
Fukui Functions for Atoms and Ions: Polarizability Justified Approach

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ABSTRACT: Recently proposed Fukui function has been tested for a collection of atoms and atomic ions. The key point of the analysis is an approximation for the softness kernel, as an extended and parameterized version of the local approximation $s(\mathbf{r},\mathbf{r}') = s(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$. The new Fukui functions lead to exact reproduction of global electronic dipole polarizability and atomic softness. The global hardness calculated with the classic definition using new Fukui functions and the hardness kernel $|\mathbf{r} - \mathbf{r}'|^{-1}$ matches the $\eta = I - A$ value with linear correlation superior to any other published hitherto. Applied approximations for the softness and hardness kernels were proved to be in perfect coherence. © 2010 Wiley Periodicals, Inc. *Int J Quantum Chem* 110:2315–2319, 2010

Key words: Fukui functions; chemical hardness; softness kernel

Introduction

Fukui function (FF) has been a target of many studies since it has first been proposed by Parr and Yang [1, 2] as a derivative:

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v = \left(\frac{\delta \mu}{\delta v(\mathbf{r})} \right)_N \quad (1)$$

where $\mu = (\partial E / \partial N)_v$ is the chemical potential, and $v(\mathbf{r}), \rho(\mathbf{r})$ stand for external potential and the electron density function of the system of N electrons,

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respectively. Chemists have soon recognized potential value of such derivative and tried to factorize it into some atomic indices [3–5]. Fukui functions condensed to atoms or chemical groups (see Ref. [6] for a formidable discussion thereof) have been used to describe electrophilic or nucleophilic character of atoms-in-molecule with some success, even despite the Fukui function itself remained ill-defined at numerical level; extensive reviews are available [7, 8].

The first trial approach for the FF was just electron density, $f(\mathbf{r}) = \rho(\mathbf{r})/N$, another common choice represents a finite difference approach, typical in conceptual density function theory [2], using densities of ions:

$$f_{+,-}(\mathbf{r}) = \frac{1}{2} [\rho^-(\mathbf{r}) - \rho^+(\mathbf{r})] \quad (2)$$

In 1995, Chattaraj et al. [9] proposed a physical analysis that motivated a gradient expansion formula satisfying most of conditions for the FF. However, the results were satisfactory for 12 selected atoms only when tested in the most evident application of the FF, i.e., relation between the global hardness $\eta = (\partial^2 E / \partial N^2)_v = I - A$ and the integrated hardness kernel $\eta(\mathbf{r}, \mathbf{r}') \cong |\mathbf{r} - \mathbf{r}'|^{-1}$, [Eq. (3)]:

$$\eta_f \cong \iint f(\mathbf{r})f(\mathbf{r}')\eta(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}' \quad (3)$$

The study of gradient expansions was continued by Fuentealba [10] and by Pacios and Gomes [11].

Calculation of hardness with the FF was also pursued by Liu et al. with the simple finite difference formula for the FF [Eq. (2)] of the collection of atoms [12] (first four rows of the periodic table, except groups IIA, VA, VIIIA). Recently, Ayers et al. have demonstrated another original a priori approach to the FF calculated from the Kohn–Sham orbital energies, however, this study was limited to the $f^+(\mathbf{r})$ (nucleophilic) and $f^-(\mathbf{r})$ (electrophilic) FF only [13, 14]. Substantial efforts were also made to produce the Fukui indices, i.e. Fukui function condensed to atoms [4, 15].

In the most recent study from this laboratory, a novel, polarizability justified approach to the FF has been introduced and successfully tested for the collection of 29 atoms (main groups), [16]. This present work is focused on extending this work to ions as well as to transition group elements.

Fukui Function and the Electronic Dipole Polarization

The key concept of the analysis (Ref. [16]) was the local electronic dipole polarizability vector defined as a local derivative of electron density over uniform electric field ε :

$$\alpha_i(\mathbf{r}) \equiv -\left(\frac{\partial \rho(\mathbf{r})}{\partial \varepsilon_i}\right)_N; \quad (i = x, y, z) \quad (4)$$

This new derivative is numerically computable by quantum-chemical methods and presents a connection between the electronic dipole polarizability tensor of a system α_e and the linear response function $\omega(\mathbf{r}, \mathbf{r}') = [\delta^2 E / \delta v(\mathbf{r})\delta v(\mathbf{r}')]_N$:

$$\alpha(\mathbf{r}) = -\int \omega(\mathbf{r}, \mathbf{r}')\mathbf{r}'d\mathbf{r}' \quad (5)$$

$$\alpha_e = \int \mathbf{r}\alpha(\mathbf{r})d\mathbf{r} \quad (6)$$

The second relation [Eq. (6)] provides a convenient test of the quality of numerical calculations for $\alpha(\mathbf{r})$, as α_e is well defined experimental quantity. Using $\alpha(\mathbf{r})$ to produce the Fukui functions is possible by exploring the Berkowitz and Parr formula for $\omega(\mathbf{r}, \mathbf{r}')$ in Eq. (5) [17]:

$$\omega(\mathbf{r}, \mathbf{r}') = -s(\mathbf{r}, \mathbf{r}') + Sf(\mathbf{r})f(\mathbf{r}') \quad (7)$$

