Comparison among Four Different Ways to Condense the Fukui Function

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Four different ways to condense the Fukui function are compared. Three of them perform a numerical integration over different basins to define the condensed Fukui function, and the other one is the most traditional Fukui function using Mulliken population analysis. The basins are chosen to be the basins of the electron density (AIM), the basins of the electron localization function (ELF), and the basins of the Fukui function itself. The use of the last two basins is new and presented for the first time here. It is found that the last three methods yield results which are stable against a change in the basis set. The condensed Fukui function using the basins of the ELF is not able to give information on the reactivity of an acceptor molecule. In general, the condensed Fukui function using the basins of the density or the basins of the Fukui function describe the reactivity trends well. The latter is preferred, because it only contains information about the Fukui function itself and it gives the right information for donor as well as acceptor centers.

Introduction

Fukui's concepts of frontier orbitals,[1] the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, are of vital importance in modern chemical reactivity theory. They were initially introduced in the context of Hartree−Fock theory and the linear combination of atomic orbital (LCAO) model. However, they have found a deeper theoretical framework in the context of density functional theory.[2] The Parr and Yang[3] definition of the Fukui function is

$$f(\vec{r}) = \left[\frac{\delta\mu}{\delta v(\vec{r})}\right]_N \tag{1}$$

where μ is the chemical potential, $v(\vec{r})$ is the external potential, and the functional derivative must be taken at a constant number of electrons N. It has been shown[3] that, in a first approximation, the Fukui function is equal to the square of the respective frontier orbital, the HOMO when the derivative is taken from the left, f^-, and the LUMO when the derivative is taken from the right, f^+. Moreover, in the Kohn−Sham scheme, one can define the Kohn−Sham Fukui function as[4]

$$f(\vec{r}) = \left[\frac{\delta\mu}{\delta v_{\mathrm{ks}}(\vec{r})}\right]_N \tag{2}$$

where $v_{\mathrm{ks}}(\vec{r})$ is the effective Kohn−Sham potential. Now, this derivative is exactly equal to the respective frontier orbital. Hence, in the Kohn−Sham scheme,

$$f^{\alpha}(\vec{r}) = |\phi^{\alpha}(\vec{r})|^2 \tag{3}$$

where ϕ^{α} is the frontier orbital (α = HOMO or LUMO), is an exact equation, and the so-implemented Fukui function is a positive definite function which normalizes to unity.[5,7,8] Therefore, in this work, the last equation has been used to calculate the Fukui function. Another related quantity is the local softness, $s(\vec{r})$

$$s(\vec{r}) = Sf(\vec{r}) \tag{4}$$

where S is the global softness. $s(\vec{r})$ is used as an intermolecular index. Two excellent reviews illustrating the usefulness of the density functional theory (DFT)-based global and local reactivity indices have recently appeared.[9,10]

For practical calculation of the Fukui function, there are also other aspects to consider. In chemistry, one usually prefers to assign a numerical value of a quantity to an atom or a fragment of a molecule instead of assigning a number to a point in space. This is necessary in order to compare a series of related molecules in the search for reactivity systematization and ordering. This simplification of reducing a three-dimensional function to one number on each atom is called the condensed function. The way to condense a function is arbitrary, as far as the definition of an atom in a molecule is arbitrary. Therefore, one can expect various different definitions, all giving reasonable results as long as one ask for trends and tendencies in a family of molecules and not for absolute values. However, the most familiar ways of condensing the Fukui function use some type of population analysis,[11] introducing two problems. The values can be negative,[5,12] which complicate the interpretation, and they are highly dependent on the basis set.[13]

To avoid the use of any population analysis, one can perform a numerical integration of the Fukui function over an a priori defined region of the space, Ω_k. The whole space is divided into various regions $\{\Omega_k\}$, and the condensed Fukui function at region k will be

$$f_k^{\alpha} = \int_{\Omega k} f_k^{\alpha}(\vec{r})\, d\vec{r} \tag{5}$$

The way to divide the space into various regions is in principle arbitrary, and one has to look to the ones with more chemical

