Polarization justified Fukui functions: The theory and applications for molecules

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The Fukui functions based on the computable local polarizability vector have been presented for a group of simple molecules. The necessary approximation for the density functional theory softness kernel has been supported by a theoretical analysis unifying and generalizing early concepts produced by the several authors. The exact relation between local polarizability vector and the derivative of the nonlocal part of the electronic potential over the electric field has been demonstrated. The resulting Fukui functions are unique and represent a reasonable refinement when compared to the classical ones that are calculated as the finite difference of the density in molecular ions. The new Fukui functions are strongly validated by their direct link to electron dipole polarizabilities that are reported experimentally and by other computational methods. © *2011 American Institute of Physics.*
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I. INTRODUCTION

The idea of the Fukui function (FF) has been introduced into the conceptual density functional theory (DFT) by Parr and Yang in 1984.[1] The derivative of the electron density has been identified via the Maxwell relation as the functional derivative of the chemical potential with respect to the external potential at point **r**. FF has been widely recognized as a potential source of information on molecular properties [Eq. (1)],[2]

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{\upsilon} = \left(\frac{\delta \mu}{\delta \upsilon(\mathbf{r})} \right)_{N}, \qquad (1)$$

$\rho(\mathbf{r})$ is the electron density function, $\upsilon(\mathbf{r})$ is the external potential, and μ is the chemical potential of the system.

Demonstrating the utility of the FF in describing chemical reactivity of molecules has been a target of numerous studies with a limited success: practical approaches have not been extended beyond the first approximations to FF based on readily computable electron density for a molecule and its respective ions,[3–5]

$$f^{EG}(\mathbf{r}) \cong \frac{\rho(\mathbf{r})}{N} \text{ the electron gas approximation,} \qquad (2)$$

$$f^{+/-}(\mathbf{r}) \cong \frac{1}{2}[\rho^{-}(\mathbf{r}) - \rho^{+}(\mathbf{r})]$$

the finite difference approximation. (3)

Practical use of the FF has been concentrated on two sets of issues: the FF condensed to atomic resolution[6,7] and generation of the actual maps of the electron density derivative.

Theoretical significance of the FF for the conceptual DFT has been brought up by many authors;[2–6] relations of the FF to other potential reactivity indices: softness, nuclear reactivity etc., have also been demonstrated.[2,8–10]

The profound theoretical work by several authors, exploring more refined approaches to the FF, has never been extended to objects other than atoms.[11–15] This situation has been stimulating the preferential use of the Fukui function in chemical reactivity studies that reproduce tentatively the electrophilicity and/or nucleophilicity of the reagents. No physical effect has ever been indicated to provide a measurable quantity leading to the Fukui functions.

The evident chemical context of the Fukui functions (and the Fukui indices for bonded atoms)[16] has stimulated theoretical chemists to concentrate on the molecule exchanging electrons. Deducing properties of a molecule from the well-defined changes of the electron density upon ionization as observed in the respective ions [Eq. (1), first part and Eq. (3)] have been a primary target of many studies.[17] The fundamental difficulty in calculating the derivatives over the discrete and variable number of electrons N has been well recognized and led Ayers, De Proft *et al.*[14] to the conclusion that, perhaps, a single (average) chemical potential does not exist since the molecular reactivity must be separately analyzed for the nucleophilic and electrophilic region. If true, this conclusion would have far reaching consequences for the whole density functional theory, based on Parr's unique idea that the chemical potential of the electrons in any system can be defined as,[2,18]

$$\mu \equiv \frac{\delta E_{\upsilon}[\rho]}{\delta \rho(\mathbf{r})} = \left(\frac{\partial E}{\partial N} \right)_{\upsilon}. \qquad (4)$$

The chemical potential, like the energy itself, must be a functional of ρ;[19] due to the latter equality in Eq. (4) it is

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a function of the external potential $\upsilon(\mathbf{r})$. While the first part of Eq. (4) is strictly defined also for a single molecule (μ_υ), the second part thereof is subject to operational approximation leading to the numerical value for μ. The result introduced by Parr *et al.* in the landmark paper[18] has been commonly used and also substantiated theoretically by Perdew *et al.*:[20] $\mu = (\partial E/\partial N)_\upsilon = -\frac{1}{2}(I + A)$. As noted by Ayers and Parr,[21] this implies using the grand canonical ensemble to extend density functional theory to nonintegral numbers of electrons and thus, it is correct in non-zero temperatures only. This result is important and widely used, as it brought density functional theory into harmony with the earlier chemical idea of electronegativity by Mulliken:[22,23] $\chi = \frac{1}{2}(I + A) = -\mu$. Also, it is consistent with the finite difference approximation or the once-explored quadratic model for $E(N)$ function[24] that still attracts some attention and that has been recently rationalized.[25] Recalling the fundamental equation of the conceptual DFT: $\mu = \upsilon(\mathbf{r}) + \delta F_{HK}[\rho]/\delta\rho(\mathbf{r})$, it should be noted that the chemical potential (the number) like the electrostatic potential $\upsilon(\mathbf{r})$, is only determined to within a constant. Other choices have also been suggested:[24,26,27] $\mu = 0$ for an isolated object in equilibrium. This choice has not yet attracted attention in the literature. The result $\mu = -\frac{1}{2}(I + A)$ has been widely accepted not only because it provided a much needed numerical value to the chemical potential but also as it is coherent with the common formula for the Fukui function [Eq. (3)] that stems from the original concept by Fukui.[16]

