

Study of atomic and condensed atomic indices for reactive sites of molecules

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Abstract. In this paper, we have introduced the atomic descriptors $s(f)_k$ to determine the local reactive sites of the molecular systems during electrophilic, nucleophilic and radical attacks. The condensed Fukui function and the newly introduced condensed atomic descriptor have been calculated for six different systems, namely glycine, alanine, aniline, BH_2Cl , *trans*-FC(O)OF and *m*-anisidine. The individual atomic charges (gross charge) calculated by the MPA scheme have been used to calculate the condensed Fukui functions (f_k) and the newly derived condensed atomic descriptors (sf_k)^a at B1-DZP level of theory. We carried out the calculation using the “stockholders” charge partitioning technique (i.e., Hirshfeld population scheme). The newly derived quantity gives the same reactive sites as the condensed Fukui functions, and the complexities associated with the negative Fukui functions are removed.

Keywords. Condensed Fukui functions; atomic descriptors; condensed atomic descriptors; electrophilic; nucleophilic; radical attacks.

1. Introduction

Density functional theory (DFT)¹ is one of the important tools of quantum chemistry to understand the popular chemical concepts like electronegativity and chemical potential,² ionization potential and electron affinity³ etc. The electron density based local reactivity descriptors; local hardness $h(r)$,⁴ local softness $s(r)$ and the Fukui function $f(r)$ ⁵ were proposed to explain the chemical selectivity or reactivity at a particular site of a chemical system. Recently, Geerlings *et al*⁶ showed that these local descriptors of DFT are essentially important in searching the “similarity of reactivity” of a group of molecules or atoms that are similar (in their structure and by extension in their electron density distribution). Electron density $\mathbf{r}(r)$ is a property that contains all of the information about the molecular system and plays an important role in calculating almost all these chemical quantities. It has also been shown that local hardness $h(r)$ is a reliable intermolecular reactivity descriptor,^{7,8} and the local softness $s(r)$ and Fukui function $f(r)$ are more reliable intramolecular site selectivity descriptors.^{9,10} Several attempts have been made to evaluate the Fukui function (FF) indices. Parr and Yang¹¹ proposed a finite difference (FD) approach to calculate FF indices i.e., nucleophilic, electrophilic, and

radical attacks. Further, number of methods and algorithms have been developed based on the partition of $\mathbf{r}(r)$ on different atoms to define Fukui functions condensed on certain atomic regions. Yang and Mortier¹² proposed three different condensed forms of $f(r)$, based on atomic charges of N , $N + 1$, and $N - 1$ electron systems. Nalewajski¹³ has studied the $f(r)$ indices in respect of atom-in-molecules (AIM). Cioslowski *et al*¹⁴ have developed an FD approach based on spin-polarized method to calculate the Fukui function indices in the framework of the AIM method of Bader.¹⁵ The atomic and group resolution of $f(r)$ indices based on semiempirical method was proposed by Komorowski *et al*¹⁶. Although these indices are successful in generating the experimentally observed intramolecular reactivity trends in many systems,^{8,9} the occurrence of negative Fukui function has remained a puzzle for a long time. Senthilkumar *et al*¹⁷ have shown the existence of negative Fukui functions in a few triatomic molecules, where they discussed the correlation between effective hardness and condensed Fukui function using AIM, *ab initio* and DFT methods. In order to solve the negative Fukui function problem, different attempts have been made by various groups.¹⁸ Two different local reactivity descriptors, “relative nucleophilicity” and “relative electrophilicity”, introduced by Roy *et al*¹⁹ based on FF indices solved the above problem. Roy *et al*^{19,20} have discussed several reasons for the appearance of negative

