

Polarization justified Fukui functions

Ludwik Komorowski,^{a)} Józef Lipiński, and Paweł Szarek

Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

(Received 15 July 2009; accepted 9 September 2009; published online 29 September 2009)

New Fukui functions have been derived within the conceptual density functional theory by the analysis of the polarization effect of a system in static electric field. Resulting Fukui functions accurately reproduce the global softness and electronic dipolar polarizability; they meet the condition $\int [f(\mathbf{r})/r] d\mathbf{r} = -(\partial\mu/\partial Z)_N$ and lead to very reasonable values of the global hardness for atoms for the group of 29 main group elements. Computational clarity makes the new Fukui functions a promising tool in studies of molecular reactivity. © 2009 American Institute of Physics. [doi:10.1063/1.3239503]

I. INTRODUCTION

Fukui function (FF) has been first introduced by Parr and Yang^{1,2} in 1984 as a derivative of the electron density, or the functional derivative of the chemical potential over the external potential function $\nu(\mathbf{r})$ in the density functional theory (DFT):

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

$\mu = (\partial E / \partial N)_\nu$ being the chemical potential of the system. Ever since FF has been a target of many studies, computational as well as chemical in nature. The widespread interest in this quantity has been stimulated by its relation to the reactivity indices in the frontier molecular orbital theory by Fukui.³ Recent extensive reviews of the general subject have been provided by Chermette,⁴ Geerlings *et al.*,⁵ and Chattaraj *et al.*⁶ Specifically, a perspective for the FF as chemical reactivity descriptor has been analyzed by Ayers and Levy.⁷ It has been recognized, that in principle, if the derivative [Eq. (1)] exists, it contains all information about the system. However, Ayers *et al.*⁸ convincingly argued, that such approach is only justified for molecules in contact with its environment at some real temperature (e.g., solution). For an isolated molecule at 0 K only derivatives “from above” and “from below” could be considered formally. This conclusion is very well consistent with the chemical tradition dating back to the Fukui reactivity indices; the electrophilic FF $f^-(\mathbf{r}) = (\partial \rho(\mathbf{r}) / \partial N)_\nu^-$ and nucleophilic FF $f^+(\mathbf{r}) = (\partial \rho(\mathbf{r}) / \partial N)_\nu^+$ have been widely explored, the radical FF $f^0(\mathbf{r})$ being the average thereof.

The variety of studies on FF calculation has been dominated by the finite difference approach. Two circumstances explain that situation. (i) The first part of the definition of the FF [Eq. (1)] seems to call for taking a finite difference derivative over N —an integral number. (ii) Connection of the FF with the frontier molecular orbital theory of reactivity by K. Fukui pushes the interest to investigation of the electron

density in real species, rather than to derivatives thereof. In consequence, while the FF and the Fukui indices (FF condensed to atoms,⁹ see also modern exhaustive analysis due to Ayers *et al.*^{10,11}) were extensively investigated, there has been less interest in studying the FF properties, e.g., its further derivatives over N and $\nu(\mathbf{r})$.⁵

First DFT computations of the FF based solely on the electron density of a neutral species were presented by Chattaraj *et al.*,¹² who proposed the gradient expansion of the electron density. An interesting contribution to the analysis has been added by Fuentealba¹³ within the local density model; the author explored the Thomas–Fermi–Dirac model. Also, Pacios and Gomes¹⁴ presented an analysis of the radial behavior of the FF calculated within the gradient expansion method and demonstrated the FF calculated with analytically modeled densities.

Recently, the second part of the definition [Eq. (1)] has been a target of the fundamental investigations, which opens a way to study the FF as a physical property, rather than as a chemical index. Ayers *et al.*^{15,16} presented an elaborate method of explicit calculations of the derivative over a local electrostatic potential $\nu(\mathbf{r})$. The authors deduced the FF from the change in Kohn–Sham orbital energies induced by perturbations in molecular external potential and have thus avoided differentiation with respect to the electron number. The authors followed the tradition of separate analysis $f^+(\mathbf{r})$ and $f^-(\mathbf{r})$ functions. They use the chemical potential from above, $\mu^+ = -A$, and from below, $\mu^- = -I$, as introduced by Ayers,¹⁷ and not the commonly used value $\mu = -\frac{1}{2}(I+A)$,¹⁸ the average of ionization energy (I) and electron affinity (A) of a system. The authors note, that their method presented a “proof of principle” rather than a tool for practical applications. A simpler, yet formally sound and computationally convenient approach is proposed in this present paper.