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TABLE 1: Donor Fukui Indexes f^-'s at B3LYP/6-311g (B1) and B3LYP/6-311++g** (B2) Levels of Theory for the Four Studied Condensation Schemes**

		f^-_{Mu}		f^-_{Ff}		f^-_{AIM}		f^-_{ELF}	
molecule	atom	B1	B2	B1	B2	B1	B2	B1	B2
H_2O	O	0.98	0.98	1.00	1.00	0.99	0.99	0.80	0.80
H_2S	S	0.99	0.99	0.98	1.00	0.96	0.96	0.80	0.80
HCN	C	0.48	0.48	0.46	0.46	0.37	0.37		
	N	0.52	0.52	0.53	0.54	0.53	0.53	0.32	0.32
CO	C	0.93	0.95	0.85	0.86	0.84	0.85	0.81	0.81
NH_2^-	N	0.98	0.98	1.00	1.00	0.96	0.95	0.70	0.68
NH_3	N	0.95	0.95	0.99	1.00	0.93	0.92	0.61	0.60
NH_2OH	N	0.74	0.73	0.75	0.76	0.72	0.72	0.51	0.51
	O	0.20	0.20	0.20	0.19	0.21	0.21	0.16	0.16
NH_2F	N	0.67	0.69	0.69	0.70	0.66	0.67	0.49	0.50
NHF_2	N	0.54	0.57	0.53	0.54	0.54	0.55	0.43	0.44
NF_3	N	0.47	0.51	0.47	0.47	0.46	0.47	0.42	0.43
Si_4	Si1=Si3	0.40	0.42	0.32[a]	0.32[a]	0.39	0.39		
	Si2=Si4	0.10	0.08			0.11	0.11		
Li_4	Li1=Li3	0.29	0.29	0.48[a]	0.48[a]	0.21	0.21		
	Li2=Li4	0.21	0.21			0.07	0.07		
	2N−At					0.22	0.23		

[a] This value is not related to any atom basins.

insight (i.e., regions which define an atom, a bond, a lone pair, etc.). In this work, we will analyze in detail three forms of dividing the space into regions. They are based on the topological analysis of different scalar functions: the electron density, $\rho(\vec{r})$, the electron localization function, ELF,[14] and the Fukui function itself. The use of the electron density to condense the Fukui function has been recently presented by some of us,[15] and other ways to divide the space have been also investigated in the past.[16,17] For a thorough presentation of the ELF, see ref 18, and for the use of the ELF to characterize donor systems, see refs 19 and 20.

The topological analysis of a scalar function in the space around a molecule has a long tradition in chemistry.[21,22] The analysis of the gradient field of any scalar function allows us to find the critical points, the set of points where the gradient vanishes. The critical points are the local minima, the saddle points, and the local maxima. The latter are called attractors, and the basin of an attractor is the set of points lying on the trajectories of the gradient field, which ends at the attractor (for a chemical introduction to the topological analysis, see ref 22).

The basins of the density define volumes which have been interpreted by Bader[22] as the atomic regions. The numerical integration of the Fukui function over these regions define the atoms in molecules (AIM)-condensed Fukui function. The basins of the ELF present several different interpretations.[23] There are basins associated to the core electrons, basins associated to bonds, and basins associated to lone pairs. The numerical integration of the Fukui function over any of these basins defines the ELF-condensed Fukui function of the core region, the bond and lone pair regions. The topological analysis of these two functions, the density and the ELF, has been studied in detail,[22,23] but to our knowledge, there is no study of the topological analysis of the Fukui function. In this work, it will be shown that the Fukui function presents basins associated to one atom and, in some cases, basins associated to a bond. It is worth mentioning that the condensation of the Fukui function over the basins of the Fukui function is the only method which uses information only from the Fukui function itself and is, therefore, more in line with the frontier orbital theory of reactivity. Notice that, in the last two kinds of condensation, the Fukui function can be associated to a region of the space which does not represent an atom, but a region of the space with chemical significance such as a bond region or a lone pair region.