Despite the disputable value for the chemical potential itself, the derivative of the chemical potential may be determined by the second part of the two equivalent definitions of the Fukui functions as shown in Eq. (1), this has been explored only recently.[14,15] The authors calculated the change in the Kohn-Sham orbital energies induced by perturbations in the molecular external potential and have thus avoided differentiation with respect to the electron number in the resulting FF, abandoning the idea of a unique chemical potential and using the one from above and from below $\mu^+ = -A$ and $\mu^- = -I$, respectively.

A analysis circumventing this limitation has been provided by the present authors.[28] It has been noted that the derivative $f(\mathbf{r}) = [\delta\mu/\delta\upsilon(\mathbf{r})]_N$ must contain an effect of the polarization of the electron density in the (uniform) electric field ε. The local polarization vector (a computable quantity) has been defined in this analysis[28] as,

$$\alpha_i(\mathbf{r}) \equiv -\left(\frac{\partial\rho(\mathbf{r})}{\partial\varepsilon_i}\right)_N \quad (i = x, y, z). \quad (5)$$

A similar concept has been explored by Kristhal, Senet, and van Alsenoy in their contemporary study of the group polarizabilities in a series of aminoacids.[29] The authors focused their attention on the local polarizability $\alpha_{ij}(\mathbf{r}) = r_j\alpha_i(\mathbf{r})$ only.

The FF have been calculated for atoms as[28]

$$f(\mathbf{r}) = d\frac{\alpha(\mathbf{r})\cdot\mathbf{r}}{r^2}\left[\int\frac{\alpha(\mathbf{r})\cdot\mathbf{r}}{r^2}d\mathbf{r}\right]^{-1} + (1 - d)\frac{\rho(\mathbf{r})}{N}. \quad (6)$$

The single parameter d (for most atoms close to 1) is readily computed for any atom by exploring the fundamental property

of the FF:[11,28] $\int f(\mathbf{r})r^{-1}d\mathbf{r} = -[\partial\mu/\partial Z]_N$. Crucial for the derivation of Eq. (6) was the approximation for the softness kernel based on the Vela and Gazquez proposal[30] (later refined by other authors[31,32]),

$$s(\mathbf{r}, \mathbf{r}') = -\left(\frac{\delta\rho(\mathbf{r})}{\delta\upsilon(\mathbf{r}')}\right)_\mu \approx Sf(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}'), \quad (7)$$

where S is molecular softness or inverse global hardness η: $\eta = (\partial^2 E/\partial N^2)_\upsilon = I - A$. FF for many atoms have been computed and discussed.[28,33] Also, the spatial properties for the softness kernel have been analyzed.[34] The resulting FF reproduces precisely the electron dipole polarization of the system and also its global softness. It has been demonstrated that this requires considerably refined functionals in the computation process of the density and its derivative [Eq. (5)].

This present work is focused on extending the approach to molecules. This is non-trivial, since the spherical symmetry of atoms greatly simplified the original analysis leading to the polarization justified Fukui functions. Therefore, the general theory is presented first, followed by the approximations and calculation method.

II. THE SOFTNESS KERNEL IN THE DFT

The energy density functional has the form (quite general),

$$E[\rho] = \int \rho(\mathbf{r}')\upsilon(\mathbf{r}')d\mathbf{r}' + F_{HK}[\rho]. \quad (8)$$

The functional derivative over the density gives the standard expression for the chemical potential,

$$\mu = \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} = \upsilon(\mathbf{r}) + u(\mathbf{r}). \quad (9)$$

Assume that the universal modified electron potential $u(\mathbf{r})$ is additively composed of two parts: $u_L(\mathbf{r})$ – local (some function of the density, like kinetic or exchange terms in the Thomas-Fermi model) and $u_{NL}(\mathbf{r})$ – nonlocal (some functional of the density, like the electron repulsion term). Then

$$\mu = \upsilon(\mathbf{r}) + u_L(\mathbf{r}) + u_{NL}(\mathbf{r}). \quad (10)$$

The functional derivative $[\delta/\delta\upsilon(\mathbf{r}')]_\mu$ leads to

$$0 = \delta(\mathbf{r} - \mathbf{r}') + \frac{du_L}{d\rho}\left[\frac{\delta\rho(\mathbf{r})}{\delta\upsilon(\mathbf{r}')}\right]_\mu + \left[\frac{\delta u_{NL}(\mathbf{r})}{\delta\upsilon(\mathbf{r}')}\right]_\mu. \quad (11)$$