$S = \eta^{-1} = (I - A)^{-1}$ stands for the softness of a system. The necessary approximation for the softness kernel $s(\mathbf{r}, \mathbf{r}') = -(\delta \rho(\mathbf{r}) / \delta v(\mathbf{r}'))_\mu$ has been tailored by extending the original idea of Vela and Gazques [18] $s(\mathbf{r}, \mathbf{r}') = s(\mathbf{r})\delta(\mathbf{r}' - \mathbf{r})$ and including further parameterization proposed by their followers: Garza and Robles [19] and Li and Evans [20]. Resulted general expression contains two parameters [16]:

$$s(\mathbf{r}, \mathbf{r}') = (1 - c)s(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') - bN\rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + b\rho(\mathbf{r})\rho(\mathbf{r}') + cSf(\mathbf{r})f(\mathbf{r}') \quad (8)$$

One of the parameters (b) can be eliminated by the formal condition $\int s(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}' = S$. The remaining one (c) is reformulated to:

$$d = \frac{S^{LA}}{S}(1 - c)^{-1} \text{ with } S^{LA} = \int \frac{\alpha(\mathbf{r}) \cdot \mathbf{r}}{r^2} d\mathbf{r} \quad (9)$$

S^{LA} is a number, approximating the softness of a system at the very local level as in Vela and Gazques' work with $s(\mathbf{r}, \mathbf{r}') = s(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$. The following result for the FF of spherically symmetric systems has been reached:

$$f(\mathbf{r}) = d\frac{\alpha(\mathbf{r}) \cdot \mathbf{r}}{r^2 S^{LA}} + (1 - d)\frac{\rho(\mathbf{r})}{N} \quad (10)$$

The parameter (d) can be calculated from the very basic property of the FF, identified by Parr and coworkers [9].

$$\int \frac{f(\mathbf{r})}{r} d\mathbf{r} = -\left(\frac{\partial \mu}{\partial Z}\right)_N \quad (11)$$

Derivative on the right side is computable, as $\mu = -(1/2)(I + A)$, hence the single parameter (d) can be identified for every atom.

Results and Discussion

The accuracy in reproducing polarizability for atoms has been used to select the appropriate computational method and the basis set within the Gaussian 03 code [21]. The best fit to experimental polarizations of atoms was obtained for the B3LYP method with *aug-cc-pvqz* basis set, Table I. Calculated as well as available experimental hardness data $\eta = I - A$ are also given in Table I. Local polarizability vector $\alpha(\mathbf{r})$ [Eq. (4)] has been calculated by the finite field procedure; results were checked by numerical integration of $\alpha(\mathbf{r}) \cdot \mathbf{r}$ to the electronic dipole polarizability of atom [Eq. (6)], leading to exact reproduction of the B3LYP calculated values. The derivative $(\partial\mu/\partial Z)_N$ has been calculated in the finite difference approximation. Calculated parameters of the Fukui function (d) and of the softness kernel (c)

TABLE I
Electronic dipole polarizability α_e and hardness η of selected atoms and ions.

Atom	α_e [a.u.]		$\eta = I - A$ [eV]	
	Calc.	Exp. ²²	Calc.	Exp. ²³
C ⁻	56.89		6.681	
N ⁻	33.43		6.288	
F ⁻	10.77	8.7–10.6 ²⁴	13.472	14.02 ^a
Si ⁻	149.01		5.046	
P ⁻	86.09		4.967	
Cl ⁻	33.48	31.4 ²⁴	10.098	9.40 ^a
Br ⁻	45.86		8.918	8.48 ^a
C ⁺	6.06		13.494	
N ⁺	3.83		15.341	
F ⁺	1.84		17.836	
Si ⁺	18.87		8.294	
P ⁺	14.27		9.358	
Cl ⁺	8.72		10.925	10.84
Br ⁺	12.66		9.625	10.0
Sc	121.89	120	6.545	6.40
Ti	102.84	98	6.892	6.74
V	89.85	84	6.330	6.2
Cr	73.74	78	6.370	6.12
Mn	71.34	63	7.967	7.44
Fe	60.37	56	6.552	7.62
Co	51.21	50	6.641	7.2
Ni	47.47	48	6.722	6.50
Cu	44.05	42	6.789	6.50
Zn	40.96	40	9.725	9.88

^aRadical hardness suggested appropriate for anions in Ref. [23].