TABLE 2: Acceptor Fukui Indexes f^+'s at B3LYP/6-311g (B1) and B3LYP/6-311++g** (B2) Levels of Theory for the Three Studied Condensation Schemes**

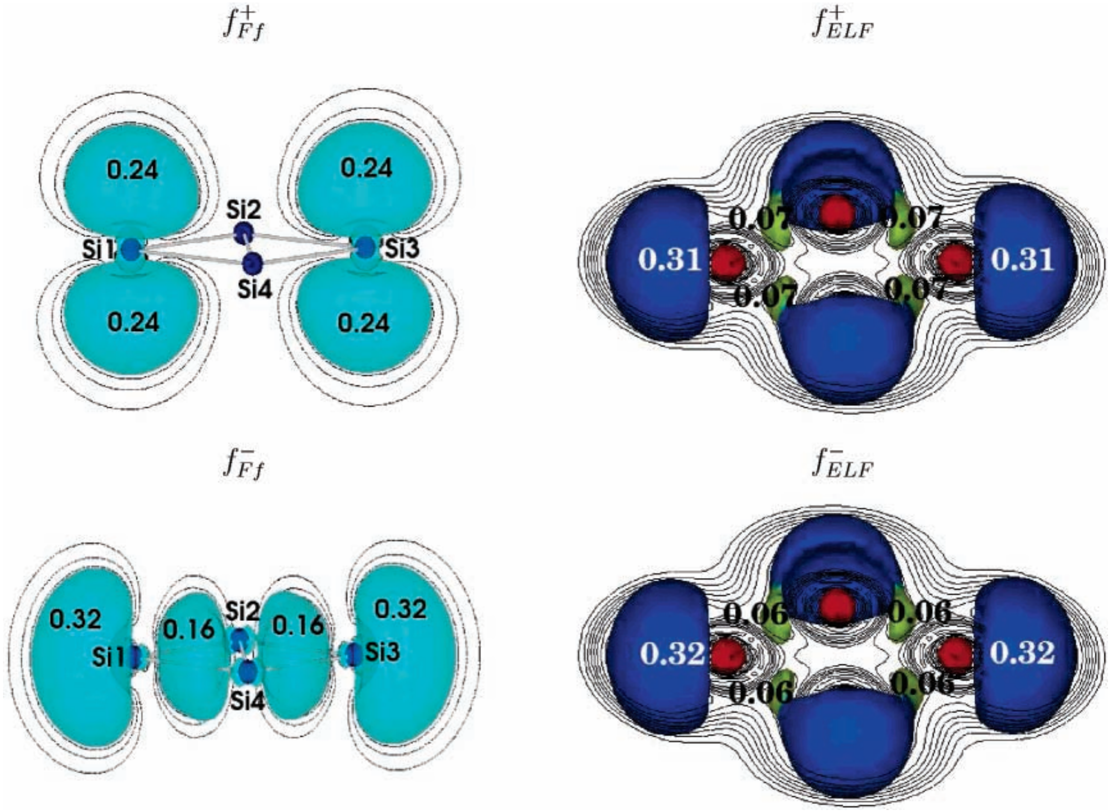
		f^+_{Mu}		f^+_{Ff}		f^+_{AIM}	
molecule	atom	B1	B2	B1	B2	B1	B2
BH_3	B	0.98	0.98	0.98	0.99	0.41	0.40
BH_2F	B	0.91	0.99	0.90	0.90	0.31	0.37
BHF_2	B	0.87	1.03	0.81	0.83	0.35	0.34
BF_3	B	0.83	1.60	0.72	0.94	0.31	0.08
BCl_3	B	0.76	0.76	0.64	0.64	0.40	0.39
CH_3^+	C	0.98	0.93	0.90	0.93	0.93	0.93
CF_3^+	C	0.69	0.71	0.62	0.62	0.48	0.48
CCl_3^+	C	0.53	0.51	0.50	0.50	0.48	0.48
CBr_3^+	C		0.50		0.49		0.48
CI_3^+	C		0.48		0.47		0.47
CO	C	0.76	0.84	0.72	0.74	0.66	0.67
OCH_2	C	0.65	0.72	0.64	0.66	0.54	0.54
$OCHCH_3$	C1	0.60	0.67	0.59	0.59	0.49	0.49
$OCClCH_3$	C1	0.57	0.57	0.54	0.53	0.47	0.47
$OC(CH_3)_2$	C1	0.53	0.49	0.52	0.50	0.44	0.44
Si_4	Si1=Si3	0.49	0.49	0.48[a]	0.48[a]	0.45	0.45
	Si2=Si4	0.01	0.01			0.05	0.05
Li_4	Li1=Li3	0.19	0.18			0.09	0.09
	Li2=Li4	0.31	0.32	0.48[a]	0.48[a]	0.26	0.26
	2N−At					0.15	0.15