Hence, the softness kernel: $s(\mathbf{r}, \mathbf{r}') = -[\delta\rho(\mathbf{r})/\delta\upsilon(\mathbf{r})]_\mu$ becomes

$$s(\mathbf{r}, \mathbf{r}') = k(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + k(\mathbf{r})\left[\frac{\delta u_{NL}(\mathbf{r})}{\delta\upsilon(\mathbf{r}')}\right]_\mu. \quad (12)$$

Integration of Eq. (12) must give the local softness. Hence

$$k(\mathbf{r}) = \left(\frac{du_L}{d\rho}\right)^{-1} = \frac{s(\mathbf{r})}{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial\mu}\right]_\upsilon}, \quad (13)$$

where the following helpful relationship has been used

$$\int \left[\frac{\delta u_{NL}(\mathbf{r})}{\delta \upsilon(\mathbf{r}')} \right]_\mu d\mathbf{r}' = -\int\int \frac{\delta u_{NL}(\mathbf{r})}{\delta \rho(\mathbf{r}'')} s(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' d\mathbf{r}''$$

$$= -\int \frac{\delta u_{NL}(\mathbf{r})}{\delta \rho(\mathbf{r}'')} s(\mathbf{r}'') d\mathbf{r}''$$

$$= -\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon. \qquad (14)$$

Using this and doing the necessary algebra leads to the expression for the softness kernel,

$$s(\mathbf{r}, \mathbf{r}') = s(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + p(\mathbf{r}, \mathbf{r}'). \qquad (15)$$

The first term on the right-hand side represents the Vela and Gazquez proposal[30] [Eq. (7)]. The second term represents the intuitive extension proposed by Garza and Robles:[31] $p(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')$ and by Li and Evans:[32] $p(\mathbf{r}, \mathbf{r}') \propto Sf(\mathbf{r})f(\mathbf{r}')$. It is now possible to have the nonlocal term $p(\mathbf{r}, \mathbf{r}')$ defined rigorously,

$$p(\mathbf{r}, \mathbf{r}') = \frac{s(\mathbf{r})}{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon} \left\{ \left[\frac{\delta u_{NL}(\mathbf{r})}{\delta \upsilon(\mathbf{r}')} \right]_\mu \right.$$

$$\left. + \delta(\mathbf{r} - \mathbf{r}') \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon \right\}. \qquad (16)$$

III. THE LOCAL POLARIZATION VECTOR AND THE FUKUI FUNCTION

The constant nuclear positions (i.e., the external potential) have been assumed in the subsequent analysis. This is a well-recognized regime for polarization phenomena, as separation of the electron and atomic polarization effects is experimentally well founded. The dipole moment of a system is (in atomic units)

$$\mathbf{M} = \sum_i^{nuclei} Z_i \mathbf{R}_i - \int \mathbf{r}\rho(\mathbf{r})d\mathbf{r} = \mathbf{M}_n - \mathbf{M}_e. \qquad (17)$$

Hence its derivatives over the number of electrons (N) and the electric field (ε) are

$$\mathbf{M}^{(N)} = \left(\frac{\partial \mathbf{M}}{\partial N} \right)_\upsilon = -\int \mathbf{r} f(\mathbf{r})d\mathbf{r} = -\mathbf{M}_e^{(N)}, \qquad (18)$$

$$\underline{\mathbf{M}}^{(\varepsilon)} = \int \mathbf{r}\alpha(\mathbf{r})d\mathbf{r} = -\int\int \mathbf{r}\mathbf{r}'\omega(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r} = \underline{\underline{\alpha_e}}. \qquad (19)$$

Here $\omega(\mathbf{r}, \mathbf{r}') = [\delta\rho(\mathbf{r})/\delta\upsilon(\mathbf{r}')]_N$ is the linear response function[35] and $\underline{\underline{\alpha_e}}$ is the electronic dipole polarizability tensor of a system.

The local polarization vector (a computable quantity) has been introduced in the preceding work[28] [Eq. (5)]. It is directly related to the linear response function,

$$\alpha(\mathbf{r}) = -\int \mathbf{r}'\omega(\mathbf{r}, \mathbf{r}')d\mathbf{r}'. \qquad (20)$$

The Berkowitz and Parr relation[36]

$$\omega(\mathbf{r}, \mathbf{r}') = -s(\mathbf{r}, \mathbf{r}') + s(\mathbf{r})f(\mathbf{r}'), \qquad (21)$$

and the general result for the softness kernel [Eqs. (15) and (16)] leads to the result,

$$\alpha(\mathbf{r}) = \int \mathbf{r}'s(\mathbf{r}, \mathbf{r}')d\mathbf{r}' - s(\mathbf{r})\mathbf{M}_e^{(N)}$$

$$= s(\mathbf{r})\left[\mathbf{r} - \mathbf{M}_e^{(N)} \right] + \mathbf{p}(\mathbf{r}), \qquad (22)$$

The $\mathbf{p}(\mathbf{r})$ vector is given as

$$\mathbf{p}(\mathbf{r}) = \int \mathbf{r}' p(\mathbf{r}, \mathbf{r}')d\mathbf{r}'. \qquad (23)$$