TABLE II
Calculated derivative $(\partial\mu/\partial Z)_N$ (a.u.) and dimensionless parameters c , d in Eq.

Atom/ion	$(\partial\mu/\partial Z)_N$	c	d
C ⁻	0.2342	-0.8326	1.0932
N ⁻	0.2665	-0.1890	1.1516
F ⁻	0.3647	-0.0893	1.3570
S ⁻	0.1752	-1.2900	0.9893
P ⁻	0.2108	-0.7482	1.0091
Cl ⁻	0.2611	-1.4094	1.0026
Br ⁻	0.2341	-1.6459	0.9551
C ⁺	0.6378	-2.2079	0.9228
N ⁺	0.7166	-1.6409	0.9504
F ⁺	0.8259	-0.4617	1.1190
Si ⁺	0.4071	-1.5699	1.0262
P ⁺	0.4510	-1.4176	1.0053
Cl ⁺	0.5181	-1.0287	1.0088
Br ⁺	0.4449	-0.8969	1.0695
Sc	0.2300	-3.5241	1.0075
Ti	0.3066	-3.4528	0.9836
V	0.3093	-2.8937	0.9725
Cr	0.2408	-2.2023	1.0053
Mn	0.2802	-3.3689	0.9861
Fe	0.2479	-1.7221	1.0139
Co	0.2591	-1.7276	1.0003
Ni	0.2713	-1.8088	0.9955
Cu	0.3416	-1.7337	0.9949
Zn	0.2394	-3.0215	1.0354

are listed in Table II. Parameter d is close to 1 for a majority of atoms/ions and parameter b is negligibly small.

Characteristic feature of the calculated new Fukui functions is very clear region of negative FF near the nucleus. Negative parts of the Fukui functions have recently focused some interest, but have not yet been demonstrated for a coherent collection of species [25]. Results of this present work are shown in Figures 1–4. For the halogen atoms and their ions (see Fig. 1), the negative region is larger for the anions and nearly (but not quite) vanishes for the cations. It becomes shallower, but gets multiplied for higher halogens; this behavior is also typical in other main groups of the periodic table (see e.g. Figs. 2 and 3). Figures 2 and 3 allow for comparing the FF for the open shell atoms/ions for the isoelectronic pairs: C/N⁺, C⁻/N, Si/P⁺, Si⁻/P. Surprisingly, the FF are similar for the pairs of original species (C/N, Si/P and their respective ions), but do not show much resemblance in isoelectronic pairs. For closed shell species, however, the Fukui functions for anion (F⁻) and isoelectronic neutral atom (Ne)

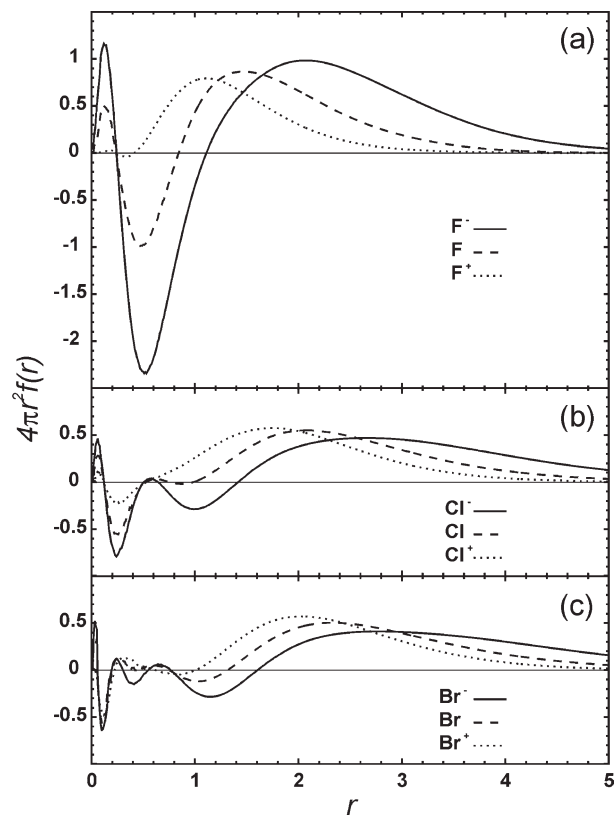


FIGURE 1. Fukui functions for neutral and ionized halogen atoms.

are very close (see Fig. 4); the difference is readily explained by the difference in their nuclear charges.