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FF values. One of the reasons, they have argued, is that according to the analytic definition of FF it is valid only when $\Delta N \rightarrow 0$. In that case, the fluctuation in the electron density distribution is minimal due to negligible relaxation in the corresponding cation and anion. However, in the definition of condensed FF's or local softness calculated by the finite difference method, we allow a change of the electron number by a large quantity, i.e., 1 and as a result there is a significant change in the electron-density distribution due to large relaxation in the corresponding cation and anion. This may cause depletion/accumulation of electron density on a particular site even though the global electron number is increased/decreased by 1. Another probable reason for the occurrence of negative FF indices might be the partitioning scheme, which we adopt to evaluate the condensed FF values. The well-known population schemes, Mulliken population analysis (MPA),²¹ natural population analysis (NPA)²² and molecular electrostatic potential (MESP) are found to produce negative FF values due to the inappropriate partitioning of charges. Roy *et al*¹⁹ proposed that the use of the stockholders' partitioning technique (Hirshfeld Population Analysis) developed by Hirshfeld²³ provides non-negative Fukui function values. The basic idea of this scheme is that the partitioning of electron density to different atoms is fixed for N , $N + 1$ and $N - 1$ electron systems. The use of constant ratio ("sharing function") in N , $N + 1$ and $N - 1$ electron systems is the probable reason behind the HPA producing reliable positive FF values where in other popularly known schemes, this partitioning is improper. Chattaraj *et al*²⁴ have proposed a "local philicity index" by generalizing both local and global electrophilicity as well as nucleophilicity, from the identity associated with the normalization of the Fukui function. Since the local philicity is a product of the FF and the global electrophilicity, it takes care of the local intramolecular (unlike FF) reactivity and site selectivity and the philicity is found to be positive everywhere. In this paper, we have established a new descriptor called "atomic descriptor" that greatly increases our understanding of the atomic sites. This newly introduced atomic descriptor not only contains profound information regarding electrophilic/nucleophilic local sites of a given molecule, but also removes the complexity associated with negative Fukui functions $f(r)$. A special treatment of the condensed atomic descriptors has been made on some small biomolecules such as glycine and alanine and some organic molecules such as aniline,

BH_2Cl , *trans*-FC(O)OF and *m*-anisidine. Due to the inherent nature of the population schemes, an attempt has been made to compare the reactive atomic sites calculated in a molecule by f_k values with that of the sites obtained by the new descriptor.

2. Theoretical aspects

2.1 Local reactivity descriptors

The Fukui function proposed by Parr and Yang¹¹ is one of the local reactivity indices that represent the system's response to a simultaneous perturbation in the total number of electrons N and the external potential $v(r)$ due to the compensating positive (nuclear) charges in the system. Fukui function $f(r)$ is defined as,

$$f(r) = (\mathbf{dm} \mathbf{dv}(r))_N = (\partial \mathbf{r}(r) / \partial N)_{v(r)}. \quad (1)$$

The local softness, which describes the response of any particular site of a chemical species (in terms of a change in electron density $\mathbf{r}(r)$ to any global change in its chemical potential), is given by

$$s(r) = (\partial \mathbf{r}(r) / \partial \mathbf{m})_{v(r)}. \quad (2)$$

where $\mathbf{r}(r)$ is the electron density at the site r , and \mathbf{m} is the chemical potential which is the negative of the electronegativity.²

The parameter $s(r)$ obeys the condition,

$$\int s(r) dr = S, \quad (3)$$

where S is the global softness which is defined as

$$S = 1/2 \mathbf{h} = (\partial N / \partial \mathbf{m})_{v(r)}. \quad (4)$$

Rewriting (3) and then combining (1), (2) and (4) we have,

$$s(r) = \left(\frac{\partial \mathbf{r}(r)}{\partial N} \right)_{v(r)} \left(\frac{\partial N}{\partial \mathbf{m}} \right)_{v(r)} = f(r) S = \left(\frac{\partial \mathbf{m}}{\partial v(r)} \right)_N S, \quad (5)$$

where $f(r)$ is the Fukui function introduced by Parr and Yang.¹¹ Thus it is clear from (5) $f(r)$ can be used to study the relative site selectivity in a molecule (intramolecular reactivity sequence) where as $s(r)$ which contains global softness, in its definition,

can be used as an indicator when comparing the reactivity of different molecules with respect to a common reaction partner.

The local softness condensed to an atom site say k , can be written as,

$$s_k^a = f_k^a S. \quad (6)$$

The Fukui function is an index of considerable importance for understanding the molecular behaviour of the species (neutral, monopositive and mononegative ions) under study. The evaluation of the Fukui function values is not straightforward due to the difficulties associated with solving the derivatives given in (1). Yang and Mortier¹² have given a simple procedure to calculate the atomic condensed Fukui function indices based on Mulliken population analysis (MPA) and on three possible forward, backward, and central finite difference approximations to the derivatives of (1), and can be written as,

$$f_k^-(r) = q_k(N) - q_k(N-1),$$

governing electrophilic attack, (7a)

$$f_k^+(r) = q_k(N+1) - q_k(N),$$

governing nucleophilic attack, (7b)

$$f_k^0(r) = \frac{1}{2}(q_k(N+1) - q_k(N-1)),$$

governing radical attack, (7c)

where f_k^- and f_k^+ describe the ability of an atom to accommodate an extra electron or to cope with the loss of an electron and f_k^0 is then considered an indicator for radical reactivity.