[a] This value is not related to any atom basins.

Results and Discussion

A set of 26 molecules has been selected to compare the 4 different ways to condense the Fukui function. The geometry of all of them has been optimized using the B3LYP density functional method and two different basis sets, namely 6-311G** and the 6-311++G**, denoted in the tables as B1 and B2, respectively. All electronic structure calculations were done using the *Gaussian 98* program,[24] and the topological analysis of the scalar functions and the calculation of the condensed Fukui function were done with a modified version of the *Top_Mod* set of programs.[25]

Tables 1 and 2 present the results for the donor and acceptor centers of the studied molecules, respectively. To do a more detailed comparison, the condensed Fukui function using the Mulliken population[5,6,26] analysis has also been computed and included in the tables. Hence, we have values for the donor and acceptor Fukui functions, f^- and f^+, respectively, condensed by means of Mulliken population analysis, $f^{\pm}_{\mathrm{Mu}}$, by means of


f^{+}_{Ff} f^{+}_{ELF}

f^{-}_{Ff} f^{-}_{ELF}

Figure 1. $f^{\pm}_{\mathrm{Ff}}$and $f^{\pm}_{\mathrm{ELF}}$ for Si_4 cluster at the B3LYP/6-311+g* level of theory. The step size of the contour line of $f^{\pm}_{\mathrm{Ff}}$ is 0.003. The ELF isosurface and the step size of the contour line of $f^{\pm}_{\mathrm{ELF}}$ are 0.82 and 0.1, respectively.

