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Condensed Fukui Functions Derived from Stockholder Charges: Assessment of Their Performance as Local Reactivity Descriptors

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Condensed Fukui function values of a number of closed-shell molecules have been calculated from Stockholder charges which were obtained using ab initio HF and DFT/B3LYP methods. The global softness parameters needed to evaluate local softness have been calculated using both Koopmans' approximation and the energy difference method. The calculated reactivity indices (condensed Fukui function and atomic softness) were used to predict the sites of electrophilic and nucleophilic attack in the molecules under investigation. In all cases, the atoms with the maximal value of condensed Fukui function and local softness are predicted to be the preferred sites of electrophilic or nucleophilic addition. The predictions thus made are in agreement with experiment and independent of the theoretical models used. The performance of the relative electrophilicity and relative nucleophilicity indices also was tested, but they were found not to have any special advantage as local reactivity descriptors.

1. Introduction

The frontier orbital (FO) theory proposed by Fukui[1] provides a general qualitative approach to understand and interpret chemical reactions. In this theory, the distribution of electron densities in the FOs (HOMO and LUMO) is recognized as the principal factor governing the stereoselective behavior of a molecule with respect to an approaching reagent. It was demonstrated by Parr and Yang[2] that the essential features of the FO theory could be rationalized in the framework of the density functional theory (DFT)[3]. They defined the Fukui function, $f(\mathbf{r})$, of a molecule reflecting the reactivity of a site as

$$f(\mathbf{r}) = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_{v(\mathbf{r})} \qquad (1)$$

where $\rho(\mathbf{r})$ is the electron density at $\mathbf{r}$, N is the number of electrons, and $v(\mathbf{r})$ is the external potential (electron−nucleus attraction potential plus any other potential applied to the system). The derivative of eq 1 is discontinuous for an atomic or molecular system. Parr and Yang[2] used a finite difference approximation (FDA) to evaluate this derivative and identified three types of Fukui functions, $f^+(\mathbf{r})$, $f^-(\mathbf{r})$, and $f^0(\mathbf{r})$, which correspond to electrophilic, nucleophilic, and free-radical attack, respectively. The explicit expressions of $f^\alpha(\mathbf{r})$ ($\alpha = +, -,$ and 0) are given by

$$f^+(\mathbf{r}) = \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r}) \qquad (2a)$$

$$f^-(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r}) \qquad (2b)$$

$$f^0(\mathbf{r}) = [\rho_{N+1}(\mathbf{r}) - \rho_{N-1}(\mathbf{r})]/2 \qquad (2c)$$

where $\rho_K(\mathbf{r})$ ($K = N - 1$, N, and $N + 1$) denotes the electron density at $\mathbf{r}$ of a K-electron system. Yang and Mortier[4] integrated $f^\alpha(\mathbf{r})$ over an atomic region and obtained numbers, which they designated as condensed Fukui functions, f_k^α, where k denotes an atom in a molecule. Because the integration of density over atomic regions gives electron population (Q_k) of atoms in a molecule, we have the following simple expressions for condensed Fukui functions.

$$f_k^+ = Q_k(N+1) - Q_k(N) \qquad (3a)$$

$$f_k^- = Q_k(N) - Q_k(N-1) \qquad (3b)$$

$$f_k^0 = [Q_k(N+1) - Q_k(N-1)]/2 \qquad (3c)$$

Meanwhile, the softness function was defined by Yang and Parr[5] by the relation

$$s(\mathbf{r}) = f(\mathbf{r})S \qquad (4)$$

where S, the global softness of a molecule is the inverse of global hardness (η). Integrating eq 4 over atomic regions leads to the definition of atomic or local softness.

$$s_k = f_k S \qquad (5)$$

Corresponding to three types of condensed Fukui functions, three types of local softness are defined from eq 5.

$$s_k^\alpha = f_k^\alpha S \qquad (6)$$

where $\alpha = +, -,$ and 0. The global softness is determined[6] using the relation

$$S = {}^1/_2\eta = 1/(I - A) \qquad (7)$$

where I is the vertical first ionization potential and A is the vertical first electron affinity of the N-electron system. It was suggested by Geerlings et al.[7] that local softness could be used

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as an intermolecular reactivity index and the Fukui function as an intramolecular index because the latter reflects the relative reactivity only among different sites in a molecule.