The behaviour of molecules as electrophiles/nucleophiles during reaction depends on the local behaviour of molecules, i.e. on how the atomic sites of the molecule react towards the approaching reagent (electrophile/nucleophile/radical). So it is very important to infer the reactivity trends of local site during electrophilic or nucleophilic attack. As we know well, the intra molecular reactivity can be explained by either $s(r)$ or $f(r)$. In the present study, we pooled the local reactivity $f(r)$ and the local site selectivity $s(r)$ given in (6) and (7), as follows.

Considering the identity that $f_k/f_k = 1$, in (6), we have,

$$s_k^a = f_k^a S.(f_k^a / f_k^a),$$

$$(sf)_k = (f_k)^2 S. \quad (8)$$

It may be noted that in (6) the function ‘‘atomic descriptor’’ $(sf)_k$, contains information on both s_k and f_k . It takes care of both the local reactivity and selectivity of a molecule. This parameter allows one to infer the behaviour of local sites during electrophilic, nucleophilic and radical attacks since it is the combination of two local descriptors s_k and f_k that concerns more about selectivity and reactivity of the atomic species in addition to the global function S .

Three different types of condensed atomic descriptors $(sf)_k^a$ can be readily obtained as,

$$(sf)_k^a = (f_k^a)^2 S, \quad (9)$$

where $a = +/-/0$ refer to nucleophilic, electrophilic and radical attacks, respectively.

i.e.

$$s_k^+ f_k^+ = (f_k^+)^2 S,$$

governing electrophilic attack, (10a)

$$s_k^- f_k^- = (f_k^-)^2 S,$$

governing nucleophilic attack, (10b)

$$s_k^0 f_k^0 = (f_k^0)^2 S, \quad \text{governing radical attack,} \quad (10c)$$

where (10a) predicts that the most electrophilic site in a molecule is the one which has the maximum $s_k^+ f_k^+$ value, which in turn is the softest region in a molecule.

3. Computational details

In the present study, we have chosen the low energy structures of two amino acids glycine and alanine^{25,26} and some organic molecules such as aniline, BH_2Cl , *trans*-FC(O)OF and *m*-anisidine to examine their preferred reactive sites in the gas phase and to examine the reliability of the newly described atomic descriptor. Since DFT method has provided comparatively good results on FF values,²⁷ we have chosen gradient corrected BLYP with LDA VWN correlation potential method for the computations. All the structures have been optimized at the gradient corrected BLYP method, with LDA VWN²⁸ correlation functionals (we represent it as B1). The Huzinaga double-zeta basis set²⁹ with polarization

(DZP) is used. For the above theory a vibrational analysis was performed for each optimized structures and in all the cases, it was verified that all the vibrational frequencies were positive indicating that all the structures were an energy minimum. Single point energy calculations have been performed at the above level of theory for the anions and cations of the conformers using the ground state optimized structure with doublet multiplicity. The individual atomic charges (gross charge) calculated by MPA have been used to calculate the Condensed Fukui functions (f_k) and the newly derived descriptors (sf_k)_k at B1-DZP level of theory using Amsterdam Density Functional program package (ADF).³⁰ In order to check the reliability of Stockholders' charge partitioning technique i.e., Hirshfeld population analysis over MPA, the reactivity descriptors have also been calculated by the gross charges of HPA at B1/DZP level of theory.

4. Results and discussion

Tables 1 to 6 show the f_k and (sf_k)_k values for the molecules, glycine, alanine, aniline, BH₂Cl, *trans*-FC(O)OF and *m*-anisidine calculated by MPA and HPA gross charges at B1/DZP level of theory. The optimized structures are shown in figure 1 in which the numbering of all the atoms is depicted.

From the tables one can find that the complexities associated with f_k values due to the negative values being removed in the (sf_k)_k values. In order to confirm that the atomic descriptor would produce the reactive sites without disturbing the trend, we have performed the calculation for the reactive sites of the stable structures of the glycine and alanine systems. The basicity of amines has been a challenge

for the DFT descriptors of reactivity. Moreover, the basicity of amines can be studied by looking at the nucleophilic sites calculated by FF values. Theoretical calculations on some organic molecules including glycine and alanine has been carried out by Patricia Pérez *et al*³¹ to study reactivity, selectivity and site activation sites. In their work, they have concluded that the N atom of the amino group is the preferred site for protonation. The explanation in favor of N₃ to be the most favourable reactive site for protonation is that (i) the hydrogen atoms of N₃ are involved in intra-molecular hydrogen bonding with O₅, which is doubly bonded with C₁, and also (ii) the oxygen atom O₅ pulls the electron density from the C₁ carbon atom due to its higher electronegativity and consequently partial charges develop on these sites (O₅ and C₁), leaving the nitrogen atom N₃ the electron-rich site for protonation. The calculated condensed FF and (sf_k)_k values of glycine are reported in table 1. Here in the case of glycine, it has been found both that the MPA and HPA schemes predict N₃ attached to C₁ has higher f_k^- value for electrophilic attack. The observed electrophilicity trend in all the conformers is N₃ > O₅ > O₄. The observation of the reactive sites by (sf_k)_k is found almost identical to f_k . Even though the (sf_k)_k values are numerically less it should be worth noting that the values are positive and the ordering of the reactivity has not been changed in any cases. Both the schemes show that C₁ and O₅ in carboxyl group as the reactive sites for receiving a nucleophile.