Quantum chemical calculations of FF and the Fukui indices condensed to atoms have been pursued in this laboratory very early, both on the semiempirical¹⁹ and *ab initio* level;²⁰ FF of the Bader AIM atoms²¹ have also been obtained.²² The goal of this present study is to relate the FF to an experimentally controlled property of a system, electronic dipole polarizability, which could provide an indepen-

^{a)} Author to whom correspondence should be addressed. Electronic mail: ludwik.komorowski@pwr.wroc.pl.

dent control for the quality of FF, before it might be applied in some chemical prediction.

II. SOFTNESS AND POLARIZABILITY

Softness of an atom, first introduced as an intuitive concept by R. G. Pearson in his classical hard and soft acids and bases (HSAB) rule, has been defined formally by Parr and Pearson²³ as the inverse global hardness $S=1/\eta$, with hardness definition coming from DFT:

$$\eta = (\partial^2 E / \partial N^2)_v = I - A. \quad (2)$$

(The original definition of global hardness included a factor $\frac{1}{2}$ for the sake of symmetry with the Mulliken electronegativity. This was later commented to be rather cumbersome, even by one of the original authors,²⁴ and will not be followed throughout this work.) A vague relation between hardness (softness) and polarizability has been outlined already by the author of the original concept²⁵ and many efforts were made to discover a relation between the two quantities, as soon as the measure for hardness has been introduced (for an early review see Ref. 26).

An electrostatic model proposed in this laboratory as a chemical approximation²⁷ first suggested a relation $1/\eta = S \cong \alpha^{1/3}$ (α stands for the electronic dipole polarizability). Theoretical support for that concept has been later presented by Simon-Manso and Fuentealba;²⁸ additional quantum-chemical wave function argument has been provided by Ayers in the framework of his extensive analysis of the HSAB principle.²⁹ Exploration of that idea allowed for calculations of hardness/softness' of bonded atoms from the data on molar refractions,³⁰ and also for softness' of bonded atoms within the framework of AIM.²²

Direct connection between the dipolar polarizability and global softness S of an atom has been first demonstrated within the rigorous DFT formalism by Vela and Gazquez.³¹ Their result for the electronic polarizability tensor was

$$\alpha_e = -S \left[\left(\int f(\mathbf{r}) \mathbf{r} d\mathbf{r} \right)^2 - \int f(\mathbf{r}) \mathbf{r} \mathbf{r} d\mathbf{r} \right]. \quad (3)$$

The authors demonstrated how the rather crude linear relationship between experimental values of α_e and $S=(I-A)^{-1}$ has been substantially improved for a series of atoms, when the FFs in Eq. (3) (the factor in brackets) has been included as $f(\mathbf{r})=1/2(\rho^- - \rho^+)$. A crucial point of their method was the strictly local approximation for the softness kernel $s(\mathbf{r}, \mathbf{r}')$ as defined in the DFT,²

$$s(\mathbf{r}, \mathbf{r}') = - \left(\frac{\delta \rho(\mathbf{r})}{\delta \nu(\mathbf{r}')_\mu} \right) \approx S f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'). \quad (4)$$

By cross checking their result they noted that in the spherical symmetry of an atom, approximation in Eq. (4) is compensated within their method of calculation of α_e ; nevertheless, their results for polarizability of atoms from Eq. (3) were too small, only ca. 50% on the average, of the expected values. Garza and Robles³² followed with further analysis of the softness kernel concluding that the proper form should rather contain the weighted local and nonlocal contributions. They

choose to generalize the local part with respect to Vela and Gazquez result:

$$s(\mathbf{r}, \mathbf{r}') \approx k(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') + t(\mathbf{r}) \rho(\mathbf{r}') \quad (5)$$

and used primitive approximation for the nonlocal part $t(\mathbf{r}) = \rho(\mathbf{r})$. The authors noted the role of the radial-induced dipole moment density in their study, but underlined the compact relation $\alpha_e = 2/Z(r^3)$ as their principal result, leading to qualitatively good α_e for atoms with $4 \leq Z \leq 36$. Subsequent step of the analysis published by Li and Evans³³ in 1995 presented another alternative nonlocal approach:

$$s(\mathbf{r}, \mathbf{r}') \approx a S f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') + b S f(\mathbf{r}) f(\mathbf{r}') \quad (6)$$

with $a + b = 1$.

This formula was used in theoretical study of chemical reactivity and stability, providing an additional support to the HSAB principle.