For $p(\mathbf{r}, \mathbf{r}')$ see Eq. (16). In order to get the final result for $\mathbf{p}(\mathbf{r})$ in a transparent form, the derivative of the nonlocal electronic potential over the field is introduced in the symbolic notation using $d\upsilon(\mathbf{r}) = \mathbf{r} \cdot d\varepsilon$ (as in Ref. 28),

$$\int \left[\frac{\delta u_{NL}(\mathbf{r})}{\delta \upsilon(\mathbf{r}')} \right]_\mu \mathbf{r}'d\mathbf{r}' = \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon} \right]_\mu. \qquad (24)$$

The derivative at constant μ (above) may be replaced by the accessible derivative at constant N (closed system). This is readily done for another important derivative, by using the Berkowitz and Parr relation again [Eq. (21)],[36]

$$\left[\frac{\partial \rho(\mathbf{r})}{\partial \varepsilon} \right]_\mu = \int \left[\frac{\delta \rho(\mathbf{r})}{\delta \upsilon(\mathbf{r}')} \right]_\mu \mathbf{r}'d\mathbf{r}' = \int \omega(\mathbf{r}, \mathbf{r}')\mathbf{r}'d\mathbf{r}'$$

$$- \int s(\mathbf{r})f(\mathbf{r}')\mathbf{r}'d\mathbf{r}' = \left[\frac{\partial \rho(\mathbf{r})}{\partial \varepsilon} \right]_N - s(\mathbf{r})\mathbf{M}_e^{(N)}. \qquad (25)$$

Using this result the required derivative is transformed,

$$\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon} \right]_\mu = \int \frac{\delta u_{NL}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \left[\frac{\partial \rho(\mathbf{r}')}{\partial \varepsilon} \right]_\mu d\mathbf{r}'$$

$$= \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon} \right]_N - \mathbf{M}_e^{(N)} \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon. \qquad (26)$$

Finally,

$$\mathbf{p}(\mathbf{r}) = \frac{s(\mathbf{r})}{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon} \left\{ \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon} \right]_N \right.$$

$$\left. + \left[\mathbf{r} - \mathbf{M}_e^{(N)} \right] \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon \right\}. \qquad (27)$$

Introducing this into Eq. (22) leads to the important and exact result that combines derivatives of the nonlocal electronic potential with other quantities: either directly computable ($\alpha(\mathbf{r})$), or accessible with some chemical intuition ($s(\mathbf{r})$, $\mathbf{M}_e^{(N)}$),

$$\alpha(\mathbf{r}) \left\{ 1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu} \right]_\upsilon \right\}$$

$$= s(\mathbf{r}) \left\{ \mathbf{r} - \mathbf{M}_e^{(N)} + \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon} \right]_N \right\}. \qquad (28)$$

This simple and appealing relation opens a way to the variety of applications. The purpose of this present work is to assess the local softness $s(\mathbf{r})$ (hence the Fukui function therein) obtained with the refined approximation to the softness kernel

and to demonstrate the limitations still hidden therein. Studying the properties of the nonlocal electronic potential through Eq. (28) is a subject of separate work.[37]

IV. THE CALCULATION METHOD

The approximation for the softness kernel successfully tested for atoms was adopted by generalizing the preceding efforts and contains complete expansion within the first order. In final form this proposal has been originally introduced in previous work,[28]

$$s(\mathbf{r}, \mathbf{r}') = (1 - c)s(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') - bN\rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$$
$$+ b\rho(\mathbf{r})\rho(\mathbf{r}') + cSf(\mathbf{r})f(\mathbf{r}'). \tag{29}$$

This is equivalent to the following arbitrary form for $p(\mathbf{r}, \mathbf{r}')$ [Eq. (16)],

$$p(\mathbf{r}, \mathbf{r}') = cs(\mathbf{r})\{f(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')\}$$
$$+ bN\rho(\mathbf{r})\left\{\frac{\rho(\mathbf{r}')}{N} - \delta(\mathbf{r} - \mathbf{r}')\right\}. \tag{30}$$

This expression contains parameters b, c to be determined. The local polarization vector within this practical approach reads

$$\alpha(\mathbf{r}) = (1 - c)s(\mathbf{r})\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right] + b\rho(\mathbf{r})\left[\mathbf{M}_e - N\mathbf{r}\right]. \tag{31}$$

In consequence, the approximation for the $\mathbf{p}(\mathbf{r})$ vector is implied in the form,

$$\mathbf{p}(\mathbf{r}) = -cs(\mathbf{r})\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right] + b\rho(\mathbf{r})\left[\mathbf{M}_e - N\mathbf{r}\right]. \tag{32}$$

Equation (31) represents considerable simplification of the general result [Eq. (28)]. A unique solution for the local softness and the Fukui function $f(\mathbf{r}) = s(\mathbf{r})/S$ from the vector equation [Eq. (31)] containing arbitrary parameters is not guaranteed. Specifically, the approximated $\mathbf{p}(\mathbf{r})$ vector may not reproduce the direction of the exact vector [Eq. (27)] at every point in space. However, since Eq. (29) was built on the assumption that b and c parameters do exist, the conditions that warrant the existence of a solution of Eq. (31) for the $s(\mathbf{r})$ function must be examined and rationalized.