In table 2, the condensed f_k and atomic descriptor (sf_k)_k values for the atoms of alanine are shown. As expected, in almost all the cases the N atom is found to the most preferred site for protonation since in this conformer there is an intra molecular interaction

Table 1. Condensed Fukui function f_k and new descriptors (sf_k)_k (10^{-2}) for glycine.

Atoms	B1-DZP/MPA				B1-DZP/HPA			
	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$
C ₁	0.2625	0.0987	1.4188	0.2006	0.2261	0.0772	0.1052	0.1227
C ₂	-0.0606	-0.0009	0.0756	0.0000	0.0676	0.0716	0.0940	0.1055
N ₃	0.0235	0.2248	0.0114	1.0405	0.0499	0.2473	0.0512	0.1259
O ₄	0.0696	0.0644	0.0997	0.0854	0.1223	0.0970	0.3078	0.1936
O ₅	0.1835	0.1801	0.6933	0.6679	0.2177	0.1824	0.9754	0.6847
H ₆	0.1605	0.0913	0.5304	0.1716	0.0915	0.0575	0.1723	0.0680
H ₇	0.1602	0.0914	0.5284	0.1720	0.0915	0.0575	0.1723	0.0680
H ₈	0.1095	0.0621	0.2469	0.0794	0.0713	0.0527	0.1046	0.0572
H ₉	0.0457	0.0941	0.0430	0.1823	0.0311	0.0783	0.0199	0.1262
H ₁₀	0.0456	0.0940	0.0428	0.1819	0.0311	0.0783	0.0199	0.1262

Table 2. Condensed Fukui function f_k and new descriptors $(sf)_k$ (10^{-2}) for alanine.

Atoms	B1-DZP/MPA				B1-DZP/HPA			
	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$
C ₁	0.1734	0.0982	0.6248	0.2004	0.1554	0.0721	0.5016	0.1080
C ₂	-0.0568	-0.0273	0.0067	0.0155	0.0468	0.0536	0.0455	0.0597
N ₃	0.0031	0.2150	0.0010	0.9605	0.0468	0.2270	0.0455	1.0703
O ₄	0.0296	0.0579	0.0182	0.0697	0.1030	0.0889	0.2203	0.1641
O ₅	0.1201	0.1694	0.2997	0.5963	0.1560	0.1708	0.5061	0.6059
H ₆	0.1666	0.0608	0.5768	0.0768	0.0902	0.0504	0.1690	0.0528
H ₇	0.1926	0.0858	0.7708	0.1529	0.0736	0.0509	0.1125	0.0538
C ₈	-0.1497	-0.0284	0.4657	0.0168	0.0686	0.0380	0.0977	0.0300
H ₉	0.0579	0.0909	0.0697	0.1717	0.0365	0.0718	0.0277	0.1071
H ₁₀	0.0728	0.0892	0.1101	0.1653	0.0385	0.0727	0.0308	0.1098
H ₁₁	0.1047	0.0528	0.2278	0.0579	0.0347	0.0279	0.0575	0.0162
H ₁₂	0.0780	0.0645	0.1264	0.0865	0.0457	0.0347	0.0434	0.0250
H ₁₃	0.2077	0.0711	0.8964	0.1051	0.0862	0.0412	0.1543	0.0353

Table 3. Condensed Fukui function f_k and new descriptors $(sf)_k$ (10^{-2}) for aniline.