Ever since their inception, the condensed Fukui functions (which we have referred to as Fukui indices for the sake of brevity) and local softness indices have received overwhelming attention[8−24] as local reactivity descriptors. A number of methods and algorithms have been proposed[25−32] to evaluate f_k^α. Yang and Mortier[4] used Mulliken population analysis (MPA)[33] to define the atomic regions. Other PA schemes, such as NPA (natural population analysis)[34] and LPA (population analysis performed in Lowdin-orthogonalized basis functions),[35] have also been used to calculate Fukui indices. Cioslowski et al.[25] developed an FDA-based spin-polarized method to calculate Fukui indices in the framework of the atoms-in-molecules (AIM) method of Bader.[36] Condensed Fukui functions have been calculated also by methods[26] based on the electronegativity equalization principle.[37] A variational method[27] and an SCF procedure[28] were proposed for the calculation of molecular hardness and Fukui indices. Balawender and Komorowski (BK)[29] developed an ab initio method where $\partial\rho/\partial N$ in eq 1 is explicitly determined via $\partial C/\partial N$ (C is the coefficient matrix of the occupied HF MOs). Some non-FDA methods for the calculation of Fukui indices were also formulated[30,31] in the framework of the Kohn−Sham (KS)[38] density functional theory. On the basis of frozen orbital approximation, Contreras et al.[32] derived expressions for Fukui functions that are identical to the ones derived by Senet.[31]

The currently used FDA-based methods for the calculation of electron populations do not guarantee that $Q_k(N+1) > Q_k(N) > Q_k(N-1)$. This implies that one can obtain also negative values of Fukui indices (see eq 3). Such cases are encountered[11,14,17,19,25] not only in MPA, LPA, NPA, and AIM calculations of Fukui indices using HF, post-HF, and DFT wave functions but also in the ab initio approach of Balawender and Komorowski[29] (note that this a non-FDA method). Because negative values of Fukui indices (consequently of atomic softness) do not have any physical significance, it is highly desirable to find some means to get rid of such values. As shown by Roy et al.,[17b] the use of Stockholder charges[39] yields only positive values of Fukui indices. They were able to correctly predict the protonation sites in aniline and some substituted anilines using Fukui indices derived from Stockholder charges. They compared the performance of HF/6-31G*, HF/6-31G**, BLYP/dnd, and BLYP/dnp methods[40,41] in this regard. However, different partitioning schemes were employed in HF (MPA) and BLYP (Stockholder) methods. The nonnegativity of the Fukui indices has recently been examined[42] in greater details. Fuentealba et al.[42a] calculated these indices for the same molecules selected in ref 17 and 19 using the definition of Contreras et al.[32] and obtained positive values in almost all cases. Using convincing analytical arguments supported by numerical data, Pal and co-workers[42b] have shown how the negative Fukui indices appear in MPA and how this problem can be averted by using the Stockholder partioning scheme. In a subsequent paper,[42c] they have further shown that nothing can be predicted about the sign of MPA charge-based Fukui indices even when evaluated using very small molecular charge.

The main purpose of the present investigation is to assess the overall performance of the Stockholder charge-derived Fukui indices as reactivity descriptors. With this objective in mind, we have studied the reactivity of a number of closed-shell molecules comprising traditional electrophiles and nucleophiles. We have used HF and B3LYP[40a,43] methods in combination with the 6-311+G** and the 6-31G** basis sets. The Stockholder partioning scheme was shown[44] to have a sound basis in the information theory.[45] It has recently been successfully used by Nalewajski[46] to explore the entropic character of the chemical bond multiplicity. Because we have used only one version, nl. B3LYP, of Kohn−Sham (KS)/DFT methods, we have henceforth referred to it as DFT.

2. Method of Calculation

All calculations have been performed using geometries optimized for the parent compounds at HF and B3LYP levels of theory using 6-31G** and 6-311+ G** basis sets. The cations and anions of the selected molecules being open-shell species, their energies and wave functions have been calculated using the single-annihilated (the quartet state is projected out for a doublet state) UHF method. These calculations were performed using the Gaussian 98 program.[47] The condensed Fukui functions (f_k^+ and f_k^-) are obtained from Stockholder charges using eq 3. The Stockholder recipe for the calculation of atomic charge has been described elsewhere[48] in detail. We present here only the essential features of the method.

In the Stockholder partitioning scheme, one locally divides the molecular density among the constituent atoms in proportion to the isolated atom share in the density of the separated atoms limit (promolecule) shifted to the nuclear position **R** in the molecule. The stockhoder charge, q_k ($q_k = Q_k - Z_k$,where Z_k is the atomic number of atom k), is obtained by integrating the atomic deformation density

$$q_k = -\int \delta\rho_k(\mathbf{r})\, dr \tag{8}$$

where

$$\delta\rho_k(\mathbf{r}) = w_k(\mathbf{r})\Delta\rho(\mathbf{r}) \tag{9}$$

with

$$\Delta\rho_k(\mathbf{r}) = \rho^{mol}(\mathbf{r}) - \rho^{pro}(\mathbf{r}) = \rho^{mol}(\mathbf{r}) - \sum_k \rho_k^{at}(\mathbf{r}) \tag{10}$$

and

$$w_k(\mathbf{r}) = \rho_k^{at}(\mathbf{r})/\rho^{pro}(\mathbf{r}) \tag{11}$$

In eqs 11 and 12, $\rho^{mol}(\mathbf{r})$ and $\rho^{pro}(\mathbf{r})$ denote molecular and promolecular density, respectively.