The valuable result by Vela and Gasquez [Eq. (3)] indicated that dipolar polarizability α_e may be decomposed into some integrable local contributions in which the local softness, $s(\mathbf{r})=Sf(\mathbf{r})$, hence the FF, plays a central role. Local contributions to polarizability have long been a subject of interest. Jameson and Buckingham³⁴ in 1980 proposed an electric polarizability density as $\alpha(\mathbf{r})=\rho^e(\mathbf{r})\mathbf{r}$ where $\rho^e(\mathbf{r})$ is the first order correction to the charge distribution in the presence of the uniform electric field ϵ , and $\alpha = \int \alpha(\mathbf{r}) d\mathbf{r}$. Stone³⁵ noted the difficulty in consistently defining a polarizability density function and concentrated on the scalar charge susceptibility $\alpha(\mathbf{r}, \mathbf{r}')$ also integrable to polarizability: $\alpha_{ij} = \int r_i \alpha(\mathbf{r}, \mathbf{r}') r_j d\mathbf{r} d\mathbf{r}'$. Bader²¹ unsuccessfully attempted to integrate local contributions into the polarizability of atomic basins. All these efforts present a valuable background to the analysis of the relation between the local polarization effect and the FF, which is the leading subject of this present study.

III. FUKUI FUNCTION FROM POLARIZATION DENSITY

In order to separate the effect of an external electric field ϵ from the nuclear potential $\nu_n(\mathbf{r})$, the classical DFT formulation must be adapted accordingly. First we assume separation of the nuclear and electronic effects, very well established for experimental data on polarizability. Since $\delta\nu(\mathbf{r}) = \delta\nu_n(\mathbf{r}) + \delta\nu_e(\mathbf{r})$, $\delta\nu_n(\mathbf{r})=0$ when the change in a local external potential is due to the external field exclusively, assuming constant nuclear positions R_i , and $\delta\nu(\mathbf{r}) = \delta\nu_e(\mathbf{r})$. Variation of the electrostatic potential at position \mathbf{r} becomes (see also Vela and Gazquez³¹) $\delta\nu_e(\mathbf{r}) = \mathbf{r} \cdot d\epsilon$ where $d\epsilon = \epsilon_x \hat{\mathbf{i}} + \epsilon_y \hat{\mathbf{j}} + \epsilon_z \hat{\mathbf{k}}$. The standard DFT electronic energy differential then becomes

$$\begin{aligned}
dE &= \mu dN + \int \rho(\mathbf{r}) \delta v(\mathbf{r}) d\mathbf{r} \\
&= \mu dN + d\boldsymbol{\varepsilon} \cdot \int \rho(\mathbf{r}) \mathbf{r} d\mathbf{r} \\
&= \mu dN + \mathbf{M}_e \cdot d\boldsymbol{\varepsilon} = \mu dN + \sum_i M_{e,i} d\varepsilon_i \quad (i = x, y, z).
\end{aligned} \tag{7}$$

$\mathbf{M}_e = \int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}$ stands for the electronic part of the dipole moment of the system; the total dipole moment is $\mathbf{M} = \mathbf{M}_n - \mathbf{M}_e$. Maxwell relation corresponding to Eq. (7) produces an important quantity, $\mathbf{M}_e^{(N)} = (\partial \mathbf{M}_e / \partial N)_{\varepsilon=0}$, a vector, to be further explored:

$$\left(\frac{\partial \mu}{\partial \varepsilon_i} \right)_N = \left(\frac{\partial M_{e,i}}{\partial N} \right)_{\varepsilon=0} \equiv M_{e,i}^{(N)} \quad (i = x, y, z). \tag{8}$$

This derivative is convenient to formulate the complementary DFT differential and corresponding Maxwell relation:

$$d\mu = \eta dN + \sum_{i=x,y,z} M_{e,i}^{(N)} d\varepsilon_i, \tag{9}$$

$$\text{hence} \quad \left(\frac{\partial \eta}{\partial \varepsilon_i} \right)_N = \left(\frac{\partial^2 M_{e,i}}{\partial N^2} \right)_{\varepsilon=0} \equiv M_{e,i}^{(NN)}. \tag{10}$$

The change in electron density due to polarization is in the language of the conceptual DFT:

$$d\rho(\mathbf{r}) = f(\mathbf{r}) dN - \boldsymbol{\alpha}(\mathbf{r}) \cdot d\boldsymbol{\varepsilon}, \tag{11}$$

where by definition, the i th component of the $\boldsymbol{\alpha}(\mathbf{r})$ vector is

$$\alpha_i(\mathbf{r}) \equiv - \left(\frac{\partial \rho(\mathbf{r})}{\partial \varepsilon_i} \right)_N \quad (i = x, y, z). \tag{12}$$