Atoms	B1-DZP/MPA				B1-DZP/HPA			
	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$
C ₁	0.1037	0.0468	0.2608	0.0531	0.1095	0.0769	0.2909	0.1435
C ₂	0.0340	0.1093	0.0280	0.2897	0.0533	0.0744	0.0689	0.1343
C ₃	0.1035	0.0471	0.2598	0.0538	0.1097	0.0768	0.2919	0.1431
C ₄	0.1161	0.0529	0.3269	0.0679	0.1184	0.0635	0.3401	0.0978
C ₅	-0.0068	0.0700	0.0011	0.1188	0.0592	0.1240	0.0850	0.3730
C ₆	0.1163	0.0531	0.3280	0.0684	0.1187	0.0634	0.3418	0.0975
N ₇	0.0447	0.1512	0.0484	0.5544	0.0597	0.1651	0.0865	0.6613
H ₈	0.0304	0.0548	0.0224	0.0728	0.0423	0.0666	0.0434	0.1076
H ₉	0.0306	0.0548	0.0227	0.0728	0.0424	0.0666	0.0436	0.1076
H ₁₀	0.0872	0.0660	0.1844	0.1056	0.0577	0.0419	0.0808	0.0426
H ₁₁	0.0916	0.0683	0.2035	0.1131	0.0621	0.0440	0.0936	0.0470
H ₁₂	0.0696	0.0915	0.1175	0.2030	0.0467	0.0515	0.0529	0.0643
H ₁₃	0.0918	0.0683	0.2044	0.1131	0.0621	0.0440	0.0936	0.0470
H ₁₄	0.0871	0.0659	0.1840	0.1053	0.0578	0.0418	0.0810	0.0424

Table 4. Condensed Fukui function f_k and new descriptors $(sf)_k$ (10^{-2}) for BH₂Cl.

Atoms	B1-DZP/MPA				B1-DZP/HPA			
	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$
B ₁	0.5752	0.1983	7.0968	0.8435	0.4651	0.1914	4.6400	0.7858
Cl ₂	0.2220	0.5090	1.0571	5.5573	0.2832	0.5106	1.7203	5.5923
H ₃	0.1014	0.1464	0.2205	0.4597	0.1258	0.1490	0.3395	0.4762
H ₄	0.1014	0.1464	0.2205	0.4597	0.1258	0.1490	0.3395	0.4762

that takes place between the N–H...O group. The order of nucleophilic site as obtained by HPA is N₃ > O₅ > O₃. The MPA scheme shows that C₁ and H₁₃ attached to carbon atom as the most reactive site

during nucleophilic attack whereas HPA shows C₁ and O₅ in carboxyl group as the reactive sites for receiving a nucleophile. Looking deeper into the reactive sites predicted by f_k and $(sf)_k$ for glycine and