Global softness (S) is evaluated using eq 7. The ionization potentials and electron affinities needed to determine S are calculated using both Koopmans' approximation ($I = -\epsilon_{HOMO}$ and $A = -\epsilon_{LUMO}$) and the energy difference (ED) method ($I = E_{n-1} - E_N$ and $A = E_N - E_{N+1}$).

3. Results and Discussion

The molecules chosen for this study are divided into the following five groups based on their structural similarity: (A) molecules containing a CO group (CO, CO_2, H_2CO, H_3CCOCH_3); (B) the anions (CN^-, NCO^-, CNO^-); (C) BX_3 (X = H, F, Cl) molecules; (D) aniline and *o*-, *m*-, and *p*-fluoroanilines; (E) molecules containing two competitive nucleophilic centers (C_6H_5NO, H_2NOH, HNO, HOF). The reactivity of these molecules will be discussed on the basis of Fukui indices (f_k^+ and f_k^-) and local softness parameters (s_k^+ and s_k^-). We also calculated the relative electrophilicity (s_k^+/s_k^-) and the relative nucleophilicity (s_k^-/s_k^+) indices, which were introduced by Roy et al.[16] These indices are, however, not tabulated because they were not found to have any special advantage. Before we present and discuss the results, some general remarks are necessary on the prevalent criteria of selecting a site for nucleophilic or electrophilic attack.

According to the guidelines proposed by Li and Evans,[49] the site of minimal (maximal) Fukui index is the preferred site for a hard (soft) reaction. This is usually known as the local HSAB (hard and soft acids and bases) principle.[50] It has been successfully applied to correlate the proton affinity of alkylamines and nicotinic acid derivatives[32] and N2-substituted *N*1,*N*1-dimethyl formamidines[18c] with the Fukui indices and local softness of the preferred sites. In hydroxylamine, aliphatic amino acids, and their methyl derivatives, the preferred site of protonation was chosen[18a] to be N (not O) because $f_N^- > f_O^-$. This is not in accordance with the local HSAB principle. In the same study, the local HSAB principle was, however, used to correlate the proton affinity of these molecules with s_N^-. Roy et al.[17b] selected the protonation site in aniline and substituted anilines using the criterion of maximal f_k^-/f_k^+ (electrophilicity index).Thus, there seems to be no unique recipe for selecting the most reactive local site in an electrophilic or a nucleophilic reaction. Once the reactive site is selected, the local HSAB principle is often applied to correlate the strength of interaction of a series of reactions with the softness indices of the selected atoms in different molecules. In this context, it may be noted that rank ordering of molecules on the basis of hardness still remains somewhat arbitrary. It is thus not possible to strictly categorize reactions as hard or soft.

With the above background information, we shall now proceed to discuss the results of the present investigation, which are summarized in Tables 1−5. A close scrutinee of these results reveals certain common features. For example, with respect to the variation of basis sets and levels of theory, the Fukui indices (f_k^-) for an electrophilic attack are generally more stable than the corresponding indices (f_k^+) for a nucleophilic attack. This variation is more pronounced in the case of CH_3COCH_3 (Table 1), CN^- (Table 2), and NH_2OH and HOF (Table 5). It was also observed that under similar variation the local softness indices in a molecule follow the same trend as that of the respective values of global softness (not tabulated). Because our main interest in this work is to choose the preferred site of reaction within a molecule, it will be sufficient to focus attention to the Fukui indices only. However, we shall occasionally refer to the other indices as well.

A. CO, CO_2, H_2CO, and CH_3COCH_3. Carbon monoxide (CO) is a soft base and carbon dioxide (CO_2) is a hard acid.[51] The latter reacts with OH^- to form HCO_3^-. The carbonyl group in H_2CO (formaldehyde) and CH_3COCH_3 (acetone) is highly susceptible to nucleophilic attack[52] by reagents, such as CN^- and NH_2OH. All four molecules can undergo protonation[51,53,54] and the pertinent reactions are exothermic. We shall interpret these reactions using the local reactivity indices of the molecules presented in Table 1. It can be seen that with the exception of f_k^+ and s_k^+ in acetone other local indices are fairly stable with respect to basis sets and levels (HF and DFT) of theory employed.