The quantitative test for the Fukui functions has been proposed in Ref. [16] through the calculation of global hardness by Eq. (3). The result

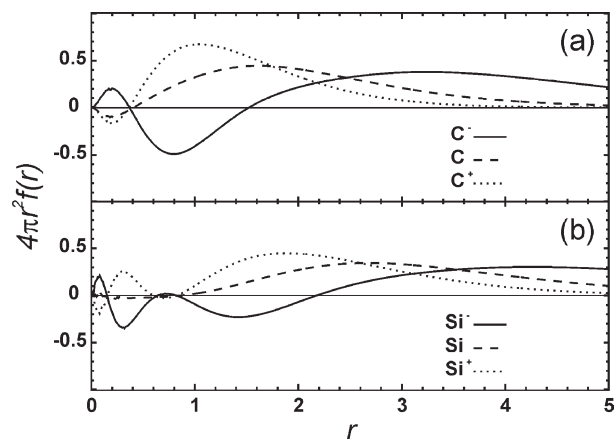


FIGURE 2. Fukui functions for carbon and silicon atoms, neutral and ionized.

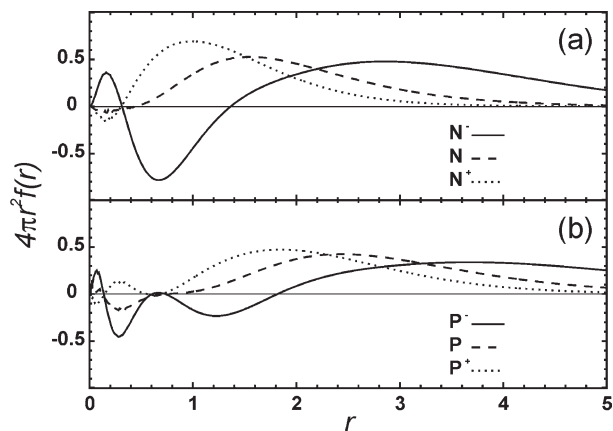


FIGURE 3. Fukui functions for nitrogen and phosphorus atoms, neutral and ionized.

should roughly correlate with the hardness calculated as $\eta = I - A$, within the approximation for the hardness kernel limited to the electronic part: $\eta(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$. Indeed, for the collection of atoms/ions in this work linear correlation was obtained as $\eta = 0.8292\eta_f + 1.2015$, ($R^2 = 0.82$ hardness in eV), with the fluorine anion being a single exception excluded. The quality of this result is same as for the correlation for 29 neutral atoms in Ref. 16, where the closed shell group VIIIA atoms also stood off the rest of the group. This is very likely to result from the unphysical nature of the negative ionization of these entities, as such process does not produce stable ions.

Another quantitative test for the quality of the resulted FF may be proposed by confronting internal results of the present method. It has been proposed long time ago [26, 27] and recently

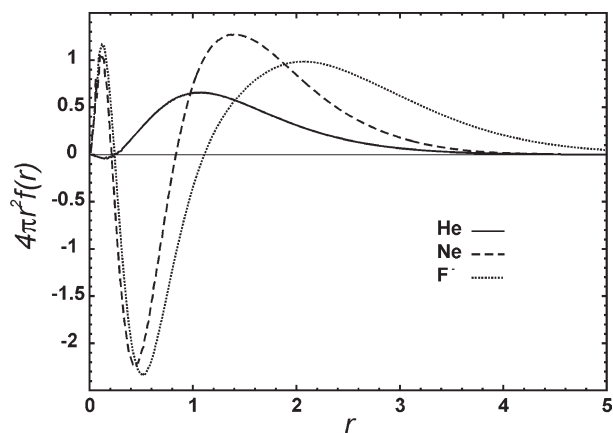


FIGURE 4. Fukui functions for isoelectronic Ne atom and F^- anion; He atom is also shown.

corroborated by formal proof by Ayers [28] that a relation between the electronic dipole polarizability for atoms and hardness is expected as:

$$(\alpha_e)^{-1/3} \propto \eta \quad (12)$$

As the FF calculated in this work are polarization justified, an exact relation between $(\alpha_e)^{-1/3}$ and η_f from Eq. (3) should be expected, and the result gives a direct measure for the quality of approximation for kernels used: $\eta(\mathbf{r},\mathbf{r}')$ in Eq. (3) and $s(\mathbf{r},\mathbf{r}')$ in Eqs. (7) and (8). This correlation has been examined on the collection of 29 atoms studied in Ref. 16 plus 24 atoms and ions in this work (excluding again He, Ne, Ar, Kr, and F⁻). The linear correlation is excellent: $(\alpha_e)^{-1/3} = 1,0446\eta_f$ ($R^2 = 0,893$). Apparently, applied approximations for the softness kernel are coherent with the commonly used formula for the hardness kernel. This result strongly supports the polarization justified calculation scheme proposed for the Fukui functions. It also calls for closer examination of the softness kernels properties, as these are crucial for the description of sensitivity of a system to an exchange of electrons in a chemical reaction.

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