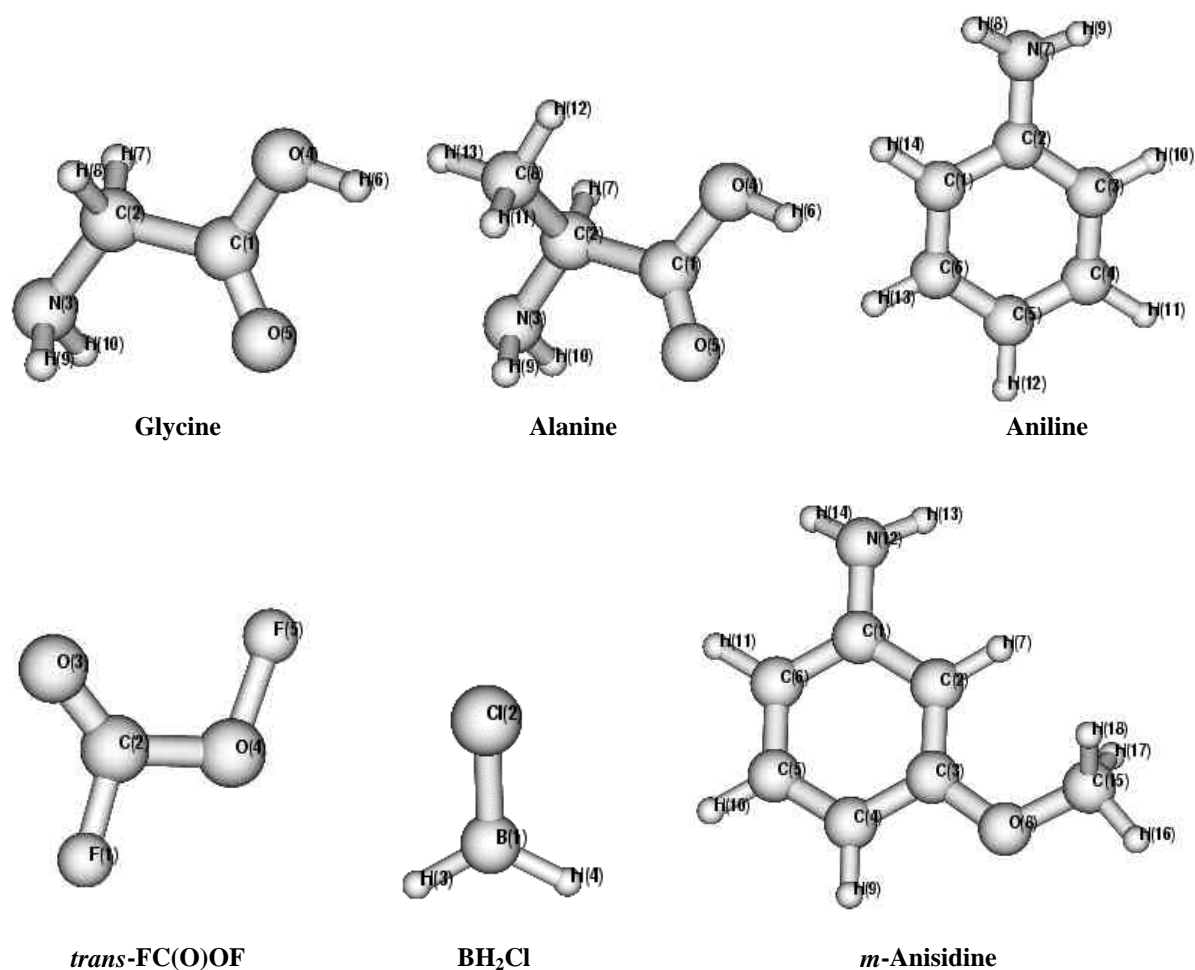


Figure 1. Equilibrium geometries of molecules taken in the present study (atomic sites are numbered).

Table 5. Condensed Fukui function f_k and new descriptors $(sf)_k$ (10^{-2}) for *trans*-FC(O)OF.

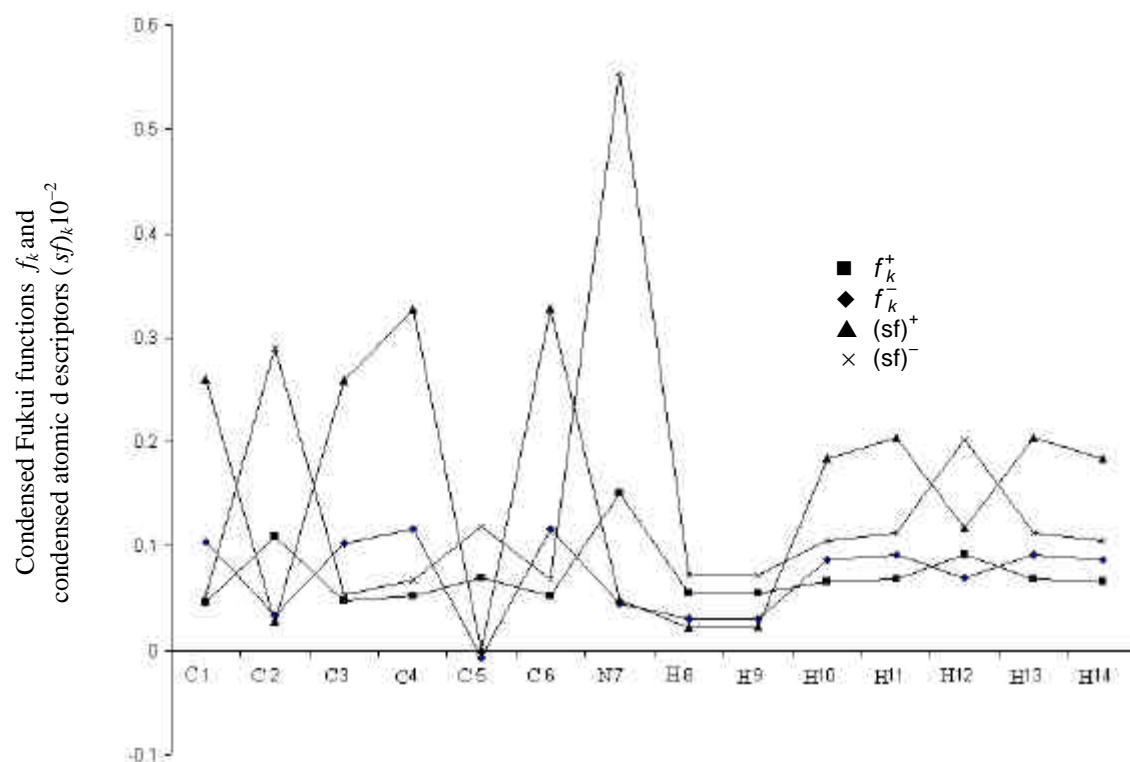
Atoms	B1-DZP/MPA				B1-DZP/HPA			
	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$
F ₁	0.0775	0.1412	0.1598	0.5305	0.1338	0.1640	0.4760	0.7157
C ₂	0.1855	0.1841	0.9157	0.9019	0.3620	0.1643	3.4871	0.7183
O ₃	0.124	0.3667	0.4092	3.5782	0.1006	0.1347	0.2693	0.4828
O ₄	0.2816	0.1544	2.1101	0.6343	0.0140	0.3720	0.5216	3.6824
F ₅	0.3313	0.1537	2.9207	0.6286	0.2636	0.1650	1.8490	0.7245