To calculate the unique value for $s(\mathbf{r})$, the vector [Eq. (31)] may be transformed into an algebraic equation by appropriate projection onto the $[\mathbf{r} - \mathbf{M}_e^{(N)}]$ vector. In order to eliminate the singularity of $s(\mathbf{r})$ at $\mathbf{r}^* = \mathbf{M}_e^{(N)}$, a unique parameter b may be calculated from

$$\alpha(\mathbf{r}^*) = b\rho(\mathbf{r}^*)[\mathbf{M}_e - N\mathbf{r}^*] \text{ for } \mathbf{r}^* = \mathbf{M}_e^{(N)}. \tag{33}$$

This yields parameter b that warrants existence of a solution for $s(\mathbf{r})$ in every point in space,

$$b = \frac{1}{\rho(\mathbf{r}^*)}\frac{\alpha(\mathbf{r}^*) \cdot [\mathbf{M}_e - N \cdot \mathbf{M}_e^{(N)}]}{\left[\mathbf{M}_e - N \cdot \mathbf{M}_e^{(N)}\right]^2}. \tag{34}$$

For centro-symmetric objects this condition must be modified, since $\mathbf{M}_e^{(N)} = 0$ and $\mathbf{M}_e = 0$. Taking the origin at the symmetry center, considering $\boldsymbol{\alpha}(0) = 0$ and expanding $\boldsymbol{\alpha}(\mathbf{r})$

vector in a series over $\mathbf{r}$ around $\mathbf{r} = 0$ we have

$$b = -\frac{1}{N\rho(0)}\left\{\left[\frac{\partial\alpha_x(\mathbf{r})}{\partial x}\right]_{\mathbf{r}=0} + \left[\frac{\partial\alpha_y(\mathbf{r})}{\partial y}\right]_{\mathbf{r}=0}\right.$$
$$\left. + \left[\frac{\partial\alpha_z(\mathbf{r})}{\partial z}\right]_{\mathbf{r}=0}\right\}. \tag{35}$$

Equations (34) and (35) provide a condition for the choice of b that warrants a unique solution for Eq. (31). To achieve the result for the Fukui function the same projection onto the $[\mathbf{r} - \mathbf{M}_e^{(N)}]$ vector must be used that validated the condition for b,

$$s(\mathbf{r}) = \frac{\alpha(\mathbf{r})\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right] - b\rho(\mathbf{r})[\mathbf{M}_e - N\mathbf{r}]\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]}{(1 - c)\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]^2}. \tag{36}$$

This is integrated to the global softness,

$$S = \int s(\mathbf{r})d\mathbf{r} \equiv \frac{K}{1 - c}, \tag{37}$$

where by definition

$$K \equiv \int \frac{\alpha(\mathbf{r})\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right] - b\rho(\mathbf{r})[\mathbf{M}_e - N\mathbf{r}]\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]}{\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]^2}d\mathbf{r}. \tag{38}$$

Hence, the Fukui function is obtained. Parameter c does not appear,

$$f(\mathbf{r}) = \frac{s(\mathbf{r})}{\int s(\mathbf{r})d\mathbf{r}} = \frac{1}{K\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]^2}$$
$$\times \{\alpha(\mathbf{r}) - b\rho(\mathbf{r})[\mathbf{M}_e - N\mathbf{r}]\}\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]. \tag{39}$$

The global softness resulting from Eq. (37) may be arbitrary, considering the approximations employed; the K integral is computable but the c parameter remains unknown. By fixing the global softness at $S = (I - A)^{-1}$, parameter c is obtained as

$$c = 1 - K/S = 1 - K(I - A). \tag{40}$$

V. RESULTS AND DISCUSSION

The electron density has been calculated by the GAUSSIAN 03 code,[38] the DFT B3LYP method. The *aug-cc-pvqz* basis set has been used. The local polarizability vector $\alpha(\mathbf{r})$ [Eq. (5)] has been calculated by the finite field procedure. The electron dipole polarizability for each molecule was obtained by numerical integration of $\alpha(\mathbf{r})\mathbf{r}$ and served the purpose of testing whether the calculation scheme or the basis set properly reproduce the polarizability of the system. The calculated energies and polarizabilities as well as the respective reference data are shown in Table I. The derivative of the electronic dipole moment was calculated by the finite difference method, based on the results for the respective molecular cation and anion. Note that the $[\mathbf{r} - \mathbf{M}_e^{(N)}]$ vector is translationally invariant, while the $\mathbf{M}_e^{(N)}$ alone is not. The calculated parameters that appear in the working approximation are collected in Table II. The resulting diagrams of the Fukui functions are shown in Figs. 1–3, together with the diagrams of classical Fukui functions $f_\pm = 1/2(\rho^- - \rho^+)$. The diagrams

TABLE I. The optimized molecular geometry, global hardness (I-A), electron dipole polarizability, and dipole moments for the set of molecules studied. The orientation of the coordinate system is found in the diagrams in Figs. 1–3. All data are presented in the atomic units.