The HCO^+ ion is predicted[54] to be more stable than HOC^+ by about 38 kcal/mol. Thus, the carbon atom is the preferred site of protonation in CO. In the other three molecules, protonation takes place at the oxygen atom.[53,54] Because f_C^- is larger than f_O^- in CO and f_O^- is larger than f_C^- in CO_2, H_2CO, and CH_3COCH_3, the experimental observation can be interpreted using the criterion that the preferred site of protonation is the site with maximal f_k^-. The proton affinities of CO (for the formation of COH^+), CO_2, and H_2CO are about 104, 129, and 142 kcal/mol, respectively.[51,53,54] The s_O^- indices in these molecules vary in the same order. For the nucleophilic addition of CN^- and NH_2OH to H_2CO and CH_3COCH_3, the preferred site is known[52] to be the C atom ($f_C^+ > f_O^+$) of the carbonyl group. The Stockholder charges for the negative ion of CH_3COCH_3 were found to exhibit a rather bizarre trend with respect to the variation of basis sets and methods of calculation. The DFT/A and HF/A methods predict O to be the preferred site, while DFT/B and HF/B predict C to be the preferred site.

TABLE 1: Condensed Fukui Functions (f_k^+ and f_k^-) and Atomic Softness Indices (s_k^+ and s_k^-) of Some Molecules with a CO Group[a]

			$s_k^{+\,b}$			$s_k^{-\,b}$	
molecule	atom, k	f_k^+	KA	ED	f_k^-	KA	ED
CO	C	0.7473	2.1661	1.3081	0.6966	2.0192	1.2194
		0.6705	1.9174	1.0657	0.6883	1.9683	1.0938
		0.7646	1.2013	1.3614	0.7003	1.1002	1.2470
		0.6801	0.9522	1.1039	0.6931	0.9709	1.1248
	O	0.2527	0.7325	0.4424	0.3034	0.8794	0.5311
		0.3295	0.9422	0.5236	0.3117	0.8913	0.4954
		0.2359	0.3698	0.4190	0.2997	0.4709	0.5336
		0.3198	0.4180	0.4864	0.3069	0.4299	0.4981
CO_2	C	0.4607	1.2577	0.8475	0.2250	0.6143	0.4139
		0.4043	1.0110	0.6183	0.2193	0.5484	0.3319
		0.4158	0.6886	0.8035	0.1736	0.2875	0.3355
		0.4211	0.5446	0.6440	0.1649	0.2140	0.2522
	O	0.2696	0.7360	0.4960	0.3876	1.0581	0.7130
		0.2979	0.7450	0.4508	0.3963	0.9758	0.5906
		0.2921	0.4837	0.5645	0.4132	0.6843	0.7985
		0.2894	0.3756	0.4426	0.4176	0.5420	0.6387
H_2CO	C	0.4278	1.9664	0.9945	0.2337	1.0470	0.5433
		0.3948	1.7539	0.8373	0.2280	1.0129	0.4836
		0.4446	0.8712	1.0682	0.2324	0.4554	0.4747
		0.4038	0.6963	0.8984	0.2277	0.3926	0.5066
	O	0.3387	1.0561	0.5317	0.4379	2.0124	1.0180
		0.3078	1.3674	0.6528	0.4319	1.9187	0.9160
		0.2033	0.3984	0.4885	0.4817	0.9439	1.0715
		0.3050	0.5259	0.6786	0.4779	0.8241	1.0633
MeCOMe[c]	C	0.0474	0.2051	0.1201	0.1177	0.5093	0.2981
		0.2388	1.0608	0.5501	0.1186	0.5269	0.2732
		0.0370	0.0777	0.0958	0.1252	0.2630	0.3242
		0.2761	0.0479	0.6492	0.1256	0.2183	0.2953
	O	0.0601	0.2601	0.1522	0.3756	1.6252	0.9513
		0.2491	1.1066	0.5738	0.3735	1.6592	0.8603
		0.0547	0.1151	0.1417	0.4437	0.9321	1.1490
		0.2632	0.4575	0.6189	0.4438	0.7711	1.0436
	C_m	0.1025	0.4435	0.2596	0.0830	0.3591	0.2102
		0.0547	0.2430	0.1260	0.0795	0.3532	0.1831
		0.1043	0.2191	0.2701	0.0657	0.1380	0.1701
		0.0489	0.0850	0.1150	0.0616	0.1070	0.1448

[a] The four sets of values against each atom refer to DFT/A, DFT/B, HF/A, and HF/B calculations, respectively, where A = 6-311+G** and B = 6-31G**. [b] The two sets of values are calculated from ionization potentials and electron affinities obtained using Koopmans' approximation (KA) and the ED method. [c] C_m denotes a carbon atom of the methyl group.