alanine, it is clear that in these systems the formation of reactive sites depend mainly on the presence of intramolecular hydrogen bonding. It is worthy of mention that the $(sf)_k$ also predict the reactivity as FF values predict, which confirms that these new atomic descriptors can also be used to study the local reactivity in molecular systems.

Analysis on the reliability of newly derived descriptor has been further extended to certain organic molecules. Calculated condensed FF values and the $(sf)_k$ values for aniline are given in table 3. Aniline and its *p*-substituted systems are found to be N-protonated and this was concluded by Summerhays *et al*³² in their experimental study. Roy *et al*¹⁹ have

Table 6. Condensed Fukui function f_k and new descriptors $(sf)_k$ (10^{-2}) for *m*-anisidine.

Atoms	B1-DZP/MPA				B1-DZP/HPA			
	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$	f_k^+	f_k^-	$s_k^+ f_k^+$	$s_k^- f_k^-$
C ₄	0.0628	0.0808	0.0942	0.1559	0.0796	0.1234	0.1513	0.3636
C ₆	0.0343	0.0681	0.0281	0.1107	0.0575	0.1104	0.0790	0.2911
N ₁₂	0.0012	0.0781	0.0000	0.1457	0.0627	0.1153	0.0939	0.3175

**Figure 2.** Condensed Fukui function and condensed atomic descriptors of aniline by MPA gross charges using B1-DZP level of theory.

proved theoretically that N is the preferred site for protonation also. It is clear from the values of FF and $(sf)_k$ that N is a possible site for protonation and the results are in agreement with previous studies. In the case of nucleophilic attack, the atoms C₄ and C₆ are found to be the most preferred sites. The graphical representation of condensed Fukui function and condensed atomic descriptors calculated by MPA charges is given in figure 2. It clearly shows that the condensed atomic descriptors predict the reactive sites as that of the condensed Fukui functions without disturbing the trend. Arulmozhiraja *et al*³³ have made a detailed study on the reactive sites of several organic molecules and some isomers based on atomic charges calculated by MPA and NPA analysis at the local sites of a molecule. We have chosen BH₂Cl and *trans*-FC(O)OF molecules to discuss the

reliability of atomic descriptors. In the case of BH₂Cl, FF and $(sf)_k$ values using different population schemes are depicted in table 4. The reactive sites evaluated³³ are as follows: f^+ , B > Cl > H; f^- , Cl > H > B. The order of reactive sites calculated in the present study matches well with the order predicted by the previous work. The calculated f_k values predict that B and Cl atoms are the possible sites for nucleophilic and electrophilic attacks, respectively. The atomic descriptors $(sf)_k$ also predicts the same reactivity with the same order and the values are found to be positive. For *trans*-FC(O)OF system the calculated FF and $(sf)_k$ values are given in table 5. The calculated condensed FF values thus predict F₅ attached to O₄ and O₄ atom attached to F₅ as possible reactive sites for nucleophilic and electrophilic attacks respectively. Hence the reactive sites and the

order of reactivity produced by the new atomic descriptor are found to be identical with that of f_k values and the values are positive. In order to discuss the importance of the atomic descriptor, the protonation site of the molecule *m*-anisidine has also been considered in this study. We have given only the most favourable reactive sites in the table 6. Both the MPA and HPA schemes predict that C₄ atom to be the most reactive site for protonation during electrophilic attack, as reported by Summerhays *et al*³² experimentally.

5. Conclusion

In this paper, we have introduced an atomic descriptor $(sf)_k$ to determine the local reactive sites for the molecular systems during electrophilic, nucleophilic and radical attacks. The results clearly show once again the superiority of HPA over MPA scheme. An analysis on the nature of newly derived “atomic descriptors” demonstrates that the issue of negative Fukui functions has been overcome. The reactive sites predicted by condensed Fukui functions f_k during electrophilic, nucleophilic and radical attacks are successfully reproduced by these new condensed atomic descriptors $(sf)_k$. This descriptor is found to be influential, since, it contains information on both the local reactivity and selectivity of a molecule. Even though the ordering of reactive sites in the molecules has not changed, the numerical values of the descriptors are found to be very low. This quantity is always positive and shows reactive trends as Fukui function predicts.