Molecule	LiH	HF	CO	N$_2$	H$_2$CO
R	3.004	1.7428	2.1236	2.1802	CO: 2.2641 CH: 2.0898
I-A	0.3203	0.5829	0.4848	0.4870	0.3410
$\alpha_{xx} = \alpha_{yy}$ calc.	30.56	5.34	12.11	10.37	$\alpha_{xx} = 13.19\ \alpha_{yy} = 18.50$
α_{zz} calc.	28.51	6.62	15.42	15.06	22.71
$\langle\alpha\rangle$ calc.	29.88	5.77	13.21	11.93	18.10
$\langle\alpha\rangle$/(reference)	28.43/(Ref. 40)	5.60/(Ref. 41)	13.09/(Ref. 41)	11.74 /(Ref. 41)	16.5/(Ref. 42)
$M_{(z)}$ [Eq. (17)]	−2.2467	−0.7114	0.0392	0	−0.9294
$M_{e(z)}$ [Eq. (17)]	−0.7572	7.6822	2.0844	0	0.9294
$M_{e(z)}^{(N)}$ [Eq. (18)]	−2.3023	−0.4541	−1.3678	0	−0.4934

TABLE II. Parameters calculated for the molecules (in a.u.).

Molecule	LiH	HF	CO	N$_2$	H$_2$CO
$b\ 10^3$ [Eqs. (34) and (35)]	− 40.893	− 27.489	− 2.257	− 6.264	− 31.776
K [Eq. (38)]	3.3704	2.1456	5.0405	4.4970	−3.8499
c [Eq. (40)]	− 0.0794	− 0.2506	− 1.4436	− 1.1900	2.3129
$\left(\partial u_{NL}/\partial\mu\right)_v$ [Eq. (43)]	0.0736	0.2004	0.5908	0.5434	1.7617
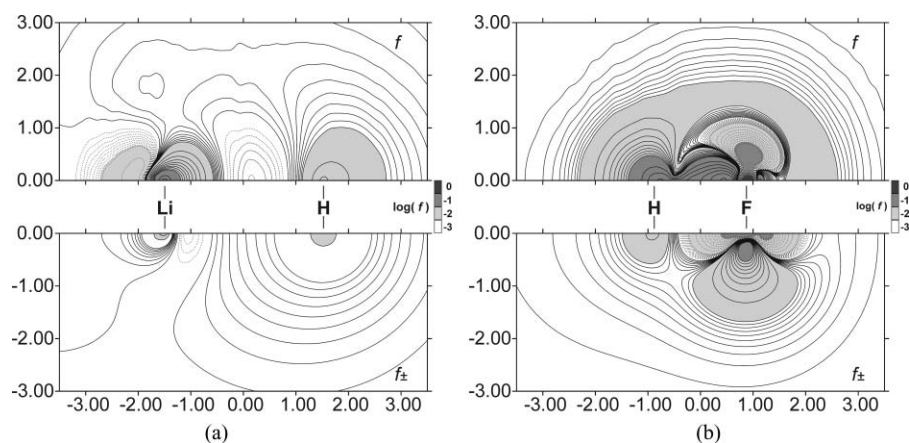
FIG. 1. The Fukui functions (in a.u.) in the xz plane for the molecules oriented with the bond along z direction (on the abscissa). The upper half: f – this work; the lower half: $f_{\pm} \cong 1/2(\rho^- - \rho^+)$. Logarithmic reduction of scale has been applied and indicated by shadows; negative values by dotted lines. (a) LiH molecule and (b) HF molecule.
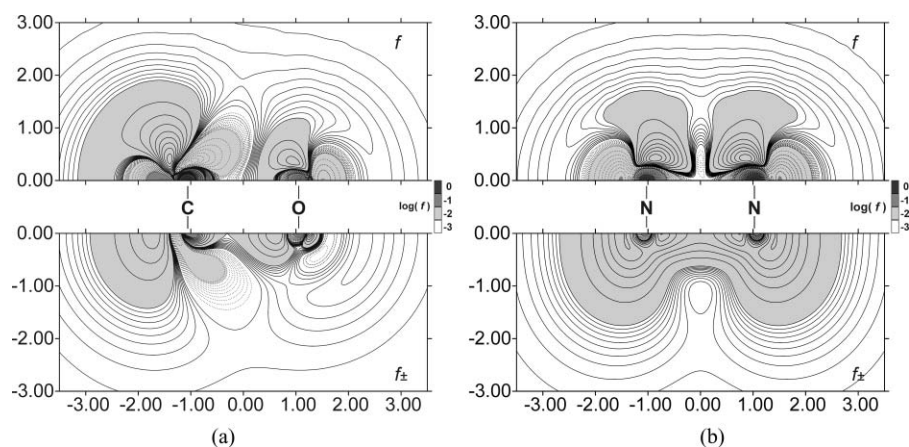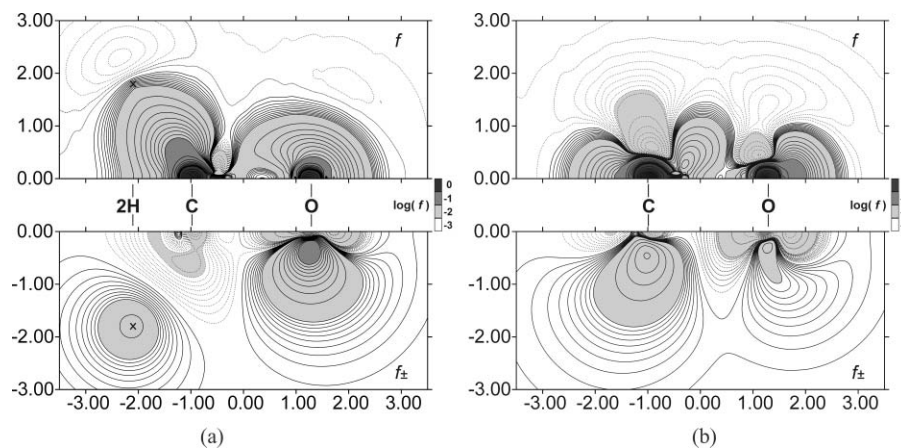