numerical integration over the basins of the density, $f^{\pm}_{\mathrm{AIM}}$, over the basins of the ELF, $f^{\pm}_{\mathrm{ELF}}$, and over the basins of the Fukui function itself, $f^{\pm}_{\mathrm{Ff}}$. For the condensed Fukui function, $f^{\pm}_{\mathrm{ELF}}$ and $f^{\pm}_{\mathrm{Ff}}$, the values are not exactly atomic basins in the sense of the AIM model.[22] For $f^{\pm}_{\mathrm{ELF}}$, they are values associated to the lone pair basins, and for $f^{\pm}_{\mathrm{Ff}}$, they are values associated to the basins which contain the nucleus. In Table 1, the results for the donor systems are presented. One can see that the 4 condensed Fukui functions yield very similar values which are not basis-set-dependent. Notice, however, that in many cases the Fukui function using the Mulliken population analysis can yield negative values for centers which are not the reactive ones; for instance, the Fukui function, f^{+}_{Mu} associated to the oxygen atom in the water molecule has a value of -0.493 at the B3LYP/6-311++g** level of theory. There are some points which are important to observe. Because in the HCN molecule, the ELF basins are centered in the bond regions and in the lone pair at the nitrogen center, and except for the core basin, there is no basin associated only to the carbon atom, f^{-}_{ELF} does not yield a unique value for the carbon atom, and there is no value associated to the reactivity of the carbon center. The Fukui function, f^{-}_{ELF}, associated to the CN bond has a value of 0.32. For the clusters Si_4 and Li_4, f^{-}_{Mu} and f^{-}_{AIM} yield values centered on the atoms, but theses clusters also present a reactivity toward an electrophilic attack through the bond zone. Si_4 has been studied by Galvan et al.,[27] who reported that the cluster can donate charge through the terminal atoms or the bond region. This is well-described by the $f^{\pm}_{\mathrm{Ff}}$ Fukui function as can be seen in Figure 1, where isosurfaces of the basins of the Fukui function are depicted. One can see that f^{-}_{Ff} presents two basins associated to the terminal atoms and two basins associated to the bond region. In the same figure, isosurfaces of the basins of the $f^{\pm}_{\mathrm{ELF}}$ Fukui function are also depicted. This function also has basins associated to the bond regions but with very low values, and only the terminal atoms are described as the reactive ones. The reactivity of Li_4 has also been studied.[28] It is known that Li_4 acts as a donor only through the bond region, a result which is perfectly reproduced by the $f^{\pm}_{\mathrm{Ff}}$ Fukui function as can be seen in Figure 2. Regarding Figures 1 and 2, the condensation of the Fukui function over the basins of the ELF deserves some criticism. One can see that both Fukui functions, $f^{\pm}$, have almost the same values when condensed over the basins of the ELF. This is due to the fact that both Fukui functions should normalize to one and the bonding basins of the ELF decay slowly to zero when the distance goes to infinity. Hence, although Figures 1 and 2 show an isosurface of the basins concentrated mainly in the region where the HOMO has a marked presence, the basins extend over the whole space, allowing the Fukui function associated to the LUMO, f^{+}_{ELF}, to normalize to one, as it should. This artifact comes from the fact that the ELF does not present basins in the region where the molecule can accept electrons. Therefore, the f^{+}_{ELF} function loses its physical meaning. To study the capability of the defined indices in describing the intermolecular reactivity, the series formed by the NH_3, NH_2F, NHF_2, and NF_3 molecules has been chosen. The binding energy of all the bases with BH_3 has been chosen as the parameter to compare with. The values have been taken from ref 29 and are theoretical calculations at the MP2/6-31G* level. As usual, the comparison is more meaningful using the condensed local softness, $s^{\pm}$, which is simply the Fukui function times the global softness of the molecule. In Figure 3, one can see that all the condensed Fukui functions are able to reproduce the correct trend.

The condensed Fukui functions for the acceptor centers are presented in Table 2. In this case, there are no values for the f^{+}_{ELF} condensed Fukui function. The ELF describes the regions

