymbol{q}_{\mathrm{B}}(0, 1) - \boldsymbol{q}_{\mathrm{B}}(0, 0)
\end{aligned} \quad (12)$$

Numbers in parentheses are the overall charges of subsystems A and B, respectively.

Noteworthy is that the definition of the CT FF can be applied to both forward and backward donations. The sum of CT FF's for both donations gives the radical CT FF

$$f_{\mathrm{r}}^{\mathrm{CT}}(\vec{r}) = f_{\mathrm{forward}}^{\mathrm{CT}}(\vec{r}) + f_{\mathrm{backward}}^{\mathrm{CT}}(\vec{r}) \quad (13)$$

Such a radical CT FF is normalized to zero, since $\int f_{\mathrm{forward}}^{\mathrm{CT}}(\vec{r})\, \mathrm{d}\vec{r}$, as well as $\int f_{\mathrm{backward}}^{\mathrm{CT}}(\vec{r})\, \mathrm{d}\vec{r}$, is equal to zero. The radical CT FF should adequately describe charge reorganization in radical processes.

3. Methods

All calculations were carried out using the Gaussian 94 suite of programs[22] on an IBM 6000. Kohn–Sham[23] (KS) calculations for interacting reactants were performed by using the self-consistent charge and configuration method for subsystems (SCCCMS).[21] The main assumption of the model is that the presence of the reaction partner is approximated by the point charge distribution. Thus, the calculations for subsystem A are performed with the background charges characterizing subsystem B ($\boldsymbol{q}_{\mathrm{B}} = \{q_1^{\mathrm{B}}, q_2^{\mathrm{B}}, ...\}$) and vice versa. The iteration scheme is repeated until the convergence in the energies and charge distributions of the subsystems is achieved. Diagonal and off-diagonal FF's were computed in local and in AIM resolutions according to eqs 7 and 12, respectively. SCCCMS calculations were performed for the following combinations of subsystem charges: $(q_{\mathrm{A}}, q_{\mathrm{B}}) = \{(-1, 0), (0, 0), (0, 1), (1, 0), (0, -1)\}$. In addition, the CT FF's of reactants were calculated via eq 9, in order to test the SCCCMS method, so the scheme was repeated for two additional combinations of subsystem charges: (−1, 1) and (1, −1).

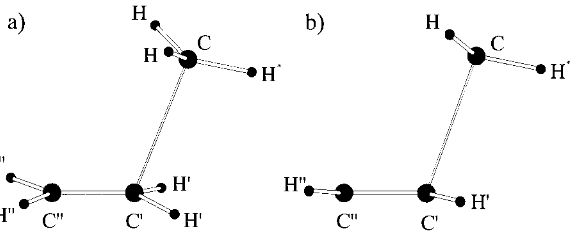

Figure 1. Perspective view of the transition state structure for methyl radical addition to ethylene (panel a) and its projection on the symmetry plane (panel b).