FIG. 2. The Fukui functions (in a.u.) in the xz plane for the molecules oriented with the bond along z direction (on the abscissa). The upper half: f – this work; the lower half: $f_{\pm} \cong 1/2(\rho^- - \rho^+)$. Logarithmic reduction of scale has been applied and indicated by shadows; negative values by dotted lines. (a) CO molecule and (b) N2 molecule.

FIG. 3. The Fukui functions (in a.u.) in the xz and yz planes for the H$_2$CO molecule oriented with the CO bond along z direction (on the abscissa). The upper half: f – this work; the lower half: $f_\pm \cong 1/2(\rho^- - \rho^+)$. Logarithmic reduction of scale has been applied; negative values by dotted lines. (a) Molecular plane (xz), with the position of the hydrogen atoms indicated ($\times$) and (b) plane perpendicular to the molecular plane (yz).

also indicate the location and orientation of the molecules in the coordinate system.

The diagrams for the calculated Fukui functions as compared to the classical ones (Figs. 1–3) demonstrate rough qualitative agreement. In all molecules studied, the new FF shows steeper slopes near nuclei than $f_\pm$. In two HX molecules (Fig. 1) f and $f_\pm$ around the hydrogen atom are much alike. They show remarkable differences in location of the negative value area near the heavy atom. In both HX molecules, the hydrogen atom tends to localize the excess charge (positive f region). In the non-polar CO and N$_2$ molecules the maps of f and $f_\pm$ match quite closely, especially at large distances from the nuclei. In the CH$_2$O molecule, the regions of negative (but exceedingly small f) Fukui functions far from the nuclei in the molecular plane are believed to be an effect of inadequate accuracy of the calculation's procedure. At intermediate distances from the nuclei, the f and $f_\pm$ functions are in a reasonable agreement. Comparing the FF in CO and in CH$_2$O molecules indicates that the π-frontier orbital FF region in CO is disturbed by the two CH σ-bonds in the formaldehyde molecule. This results in a displacement of the π-Fukui function region further from the CO bond axis and out of the molecular plane; also the reduction and subdivision of this region in the molecular plane due to the two neighboring C-H and one C-O σ-bonds is observed.

The inspection of the detailed differences between f and $f_\pm$ calls for further testing of the polarization justified FF's in the studies of the reaction path, as they contain direct information on the response of the actual density in the molecule to the external potential due to the approaching agent. This appears to be a much superior source of information as compared to the average density of ions, that served to estimate of the classical $f_\pm$ functions. As demonstrated recently by Tozer and De Proft,[39] the density of the molecular ion (ρ^-) is of questionable value for many molecules with unstable anions. The authors indicated a way to overcome this difficulty but the result will still be sensitive to the choice of the basis set. The new FF proposed in this work is only dependent on the basis set through the $\alpha(\mathbf{r})$ derivative. This dependence is controlled by using a basis set sufficient for the proper reproduction of

the electron dipole polarizability, obtained independently; the result needs no additional refinement.