The new vector derivative $\boldsymbol{\alpha}(\mathbf{r})$ is most essential for this work; it will be referred to as the local polarization vector. The Maxwell relation follows

$$\left(\frac{\partial f(\mathbf{r})}{\partial \varepsilon_i} \right)_N = - \left(\frac{\partial \alpha_i(\mathbf{r})}{\partial N} \right)_{\varepsilon=0} \quad (i = x, y, z). \tag{13}$$

The dipole polarization tensor $\boldsymbol{\alpha}$ is by classical definition $\mathbf{M} = \mathbf{M}_0 + \boldsymbol{\alpha} \cdot \boldsymbol{\varepsilon}$, and thus for the electronic polarization we have

$$d\mathbf{M}_e = - \boldsymbol{\alpha}_e \cdot d\boldsymbol{\varepsilon}. \tag{14}$$

Electronic dipole polarization tensor $\boldsymbol{\alpha}_e$ is directly related to the vector $\boldsymbol{\alpha}(\mathbf{r})$ when the nuclear positions are frozen:

$$d\mathbf{M}_e = - d\boldsymbol{\varepsilon} \cdot \int \mathbf{r} \boldsymbol{\alpha}(\mathbf{r}) d\mathbf{r} = \int \mathbf{r} d\rho(\mathbf{r}) d\mathbf{r} \tag{15}$$

and

$$\boldsymbol{\alpha}_e = \int \mathbf{r} \boldsymbol{\alpha}(\mathbf{r}) d\mathbf{r}. \tag{16}$$

Also, by the definition of the linear response function:

$$\omega(\mathbf{r}, \mathbf{r}') = \left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_N. \tag{17}$$

Hence, alternatively [Eq. (15)]

$$\begin{aligned}
d\mathbf{M}_e &= \int \mathbf{r} d\rho(\mathbf{r}) d\mathbf{r} = \int \mathbf{r} d\mathbf{r} \int \left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')} \right]_N \delta v(\mathbf{r}') d\mathbf{r}' \\
&= d\boldsymbol{\varepsilon} \cdot \int \int \mathbf{r} \omega(\mathbf{r}, \mathbf{r}') \mathbf{r}' d\mathbf{r} d\mathbf{r}'
\end{aligned} \tag{18}$$

and

$$\boldsymbol{\alpha}(\mathbf{r}) = - \int \omega(\mathbf{r}, \mathbf{r}') \mathbf{r}' d\mathbf{r}'. \tag{19}$$

The local polarization vector $\boldsymbol{\alpha}(\mathbf{r})$ can be readily calculated by the finite field procedure [Eq. (12)] by numerical derivation of the results for electron density $\rho(\mathbf{r})$ in an external uniform electric field $\boldsymbol{\varepsilon}$. Vector $\boldsymbol{\alpha}(\mathbf{r})$ is translationally invariant and $\int \boldsymbol{\alpha}(\mathbf{r}) d\mathbf{r} = 0$. The product $\boldsymbol{\alpha}(\mathbf{r}) \mathbf{r}$ has a meaning of local polarizability as originally proposed by Jameson and Buckingham.³⁴ It is generally a diade (tensor) and is not translationally invariant but gives invariant electron polarizability upon integration [Eq. (16)]. We now aim at producing a workable link of $\boldsymbol{\alpha}(\mathbf{r})$ to the FF.

The Berkowitz and Parr³⁶ formula provides the relation between the linear response function $\omega(\mathbf{r}, \mathbf{r}')$ and the softness kernel $s(\mathbf{r}, \mathbf{r}')$:

$$\omega(\mathbf{r}, \mathbf{r}') = - s(\mathbf{r}, \mathbf{r}') + s(\mathbf{r}) f(\mathbf{r}'). \tag{20}$$

By definition of the dipole moment, the derivative $\mathbf{M}_e^{(N)}$ can be related to the FF:

$$\mathbf{M}_e^{(N)} = \int \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v \mathbf{r} d\mathbf{r} = \int f(\mathbf{r}) \mathbf{r} d\mathbf{r}. \tag{21}$$

Using Eqs. (20) and (21) in Eq. (19) the concluding result is

$$\boldsymbol{\alpha}(\mathbf{r}) = - s(\mathbf{r}) \mathbf{M}_e^{(N)} + \int s(\mathbf{r}, \mathbf{r}') \mathbf{r}' d\mathbf{r}'. \tag{22}$$

This formula requires a resolution for the softness kernel $s(\mathbf{r}, \mathbf{r}')$ before it could be applied in practice. The local density approximation successfully used by Vela and Gazquez³¹ [Eq. (4)] leads to

$$\boldsymbol{\alpha}(\mathbf{r}) = s(\mathbf{r}) [\mathbf{r} - \mathbf{M}_e^{(N)}]. \tag{23}$$