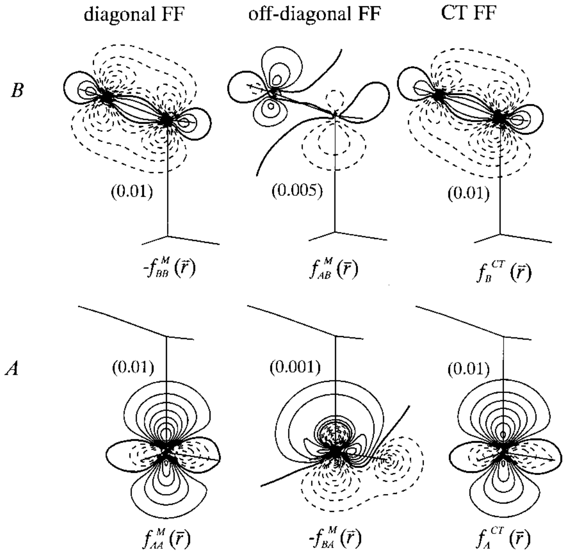

Figure 2. Contour maps of the CT FF of reactants [$f_{\mathrm{B}}^{\mathrm{CT}}(\vec{r})$, $f_{\mathrm{A}}^{\mathrm{CT}}(\vec{r})$] (third column) together with its diagonal [$-f_{\mathrm{BB}}^{\mathrm{M}}(\vec{r})$, $f_{\mathrm{AA}}^{\mathrm{M}}(\vec{r})$] (first column) and off-diagonal [$f_{\mathrm{AB}}^{\mathrm{M}}(\vec{r})$, $-f_{\mathrm{BA}}^{\mathrm{M}}(\vec{r})$] (second column) contributions. The first row corresponds to ethylene (B) and the second row to the methyl radical (A). The CT from ethylene to the methyl radical, B → A, is assumed (forward CT). Solid and broken lines represent positive and negative values. Bold solid lines are the zero contours. The positive and negative values indicate increase and decrease in electron density during CT. The numbers in parentheses are the contour intervals. Letters "A" and "B" correspond to acid and base, respectively. Contour maps are plotted in the surface spanned by the carbon skeleton (see Figure 1b). In all contour maps, molecular frames are included for reasons of clarity.

The transition state structure for methyl radical addition to ethylene was given in our previous paper.[18] A perspective view of this transition state and its projection on the symmetry plane are shown in Figure 1. The SCCCMS calculations for interacting methyl radical and ethylene are performed at the B3PW91/6-31G* level of theory. This computational level was shown to describe adequately activation energies for the methyl radical/ethylene system.[18]

4. Results and Discussion

Figures 2 and 3 display the CT FF's of the transition state for addition of the methyl radical to ethylene. Diagonal and off-diagonal components of the CT FF's are shown as well. Figures 2 and 3 correspond to forward and backward donations, respectively. For reasons of clarity, the signs of $f_{\mathrm{BB}}^{\mathrm{M}}$ and $f_{\mathrm{BA}}^{\mathrm{M}}$

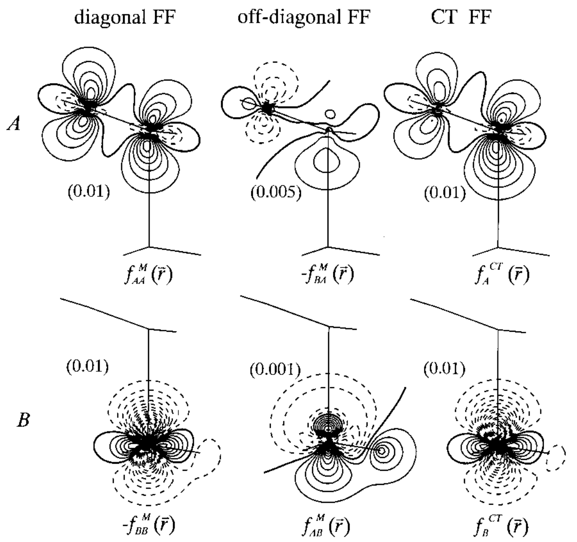

Figure 3. The same as in Figure 2, but for CT in the opposite direction, i.e., from the methyl radical (B) to ethylene (A) (backward CT).

are changed (see eq 6b). After this modification, positive and negative contours indicate increase and decrease in electron density during CT, respectively.

For forward donation (Figure 2), the diagonal FF of ethylene $f_{\mathrm{BB}}^{\mathrm{M}}$ is dominated by the HOMO density (see eq 8d). The geometry deformation of ethylene from planarity in the transition state is rather small. However, increase in electron density between the carbon atoms of the double bond is due to relaxation of the CC σ molecular orbital during "oxidation" (second component of the sum in eq 8d). Such a pattern in the diagonal FF clearly demonstrates importance of σ/π polarization during alkene oxidation. The off-diagonal FF $f_{\mathrm{AB}}^{\mathrm{M}}$ can be called the "chemical channel". Densities of hybrid-type orbitals are visible on both carbon atoms. Such a pattern in the charge reorganization agrees well with chemical intuition. Namely, rehybridization on the attacked carbon atom can be considered as the incipient step in forming a localized σ orbital with a radical carbon atom. Rehybridization is also recognized on the second carbon atom of ethylene where an unpaired electron will be placed after the CT.