B. CN^-, NCO^-, and CNO^-. These are all nucleophilic reagents. The calculated local indices of these ionic species are summarized in Table 2. According to the first-principles calculations (ab initio HF/6-31G*) of Balawender and Komorowski,[29] the s_C^- indices vary in the order CO > NCO^- > H_2CO and CNO^- > NCO^-. For the s_O^- and s_N^- indices, they observed the following order: H_2CO > NCO^- > CO and NCO^- > CN^- > CNO^-, respectively. The calculated values of local softness given in Tables 1 and 2 are in agreement with these sequences. Because HCN is more stable than HNC protonation of CN^- takes place preferably at the carbon (note that $f_C^+ >$

TABLE 2: Condensed Fukui Functions (f_k^+ and f_k^-)[a] and Atomic Softness Indices (s_k^+ and s_k^-)[b] of the Anions Studied in This Work

			s_k^+			s_k^-	
molecule	atom, k	f_k^+	KA	ED	f_k^-	KA	ED
CN^-	C	0.6362	2.6608	1.5310	0.6236	2.6081	1.5006
		0.5993	1.7847	1.0204	0.6024	1.7939	1.0256
		0.8674	1.9849	2.3071	0.6585	1.5068	1.7514
		0.6046	0.8941	1.0428	0.6376	0.9429	1.0997
	N	0.3638	1.5216	0.8754	0.3764	1.5743	0.9058
		0.4007	1.1933	0.6822	0.3976	1.1840	0.6770
		0.1326	0.3034	0.3527	0.3415	0.7815	0.9083
		0.3954	0.5845	0.6820	0.3624	0.5359	0.6251
NCO^-	N	0.3333	1.6607	0.9738	0.4270	2.1276	1.2476
		0.3854	1.0826	0.6472	0.4270	1.1994	0.7171
		0.3586	0.9309	1.1425	0.4234	1.0991	1.3490
		0.3884	0.5651	0.6540	0.4209	0.6189	0.7155
	C	0.3836	1.9113	1.2076	0.2324	1.1579	0.7316
		0.3644	1.0236	0.6120	0.2249	0.6317	0.3776
		0.3530	0.9164	1.1247	0.1891	0.4909	0.6025
		0.3777	0.5485	0.6348	0.1740	2.5320	0.2928
	O	0.2832	1.4140	0.8274	0.3405	1.6966	0.9948
		0.2501	0.7025	0.4200	0.3481	0.9778	0.5846
		0.2883	0.7484	0.9186	0.3875	1.0060	1.2316
		0.2339	0.3403	0.3939	0.4011	0.5836	0.6754
CNO^-	C	0.5196	2.5928	1.5417	0.4374	2.1826	1.2978
		0.5503	1.8497	1.0386	0.4344	1.4601	0.8198
		0.5353	1.3947	1.7927	0.3877	1.0102	1.2984
		0.5756	0.9376	1.1368	0.3877	0.6316	0.7657
	N	0.1389	0.6921	0.4121	0.1326	0.6617	0.3934
		0.2237	0.7519	0.4222	0.1452	0.4881	0.2740
		0.1238	0.3226	0.4447	0.0669	0.1730	0.2386
		0.2289	0.3727	0.4501	0.0728	0.1186	0.1438
	O	0.3415	1.7041	1.0132	0.4300	2.1457	1.2759
		0.2501	0.8407	0.4720	0.4204	1.4131	0.7934
		0.3409	0.882	1.1417	0.5459	1.4223	1.8282
		0.1955	0.3185	0.3861	0.5395	0.8788	1.0655

[a] The four sets of values against each atom refer to DFT/A, DFT/B, HF/A, and HF/B calculations, respectively, where A = 6-311+G** and B = 6-31G**. [b] The two sets of values are calculated from ionization potentials and electron affinities obtained using Koopmans' approximation (KA) and the ED method.

TABLE 3: Condensed Fukui Functions (f_k^+ and f_k^-)[a] and Atomic Softness Indices (s_k^+ and s_k^-)[b] of BX_3 (X = H, F, Cl) Molecules

			s_k^+			s_k^-	
molecule	atom, k	f_k^+	KA	ED	f_k^-	KA	ED
BH_3	B	0.6081	2.2048	1.2600	0.3390	1.2291	0.7043
		0.6059	1.8934	1.1676	0.3505	1.2311	0.6754
		0.6070	1.1327	1.2489	0.3399	0.6343	0.6993
		0.6114	1.0444	1.1739	0.3326	0.5681	0.6386
BF_3	B	0.2869	1.1331	0.6862	0.0581	0.2295	0.1390
		0.2896	1.1393	0.6770	0.0485	0.1908	0.1134
		0.3256	0.6416	0.7287	0.0383	0.0755	0.0857
		0.3263	0.6085	0.7204	0.0297	0.0554	0.0656
BCl_3	B	0.5405	1.2790	0.9124	0.1679	0.3973	0.2834
		0.5266	1.1702	0.7594	0.1573	0.3496	0.2268
		0.4599	0.6413	0.7246	0.1312	0.1829	0.2067
		0.5563	0.6479	0.7447	0.1198	0.1395	0.1604

[a] The four sets of values against each atom refer to DFT/A, DFT/B, HF/A, and HF/B calculations, respectively, where A = 6-311+G** and B = 6-31G**. [b] The two sets of values are calculated from ionization potentials and electron affinities obtained using Koopmans' approximation (KA) and the ED method.