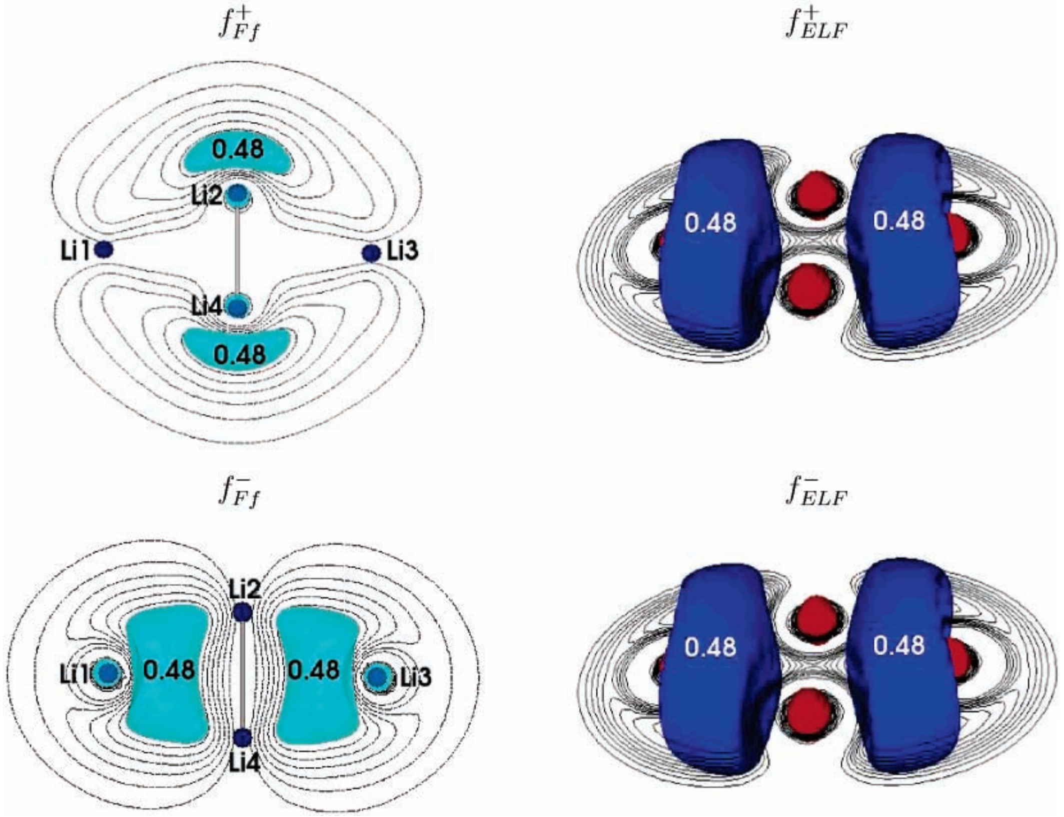


Figure 2. $f_{\mathrm{Ff}}^{\pm}$and $f_{\mathrm{ELF}}^{\pm}$ for $\mathrm{Li_4}$ cluster at the B3LYP/6-311+g* level of theory. The step size of the contour line of $f_{\mathrm{Ff}}^{\pm}$ is 0.003. The ELF isosurface and the step size of the contour line of $f_{\mathrm{ELF}}^{\pm}$ are 0.92 and 0.1, respectively.

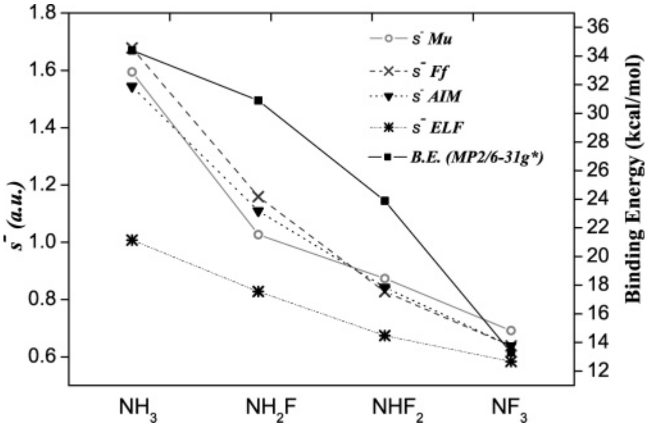


Figure 3. Comparison between local donor softness s^{-} condensed at the nitrogen center and binding energies of the complex[29] formed by the basis and $\mathrm{BH_3}$. The data used were the B3LYP/6-311++g** results.