The last plot in the first row of Figure 2 presents the forward CT FF of ethylene, $f_{\mathrm{B}}^{\mathrm{CT}} = f_{\mathrm{AB}}^{\mathrm{M}} - f_{\mathrm{BB}}^{\mathrm{M}}$. It describes charge reorganization accompanying the shift of an electron from ethylene to the methyl radical. The π-electron system of ethylene is destroyed (decrease in electron density). At the same time, there is increase in electron density between the carbon atoms. One should observe that the diagonal and off-diagonal responses act in phase on the attacked carbon atom, while on the neighboring carbon atom the diagonal and off-diagonal contributions are out of phase. Thus, the HOMO density in $f_{\mathrm{B}}^{\mathrm{CT}}$ is slightly more expanded toward the radical.

The diagonal FF of the methyl radical for forward donation, $f_{\mathrm{AA}}^{\mathrm{M}}$ (first map in the second row of Figure 2), is dominated by the nonbonding SOMO (singly occupied molecular orbital). Orbital relaxation during reduction causes a significant contribution of the CH bond to the diagonal FF. Mixing of 2s and 2p orbitals of the radical carbon atom (partial hybridization) is observed. The contours are more expanded toward the ethylene carbon atom. The off-diagonal response $f_{\mathrm{BA}}^{\mathrm{M}}$ is insignificant; the small contour interval (0.001) was taken in order to show its topology, which is rather complex. Thus, $f_{\mathrm{A}}^{\mathrm{CT}}$ for the methyl radical is dominated by the diagonal component.

TABLE 1: Fukui Function Indices in AIM Resolution for the Methyl Radical/Ethylene System in the Transition State Structure[a]

methyl atom	forward CT (ethylene → methyl)			backward CT (methyl → ethylene)		
	$-f_{\mathrm{BA}}^{\mathrm{M}}$	$f_{\mathrm{AA}}^{\mathrm{M}}$	$f_{\mathrm{A}}^{\mathrm{CT}}$	$f_{\mathrm{AB}}^{\mathrm{M}}$	$-f_{\mathrm{BB}}^{\mathrm{M}}$	$f_{\mathrm{B}}^{\mathrm{CT}}$
C	0.151	0.423	0.573	−0.146	−0.454	−0.600
H*	−0.059	0.198	0.139	0.058	−0.187	−0.129
H	−0.046	0.190	0.144	0.044	−0.180	−0.135

ethylene atom	forward CT (ethylene → methyl)			backward CT (methyl → ethylene)		
	$f_{\mathrm{AB}}^{\mathrm{M}}$	$-f_{\mathrm{BB}}^{\mathrm{M}}$	$f_{\mathrm{B}}^{\mathrm{CT}}$	$-f_{\mathrm{BA}}^{\mathrm{M}}$	$f_{\mathrm{AA}}^{\mathrm{M}}$	$f_{\mathrm{A}}^{\mathrm{CT}}$
C′	−0.240	−0.185	−0.425	0.265	0.157	0.423
C″	0.048	−0.190	−0.142	−0.065	0.143	0.079
H′	0.057	−0.157	−0.100	−0.056	0.174	0.119
H″	0.039	−0.155	−0.116	−0.045	0.175	0.130

[a] The transition state structure has C_s symmetry (see Figure 1). The carbon skeleton is located on the symmetry plane. The radical H* atom is located on the symmetry plane. H′ and H″ are bonded to C′ and C″, respectively. The methyl radical approaches ethylene from the C′ side.

CT FF's for the opposite direction of CT (backward CT), i.e., from the methyl radical to ethylene, are shown in Figure 3. Now, the radical acts as a base (B), while ethylene acts as an acid (A). For the methyl radical (second row), diagonal and off-diagonal components, as well as the CT FF, in backward donation give qualitatively the same plots as those in forward donation but the sign is reversed. This is connected with the fact that the SOMO is involved in CT for both directions. One should notice that the magnitude of diagonal response ($f_{\mathrm{BB}}^{\mathrm{M}}$) is much higher (maximum contour is equal to 0.13) for the backward donation than for the forward donation shown in Figure 2 (maximum contour is equal to 0.07). This is due to a stronger self-relaxation of the SOMO during radical oxidation as compared to that in the reduction.

For ethylene, the off-diagonal FF in backward donation has qualitatively the same features as that in forward donation. In contrast, diagonal FF's of ethylene are quite different from each other. In backward donation, the diagonal FF is dominated by the LUMO density (see eq 8a), while the HOMO dominates in forward donation. The contours are more expanded toward the radical due to mixing with the carbon 2s orbital. There is no significant increase or decrease in electron density between carbon atoms. Thus, σ/π polarization is unimportant during reduction of ethylene.