TABLE 4: Condensed Fukui Functions (f_k^+ and f_k^-)[a] and Atomic Softness Indices (s_k^+ and s_k^-)[b] of Aniline and Fluoroanilines

			s_k^+			s_k^-	
molecule	atom, k[c]	f_k^+	KA	ED	f_k^-	KA	ED
$C_6H_5NH_2$	C4	0.0499	0.2500	0.1531	0.1307	0.6565	0.4009
		0.0543	0.2628	0.1489	0.1306	0.6321	0.3582
		0.0418	0.1149	0.1239	0.1187	0.3263	0.3518
		0.0344	0.0784	0.0966	0.1179	0.2687	0.3312
	N	0.0650	0.3264	0.1994	0.1604	0.8056	0.4920
		0.0378	0.3146	0.1037	0.1649	0.7981	0.4522
		0.0300	0.0825	0.0899	0.1749	0.4805	0.5184
		0.0362	0.0825	0.1017	0.1802	0.4107	0.5063
m-F-$C_6H_4NH_2$	C4	0.0502	0.2474	0.1513	0.1349	0.6649	0.4065
		0.0761	0.3617	0.2066	0.1361	0.6469	0.3694
		0.0515	0.1387	0.1498	0.1293	0.3481	0.3760
		0.0897	0.2015	0.2469	0.1305	0.2931	0.3593
	N	0.0672	0.3312	0.2025	0.1573	0.7753	0.4740
		0.0449	0.2124	0.1219	0.1601	0.7609	0.4345
		0.0329	0.0886	0.0957	0.1775	0.4779	0.5162
		0.0387	0.0869	0.1065	0.1822	0.4093	0.5014
o-F-$C_6H_4NH_2$	C4	0.0544	0.2713	0.1633	0.1257	0.6269	0.3773
		0.0715	0.3447	0.1952	0.1243	0.5984	0.3394
		0.0837	0.2244	0.2614	0.1107	0.2968	0.3457
		0.0440	0.0995	0.1214	0.1093	0.2473	0.3017
	N	0.0656	0.3272	0.1969	0.1603	0.7995	0.4812
		0.0467	0.2248	0.1275	0.1649	0.7937	0.4503
		0.0401	0.1075	0.1252	0.1929	0.5174	0.6024
		0.0316	0.0715	0.0872	0.2012	0.4552	0.5533
p-F-$C_6H_4NH_2$	C4	0.0316	0.3543	0.0970	0.1070	0.5667	0.3283
		0.0501	0.2573	0.1418	0.1069	0.5491	0.3026
		0.0394	0.1078	0.1189	0.0948	0.2592	0.2860
		0.0333	0.0781	0.0954	0.0945	0.2215	0.2717
	N	0.0669	0.3543	0.2053	0.1565	0.8289	0.4802
		0.0373	0.1916	0.1056	0.1586	0.8146	0.4489
		0.0288	0.0788	0.0869	0.1797	0.4919	0.5722
		0.0273	0.0640	0.0785	0.1836	0.4305	0.5279

[a] The four sets of values against each atom refer to DFT/A, DFT/B, HF/A, and HF/B calculations, respectively, where A = 6-311+G** and B = 6-31G**. [b] The two sets of values are calculated from ionization potentials and electron affinities obtained using Koopmans' approximation (KA) and the ED method. [c] N is bonded to the carbon atom numbered 1 (i.e., to C1) and atom C4 is in the para position to C1.

f_N^-) end. For the same reason, the C atom of CN^- is attached to the C atom of aldehydes and ketones ($f_C^+ > f_O^+$; see Table 1) in the formation of cyanohydrins. Of the two isomeric species, NCO^- is far more stable than CNO^-. Although the N atom in NCO^- has the highest value of f_k^- and s_k^-, electrophilic attack to this molecule can take place[55] at both N and O depending upon the nature of the attacking reagent. For example, the proton (the hardest acid) is attached to the N atom (HNCO is more stable than HOCN by about 28.5 kcal/mol[56]), but softer acids such as K^+ and NH_4^+ ions are attached to the oxygen atom of NCO^-. Exception occurs in the reaction of NCO^- with Ag^+ (a soft acid), which gives rise to the product, AgNCO.