of the space where it is most probable to localize electrons. Therefore, it does not present any basins in the regions where the molecule is deficient in electrons. The f_{Ff}^{+} and f_{AIM}^{+} condensed Fukui functions again show great stability against a change in the basis set. However, the f_{Mu}^{+} condensed Fukui function shows, in some cases, a strong basis-set dependence. $\mathrm{BF_3}$ is a special case, for the LUMO changes from a′ to e″ symmetry in going from basis set B1 to B2, thereby explaining the large variation in the Fukui function even when calculated by numerical integration over the AIM basins. It is also worth noticing that, for the series $\mathrm{CH_3}^{+}$, $\mathrm{CF_3}^{+}$, $\mathrm{CCl_3}^{+}$, $\mathrm{CBr_3}^{+}$, and $\mathrm{CI_3}^{+}$, f_{AIM}^{+} is not able to discriminate among the different molecules. For the series $\mathrm{BH_2F}$, $\mathrm{BHF_2}$, $\mathrm{BH_3}$, $\mathrm{BCl_3}$, and $\mathrm{BF_3}$, the intermolecular reactivity is studied using the condensed local softness, s^{+}. Again, the comparison is done with the binding energy of the complex formed by the studied acids with $\mathrm{NH_3}$. The values are taken from ref 29 and correspond to theoretical calculations at the MP2/6-31G* level. The results are depicted in Figure 4. For the f_{Mu}^{+} condensed Fukui function, the values calculated with both basis sets are shown, to emphasize the fact that this way of condensing is highly basis-set-dependent and is not able to reproduce the correct trend with both basis sets. The other methods yield qualitatively correct results except for the value of $f_{\mathrm{AIM}}^{\pm}$ for $\mathrm{BCl_3}$.

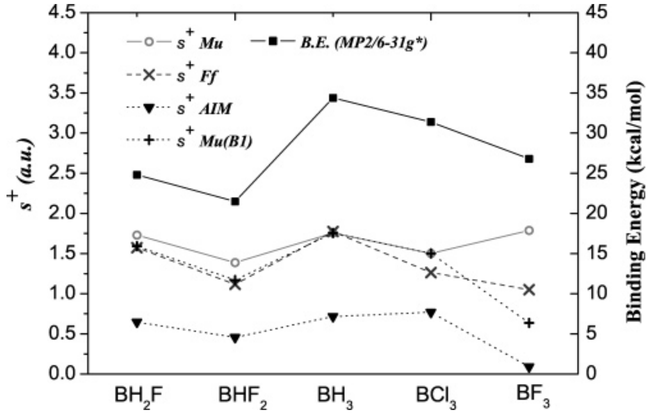


Figure 4. Comparison between local acceptor softness s^{+} condensed at the boron center and binding energies of the complex[29] formed by the acids and $\mathrm{NH_3}$.The data used were the B3LYP/6-311++g** and B3LYP/6-311g** (B1) results.

Concluding Remarks

It has been confirmed that the condensation by means of numerical integration yields numbers which are not so dependent on the basis set. $f_{\mathrm{Mu}}^{\pm}$ is basis-set-dependent and should be used with caution, especially when diffuse functions are included in the basis set. As it is based on the Mulliken population analysis, it will fail in all the cases where the Mulliken population analysis fails. $f_{\mathrm{ELF}}^{\pm}$ and $f_{\mathrm{Ff}}^{\pm}$ are able to condense the Fukui function in regions of the space which does not necessarily represent an atom, but the region of a bond or a lone pair, and only in the cases where this region are relevant for the chemical reactivity. For instance, the $f_{\mathrm{Ff}}^{\pm}$ function produces nonatomic values for the Li_4 cluster; they are located in the region of the three-center two-electrons bond,[28] which is precisely the reactive zone. It is also important to note that $f_{\mathrm{ELF}}^{\pm}$ will not yield reasonable results at the acceptor regions of a molecule, because the ELF does not present basins in the regions of the space where there is a deficiency of electrons. To our knowledge, the topological analysis of the Fukui function is new and deserves a more detailed study in order to investigate the possible chemical meaning of the basins. The present study is not completely conclusive as to what is the best way to condense the Fukui function, but it gives indications about the best choice among $f_{\mathrm{Ff}}^{\pm}$ or $f_{\mathrm{AIM}}^{\pm}$ condensed functions. $f_{\mathrm{Mu}}^{\pm}$ presents a dangerous basis-set dependence, and $f_{\mathrm{ELF}}^{\pm}$ is not able to give information on electrophilic systems. From a more formal point of view, $f_{\mathrm{Ff}}^{\pm}$ should be preferred, because it only contains information from the Fukui function itself and is able to condense in regions of the space of chemical significance, like the bond regions.

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