References

- Hohenberg P and Kohn W 1964 *Phys. Rev.* **B136** 864
- Parr R G, Donnelly R A, Levy M and Palke W E J 1978 *Chem. Phys.* **68** 3801
- Perdew J P, Parr R G, Levy M and Balduz J L 1982 *Phys. Rev. Lett.* **49** 1691; Pal S, Roy R K and Chandra 1994 *J. Phys. Chem.* **98** 2314
- Gosh S K and Berkowitz M 1985 *J. Chem. Phys.* **83** 2976
- Yang W and Parr R G 1985 *Proc. Natl. Acad. Sci. USA* **82** 6723
- Geerlings P, Boon G, van Alsenoy C and De Proft F 2005 *Int. J. Quantum Chem.* **101** 722
- Langenaekar W, De Proft F and Geerlings P 1995 *J. Phys. Chem.* **99** 6424
- Roy R K, Krishnamurti S, Geerlings P and Pal S 1998 *J. Phys. Chem.* **102** 3746
- De Proft F, Langenaekar W and Geerlings P 1993 *J. Phys. Chem.* **97** 1876; Langenaekar W, Coussement N, De Proft F and Geerlings P 1994 *J. Phys. Chem.* **98** 3010; De Proft F, Amira S, Choho K and Geerlings P 1994 *J. Phys. Chem.* **98** 5227; Langenaekar W, Demel K and Geerlings P 1992 *J. Mol. Struct: Theochem.* **259** 317; Langenaekar W, Demel K and Geerlings P 1991 *J. Mol. Struct: Theochem.* **234** 329; Baeten A, De Proft F, Langenaekar W and Geerlings P 1994 *J. Mol. Struct: Theochem.* **306** 203; Chandra A K, Geerlings P and Nguyen M T 1997 *J. Org. Chem.* **62** 6417; Sengupta D, Chandra A K and Nguyen M T 1997 *J. Org. Chem.* **62** 6404
- Krishnamurti S, Roy R K, Vetrivel R, Iwata S and Pal S 1997 *J. Phys. Chem.* **101** 7253
- Parr R G and Yang W J 1984 *Am. Chem. Soc.* **106** 4049
- Yang W and Mortier W J 1986 *J. Am. Chem. Soc.* **108** 5708
- Nalewajski R F 1993 *Structure and bonding* (Berlin: Springer) vol. 80, p. 115
- Cioslowski J, Martinov M and Mixon S T 1993 *J. Phys. Chem.* **97** 10948
- Bader R W F 1990 *Atoms in molecules a quantum theory*, Oxford Science Publications (London: Clarendon)
- Komorowski L, Lipinski J and Pyka M J 1993 *J. Phys. Chem.* **97** 3166; Komorowski L 1993 *Structure and bonding* (Berlin: Springer) vol. 80, p. 46
- Senthilkumar L and Kolandaivel P 2005 *Mol. Phys.* **103** 547
- Roy R K, Hirao K, Krishnamurti S and Pal S J 2001 *Chem. Phys.* **115** 2901; Bultinck P, Carbó-Dorca R and Langenaekar W J 2003 *Chem. Phys.* **118** 4349; Bultinck P and Carbó-Dorca R J 2003 *Math. Chem.* **34** 67
- Roy R K, Pal S and Hirao K 1999 *J. Chem. Phys.* **110** 8236
- Roy R K, Hirao K and Pal S 2000 *J. Chem. Phys.* **113** 1372
- Mulliken R S 1955 *J. Chem. Phys.* **23** 1833
- Reed A E and Weinhold F 1983 *J. Chem. Phys.* **F8** 4066
- Hirshfeld F L 1977 *Theor. Chim. Acta* **44** 129
- Chattaraj P K, Maiti B and Sarkar U 2003 *J. Phys. Chem.* **A107** 4873
- Császár A G 1992 *J. Am. Chem. Soc.* **114** 9568
- Császár A G 1996 *J. Phys. Chem.* **100** 3541
- De Proft F, Jan Martin M L and Geerlings P 1996 *Chem. Phys. Lett.* **256** 400
- Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
- Huzinaga S 1965 *J. Chem. Phys.* **42** 1293
- Baerends E J *et al* 2004 Amsterdam Density Functional Package, ADF 2004.01
- Pérez P, Parra-Mouchet J and Contreras R R 2004 *J. Chilean Chem. Soc.* **49**
- Summerhays K D, Pollack S K, Taft R W and Hehre W J 1977 *J. Am. Chem. Soc.* **99** 9585
- Arulmozhiraja S and Kolandaivel P 1997 *Mol. Phys.* **90** 55