C. BX_3 (X = H, F, Cl) Molecules. The calculated values of the local reactivity indices of the BX_3 molecules are given in Table 3. Because of Jahn−Teller (JT) distortion caused by the double degeneracy of the HOMOs of BH_3, the symmetry of BH_3^+ is reduced and one of the three H atoms is predicted to have a different charge. The JT effect is observed in all four models used. Because the BX_3 molecules are electron-deficient species, they readily react with an electron-rich molecule like NH_3 forming a compound of the type $H_3N{\rightarrow}BX_3$. We are thus concerned with f_B^+ and s_B^+ indices. These indices will not be affected by the JT effect because it is not observed in BH_3^-. The relative electrophilic index (s_B^+/s_B^-) may, however, be affected marginally through s_B^-.

The classical sequence of the reactivity for boron-containing Lewis acids (BX_3) was recovered by Balawender and Komorowski[29] in the following form: $s_B^+(BH_3) > s_{Cl}^+(BCl_3) > s_F^+(BF_3)$. This is not a useful result because B is the electro-

TABLE 5: Condensed Fukui Functions (f_k^+ and f_k^-)[a] and Atomic Softness Indices (s_k^+ and s_k^-)[b] of Some Molecules with Two Competitive Nucleophilic Centers

			s_k^+			s_k^-	
molecule	atom, k[c]	f_k^+	KA	ED	f_k^-	KA	ED
NH_2OH[c]	N	0.1443	0.5076	0.3112	0.4096	1.4407	0.8835
		0.1661	0.4938	0.2972	0.4139	1.2274	0.7388
		0.1480	0.2821	0.3336	0.4556	0.8700	1.0291
		0.1844	0.2839	0.3282	0.4603	0.7083	0.8193
	O	0.1256	0.4418	0.2709	0.2283	0.8030	0.4924
		0.1475	0.4385	0.2818	0.2357	0.7007	0.4218
		0.0875	0.1668	0.1973	0.1939	0.3696	0.4371
		0.0930	0.1432	0.1655	0.2000	0.3080	0.3560
	H_a	0.2569	0.9036	0.5541	0.1283	0.4513	0.2767
		0.2345	0.6971	0.4195	0.1266	0.3763	0.2265
		0.3389	0.6459	0.7640	0.1318	0.2512	0.2971
		0.3318	0.5109	0.5906	0.1288	0.1983	0.2293
	H_h	0.2164	0.7612	0.4668	0.1033	0.3633	0.2228
		0.2171	0.6454	0.3884	0.0982	0.2919	0.1757
		0.0868	0.1654	0.1959	0.0859	0.1637	0.1936
		0.0590	0.0908	0.1050	0.0811	0.1260	0.1444
C_6H_5NO	N	0.2053	1.7339	0.7455	0.1951	1.6478	0.7085
		0.2082	1.7437	0.6472	0.1993	1.6832	0.6195
		0.2802	0.6881	1.1529	0.1575	0.3368	0.6481
		0.2844	0.6792	0.9759	0.1494	0.3568	0.5127
	O	0.2149	1.8150	0.7804	0.2680	2.2635	0.9732
		0.2120	1.7755	0.6590	0.2662	2.2295	0.8274
		0.2722	0.6684	1.1200	0.3226	0.8045	1.3430
		0.2668	0.6372	0.9155	0.3219	0.7688	1.1046
HNO	H	0.1932	1.4290	0.5040	0.2008	1.4852	0.5238
		0.1983	1.4453	0.4793	0.2059	1.5007	0.4977
		0.1793	0.3605	0.4724	0.1754	0.3526	0.4621
		0.1832	0.3519	0.4588	0.1751	0.3363	0.4356
	N	0.4303	3.1827	1.1225	0.3739	2.7655	0.9754
		0.4209	3.0678	1.0174	0.3724	2.7143	0.9001
		0.4380	0.8806	1.1539	0.3416	0.6868	0.8999
		0.4312	0.8282	1.0728	0.3441	0.6610	0.8561
	O	0.3764	2.7840	0.9819	0.4254	3.1464	1.1097
		0.3809	2.7762	0.9207	0.4217	3.0736	1.0193
		0.3829	0.7698	1.0064	0.4830	0.9711	1.2725
		0.3857	0.7409	0.9596	0.4807	0.9234	1.1960
HOF	H	0.2221	0.8748	0.4301	0.1444	0.5687	0.2797
		0.2438	0.9179	0.4275	0.1385	0.5215	0.2429
		0.4910	0.7325	0.8817	0.1459	0.2177	0.2620
		0.6918	0.9548	0.3261	0.1053	0.1453	0.2364
	O	0.3913	1.5404	0.7578	0.4968	1.9567	0.9621
		0.3866	1.4556	0.6779	0.5006	1.8848	0.8778
		0.3009	0.4489	0.5403	0.5586	0.8334	1.0031
		0.4146	0.5048	0.7001	0.5637	0.6863	0.9519
HOF	F	0.3866	1.5227	0.7487	0.3588	1.4132	0.6949
		0.3696	1.3916	0.6481	0.3617	1.3618	0.6342
		0.2081	0.3105	0.3737	0.2954	0.4407	0.5304
		0.3923	0.1870	0.6624	0.2963	0.3899	0.5003