The CT FF and its components condensed to the AIM resolution are collected in Table 1. Data for CT in both directions are reported. Similarly to the plots of CT FF's, we present the negative vectors $\boldsymbol{f}_{\mathrm{BB}}^{\mathrm{M}}$ and $\boldsymbol{f}_{\mathrm{BA}}^{\mathrm{M}}$ (see eq 10). After this modification, positive (negative) values correspond to inflow (outflow) of electrons into (from) a given atom. Noteworthy is that only for C and C′ atoms do diagonal and off-diagonal contributions act in phase. Thus, off-diagonal FF indices additionally strengthen diagonal components of the overall CT FF. For the remaining atoms, off-diagonal FF responses weaken diagonal FF indices. These observations are true for CT in both directions. Thus, magnitudes of CT FF indices of the interacting carbon atoms (C and C′ in Table 1) are significantly higher than those of the remaining atoms. Nevertheless, this is not only due to the fact that diagonal and off-diagonal responses act in phase but also due to the highest magnitude of off-diagonal components.

The total CT FF of the whole reactive system is given as sum of CT FF's of the subsystems A and B: $f^{\mathrm{CT}} = f_{\mathrm{A}}^{\mathrm{CT}} + f_{\mathrm{B}}^{\mathrm{CT}}$. Parts a and b of Figure 4 show contour maps of total CT FF's

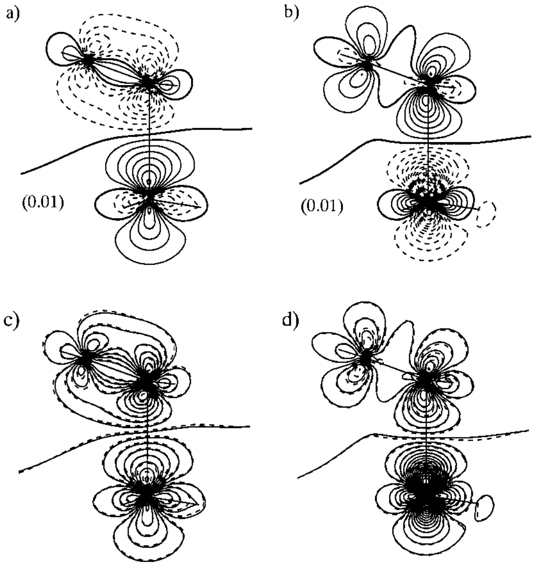

Figure 4. Contour maps of the total CT FF [$f^{\mathrm{CT}}(\vec{r})$]. On the left-hand side (panels a and c), CT from ethylene (B) to the methyl radical (A) is assumed (forward CT), while on the right-hand side (panels b and d), CT from the methyl radical (B) to ethylene (A) is assumed (backward CT). In the first row, $f^{\mathrm{CT}}(\vec{r})$ is computed by eq 6b. In the second row, comparison between the CT FF obtained from eq 6b (solid line) and that obtained from eq 9 (broken line) is given.

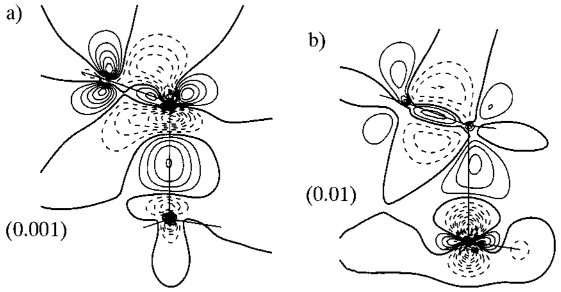

Figure 5. Contour maps describing the change in electron density, $\Delta\rho(\vec{r}) = \rho^{(\mathrm{A}\vdots\mathrm{B})}(\vec{r}) - \rho^{(\mathrm{A|B})}(\vec{r})$ (panel a), and the radical CT FF, $f_{\mathrm{r}}^{\mathrm{CT}}(\vec{r}) = f_{\mathrm{ethylene}\rightarrow\mathrm{radical}}^{\mathrm{CT}}(\vec{r}) + f_{\mathrm{radical}\rightarrow\mathrm{ethylene}}^{\mathrm{CT}}(\vec{r})$ (panel b).