The calculation scheme described in Sec. IV has been built on the refined approximation to the softness kernel with two arbitrary parameters b, c. They have been determined in the calculation procedure and are shown in Table II. The general and exact result [Eq. (28)] connecting the computable vector derivative $\alpha(\mathbf{r})$ to the unknown derivatives of the nonlocal electronic potential now allows for calculation of the later. This will be done by identifying expressions for the $\mathbf{p}(\mathbf{r})$ vector: the approximate [Eq. (32)], and the exact one below [transformed [Eq. (27)]

$$\mathbf{p}(\mathbf{r}) = \frac{\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v}{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v} s(\mathbf{r})\left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]$$
$$+ \frac{s(\mathbf{r})}{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v}\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon}\right]_N. \quad (41)$$

Equations (32) and (41) represent vectors with first components being identical, hence it must be

$$\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v \left\{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v\right\}^{-1} = -c. \quad (42)$$

This imposes an approximation

$$\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v \cong \left(\overline{\frac{\partial u_{NL}}{\partial \mu}}\right)_v = \frac{c}{c-1}. \quad (43)$$

Comparing the second vector terms in Eqs. (32) and (41) leads to

$$\frac{s(\mathbf{r})}{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_v}\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon}\right]_N = b\rho(\mathbf{r})\left[\mathbf{M}_e - N\mathbf{r}\right]. \quad (44)$$

This shows the implied approximation for the derivative [with the use of Eqs. (43) and (40)],

$$\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon}\right]_N = b\,[K(I-A)]^{-1}\,\frac{\rho(\mathbf{r})}{s(\mathbf{r})}\,[\mathbf{M}_e - N\mathbf{r}]. \tag{45}$$

Equations (43) and (45) demonstrate the consequences of the applied approximation for the softness kernel [Eq. (29)]. Calculated values for the spatially averaged derivative $(\partial u_{NL}/\partial \mu)_\upsilon$ are presented in Table II. These data may be cross-referenced assuming that the contribution from the coulomb potential is a substantial part of this derivative,

$$u_{NL}(\mathbf{r}) \approx \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{46}$$

Hence, the derivative should be related to the electrostatic potential of the Fukui function,[11]

$$\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_\upsilon \approx S \int \frac{f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{47}$$

Numerical data for the integral in Eq. (47) have been known for atoms (e.g., Ref. 11). They are positive numbers with moderate variation from a maximum near the nucleus (~ 1.0 a.u.) to ~ 0.1 a.u.; they tend to increase with increasing numbers of electrons in the system. The numerical results for $(\partial u_{NL}/\partial \mu)_\upsilon$ in Table II must be considered very reasonable for an average value of this derivative.

The consequences of the approximation for the vector derivative $(\partial u_{NL}/\partial \varepsilon)_N$ in Eq. (45) are more complex. To appreciate this, Eq. (45) must be reconciled with the expectation from the exact Eq. (28),

$$\left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \varepsilon}\right]_N = \frac{\alpha(\mathbf{r})}{s(\mathbf{r})}\left\{1 - \left[\frac{\partial u_{NL}(\mathbf{r})}{\partial \mu}\right]_\upsilon\right\} - \left[\mathbf{r} - \mathbf{M}_e^{(N)}\right]. \tag{48}$$

This exact vector derivative represents a sum of the two well-defined vector contributions and unveils an interesting general property of the derivative of the total nonlocal electronic potential. In any electronic system, the vector $[\partial u_{NL}(\mathbf{r})/\partial \varepsilon]_N$ at every point $\mathbf{r}$ must be in plane defined by the pair of the well-defined vectors: $\alpha(\mathbf{r})$ and $[\mathbf{r} - \mathbf{M}_e^{(N)}]$. This condition is not affected by whatever approximation for $(\partial u_{NL}/\partial \mu)_\upsilon$ is employed in order to evaluate $s(\mathbf{r})$. Comparing Eq. (48) to Eq. (45) it becomes clear that, in general, the working approximation applied in Eq. (45) (cf., Sec. IV) would not warrant compliance with the above requirement. On the other hand, the condition is trivially met for an atom: due to its spherical symmetry $\mathbf{M}_e = 0$ and $\mathbf{M}_e^{(N)} = 0$; hence the vector derivatives in Eqs. (45) and (48) are collinear. In consequence, the solution for $s(\mathbf{r})$ in the basic vector equation [Eq. (31)] is guaranteed for an atom as demonstrated in earlier works.[28,33] In a system of lower symmetry, the vector given by Eq. (45) and used in Eq. (31) may not meet the requirement of Eq. (48). To warrant a solution and a unique numerical value for $s(\mathbf{r})$ from the approximate vector equation [Eq. (31)] an additional projection procedure was necessary.

VI. CONCLUSION

A theoretical analysis has been presented, leading to the general exact relation between the local polarization vector and the derivatives of the nonlocal electronic potential. Calculation of the Fukui function for molecules was subjected to more extensive approximations than was possible for atoms. A proposed calculation procedure for the molecules produced Fukui functions that reproduce qualitative expectations for the collection of simple species, and contain information on the properties of the electron density in a molecule itself, without direct reference to the densities of its ions. Only minor increase in computer costs is involved of the order of a self-consistent field run to calculate the $\alpha(\mathbf{r})$ vector components. The novel property of the derivative $[\partial u_{NL}(\mathbf{r})/\partial \varepsilon]_N$ of the nonlocal electronic potential is reported that may be of interest in studying the requirements for the approximations for the energy density functional.

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