[a] The four sets of values against each atom refer to DFT/A, DFT/B, HF/A, and HF/B calculations, respectively, where A = 6-311+G** and B = 6-31G**. [b] The two sets of values are calculated from ionization potentials and electron affinities obtained using Koopmans' approximation (KA) and the ED method. [c] H_a is a hydrogen atom of the amine group and H_h is a hydroxyl hydrogen atom.

philic center in BX_3. According to the present calculations, the s_B^+ values in these molecules vary in the order $BH_3 > BCl_3 > BF_3$. This is in agreement with the ab initio MP2/6-311+G(d,p) calculations of Mo and Gao.[57] They found that the interaction between BH_3 and NH_3 is stronger than that between BF_3 and NH_3 by about 8.6 kcal/mol. The s_B^+/s_B^- indices (not tabulated) do not support the theoretical trend.

D. Aniline ($C_6H_5NH_2$) and *o*-, *m*-, and *p*-Fluoroanilines ($F-C_6H_4NH_2$). The protonation reaction of these molecules (ortho isomer excluded) was studied by Roy et al.[17b] using Fukui indices derived from Mulliken and Stockholder charges and more recently by Fuentealba et al.[44] In the latter study, the non-FDA definition of Fukui functions given by Contereas et al.[31] was used. Because the N atom attached to C1 (carbon atom numbered 1) and the carbon atom C4 occupying the para position with respect to C1 are the competitive sites of protonation, Table 5 includes the calculated local indices of these two atoms only. In all of the molecules, f_k^- and s_k^- of N are larger than the corresponding values of C4. Thus, the N-protonation in these molecules is a more favorable process than the protonation on the ring. This prediction is in agreement with the experimental observation.[58]

E. C_6H_5NO, H_2NOH, HNO, and HOF. All of these four molecules contain two competitive nucleophilic centers. Pilepic and Ursic[24] recently studied the nucleophilic reactivity of C_6H_5NO using Fukui and related indices calculated from MPA, NPA, and the electrostatic potential-derived (CHELP[59] and CHELPG[60]) charges. The H-bonded dimers of H_2NOH, HNO, and HOF have been shown[61] to have higher stability when the less electronegative atom is involved in H-bonding. We have interpreted these reactivity trends using the local indices given in Table 5.

In C_6H_5NO, both the nucleophilic local indices (f_k^-, s_k^-) of O are predicted to be larger than those of N. Hence, oxygen should be the preferred site of nucleophilic attack as predicted by Pilepic and Ursic[24] on the basis of local quantities derived from MPA and NPA charges. The corresponding indices calculated from electrostatic potential-derived charges, however, indicated that N should be the preferred site. Their final conclusion is that both N and O are equally suitable sites for an electrophilic attack. The preferred site of protonation in NH_2OH is N because the associated local indices for the electrophilic attack are larger than the corresponding values for oxygen. For the same reason, the N atom of NH_2OH is attached to the C atom of aldehydes and ketones ($f_C^+ > f_O^+$; see Table 1) in the formation of oximes. Intermolecular H-bonding can be regarded as a type of electrophile−nucleophile interaction in which an electronegative atom serves as the nucleophilic center and the partially positively charged H-atom as the electrophilic reagent. It can be seen from Table 6 that in NH_2OH and HNO $f_N^- > f_O^-$ and in HOF $f_O^- > f_F^-$. This suggests that H-bonding will preferably take place through N in NH_2OH and HNO and through O in HOF. This is in agreement with the theoretical predictions of Peters.[61]

4. Concluding Remarks

The aim of the present investigation was to assess the performance of the local reactivity indices derived from Stockholder charges. For this purpose, we selected a number of closed-shell molecules that are traditionally known to act as electrophiles, nucleophiles, or both. In all cases, the atomic centers with the maximal values of Fukui and related indices are found to be the preferred sites for electrophilic or nucleophilic attack. The conclusions of the present study are independent of basis sets and the levels of theory (HF and DFT) employed.

The results of the present study do not follow the local HSAB principle. Despite the sound theoretical basis of the Stockholder partitioning scheme, the atomic charges for some anions were not predicted satisfactorily. This might stem from the inadequacy of the basis sets to properly describe the anions, which usually have an expanded charge distribution.

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