for forward and backward donations, respectively. To obtain these plots, CT FF's derived from diagonal and off-diagonal components were employed. Namely, the plots in Figure 4a,b are based on the plots of CT FF's shown in Figures 2 and 3. As pointed out in section 2, the CT FF can also be obtained directly from eq 9. In Figure 4c,d, the contour plots of the total CT FF's obtained from direct calculations (according to eq 9) are superimposed on those derived from diagonal and off-diagonal components. The former are plotted in broken lines and the latter in solid lines. The contour plots obtained in both methods are almost indistinguishable from each other for forward (Figure 4c) and backward (Figure 4d) donations. Thus, we can safely conclude that the SCCCMS scheme adequately describes mutual polarization of subsystems (reactants). The CT FF obtained from SCCCMS calculations can be considered as a "function of state".

Reorganization of electron density caused by CT can be considered as $\Delta\rho(\vec{r}) = \rho^{(\mathrm{A}\vdots\mathrm{B})}(\vec{r}) - \rho^{(\mathrm{A|B})}(\vec{r})$, i.e., the difference between electron density calculated for the supermolecule, M = (A⋮B), and that calculated for a hypothetical stage in which subsystems are mutually closed but polarized, M = (A|B). The SCCCMS scheme gives electron density for M = (A|B). Figure 5a shows $\Delta\rho(\vec{r})$ for the addition of a methyl radical to ethylene in the transition state configuration. Reorganization in electron density due to CT should be proportional to the CT FF, $\Delta\rho(\vec{r}) = f^{\mathrm{CT}}(\vec{r})\,\mathrm{d}N_{\mathrm{CT}}$. However, $\Delta\rho(\vec{r})$ shown in Figure 5a does not resemble either the plot of the forward CT FF (Figure 4a) or that of the backward CT FF (Figure 4b). It is noteworthy that the sum of forward and backward CT FF's, i.e., the radical CT FF shown in Figure 5b (see eq 13), reproduces quite well the characteristic features (positive and negative basins) of the contour plot of Figure 5a. Thus, it can be concluded that forward and backward CT channels are both important in the transition state for the addition of a methyl radical to ethylene. In general, the expression $\Delta\rho(\vec{r}) = f_{\mathrm{alkene}\rightarrow\mathrm{radical}}^{\mathrm{CT}}(\vec{r})\,\mathrm{d}N_{\mathrm{CT}} + f_{\mathrm{radical}\rightarrow\mathrm{alkene}}^{\mathrm{CT}}(\vec{r})\,\mathrm{d}N'_{\mathrm{CT}}$ should better describe reorganization of electron density due to CT. The least-squares fitting gives $\mathrm{d}N_{\mathrm{CT}} = 0.10$ and $\mathrm{d}N'_{\mathrm{CT}} = 0.07$. Thus, there is a net donation from alkene to radical (0.03). Consequently, the HOMO/SOMO interaction dominates the LUMO/SOMO interaction. These findings are in accord with chemical potentials of the methyl radical and ethylene[21] and are also consistent with the results of supermolecule calculations.

5. Conclusions

In this paper, the finite-difference approach has been used to derive expressions for the charge transfer Fukui function in local and in AIM resolutions. The obtained results extend the known approach of Parr and Yang[1,2] or Yang and Mortier[3] to reactive systems. Our formalism can be applied to follow reorganization of electron density during reactive chemical interactions.

Addition of a methyl radical to ethylene has been taken as an illustrative example. The results clearly show that the SCCCMS scheme correctly describes polarized reactants (before CT); the CT FF obtained for two-step process and that obtained for a one-step process are almost indistinguishable. Decomposition of the CT FF of reactants into diagonal and off-diagonal responses gives additional information about charge reorganization. The off-diagonal CT FF's of ethylene are strongly localized and resemble densities of hybrid-type orbitals. They have significant contributions to the CT FF's. This is especially emphasized in the AIM resolution, where the off-diagonal responses of interacting atoms have greater contributions than diagonal responses. Such off-diagonal contributions to overall CT FF's should be of great importance in π-electron systems and should significantly modify diagonal FF's. The radical CT FF, which is the sum of forward and backward CT FF's, reproduces well the reorganization of electron density due to CT. Thus, forward (ethylene → methyl radical) and backward (methyl radical → ethylene) donations are both important in methyl radical addition to ethylene. However, the former donation slightly dominates the latter.

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