This result in principle allows for calculation the local softness $s(\mathbf{r}) = S f(\mathbf{r})$ for any electronic system; the $\mathbf{M}_e^{(N)}$ vector is defined by Eq. (8). The FF in this local approach (LA) becomes

$$f^{LA}(\mathbf{r}) = \frac{\boldsymbol{\alpha}(\mathbf{r}) \cdot \mathbf{r}}{r^2 - \mathbf{M}_e^{(N)} \cdot \mathbf{r}} \left(\frac{1}{S^{LA}} \right). \tag{24}$$

Since the FF must integrate to unity, the global softness in this model is available as

$$S^{\text{LA}} = \int \frac{\boldsymbol{\alpha}(\mathbf{r}) \cdot \mathbf{r}}{(r^2 - \mathbf{M}_e^{(N)} \cdot \mathbf{r})} d\mathbf{r}. \quad (25)$$

This strictly local approach may be modified by using the nonlocal extension for $s(\mathbf{r}, \mathbf{r}')$ as proposed by Li and Evans [Eq. (6)]:

$$s(\mathbf{r}, \mathbf{r}') = as(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + (1 - a)s(\mathbf{r})f(\mathbf{r}'). \quad (26)$$

a is an arbitrary parameter, which introduces a balance between the local and nonlocal contributions to $s(\mathbf{r}, \mathbf{r}')$. Using Eq. (26) in Eq. (22) the result for $\boldsymbol{\alpha}(\mathbf{r})$ is

$$\boldsymbol{\alpha}(\mathbf{r}) = as(\mathbf{r})[\mathbf{r} - \mathbf{M}_e^{(N)}]. \quad (27)$$

This leads to identical result for the FF as in Eq. (24). However, since $f(\mathbf{r})$ must again integrate to 1, we may now look for the choice of a that warrants that global softness reproduces exactly the expected $S=1/(I-A)$. Then a must be

$$a = S^{\text{LA}}/S = S^{\text{LA}}(I - A). \quad (28)$$

Considerable progress in this analysis is possible when the fully nonlocal model is adopted. For the purpose of this work we note, that a more general solution in Garza and Robles proposal [Eq. (5)] is $t(\mathbf{r})=b\rho(\mathbf{r})$ with constant b to be determined. By combining Eq. (5) with the Li and Evans result [Eq. (26)] the general *a priori* formula for the softness kernel is formulated as:

$$s(\mathbf{r}, \mathbf{r}') = k(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') + b\rho(\mathbf{r})\rho(\mathbf{r}') + cSf(\mathbf{r})f(\mathbf{r}'). \quad (29)$$

The unknown local function $k(\mathbf{r}')$ need not be calculated here, as it can be eliminated using the fundamental condition for the softness kernel:²

$$\int s(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = s(\mathbf{r}). \quad (30)$$

Hence

$$k(\mathbf{r}) = (1 - c)s(\mathbf{r}) - bN\rho(\mathbf{r}) \quad (31)$$

and the basic expression for the softness kernel reads:

$$s(\mathbf{r}, \mathbf{r}') = (1 - c)s(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') - bN\rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + b\rho(\mathbf{r})\rho(\mathbf{r}') + cSf(\mathbf{r})f(\mathbf{r}'). \quad (32)$$

Using this in Eq. (22) we obtain the local polarizability function:

$$\boldsymbol{\alpha}(\mathbf{r}) = (1 - c)s(\mathbf{r})[\mathbf{r} - \mathbf{M}_e^{(N)}] + b\rho(\mathbf{r})[\mathbf{M}_e - N\mathbf{r}]. \quad (33)$$

Parameter b can also be eliminated imposing once again a condition, that the global softness meets expectation for the global system $S=1/(I-A)$; integration of local softness $s(\mathbf{r})$ from Eq. (33) leads to the final result, where for the sake of clarity, the parameter a is used again [Eq. (28)]:

$$b = \left[\left(\frac{a}{1 - c} \right)^{-1} - 1 \right] \left(\int Y(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \right)^{-1} S^{\text{LA}}, \quad (34)$$

where

$$Y(\mathbf{r}) = \frac{Nr^2 - \mathbf{M}_e \cdot \mathbf{r}}{r^2 - \mathbf{M}_e^{(N)} \cdot \mathbf{r}}. \quad (35)$$

The final form for the FF in the general nonlocal approximation becomes

$$f(\mathbf{r}) = d \cdot f^{\text{LA}}(\mathbf{r}) + (1 - d)f^{\text{p}}(\mathbf{r}) \quad (36)$$

with one single parameter left $d=a/1-c$. $f^{\text{LA}}(\mathbf{r})$ is given by Eqs. (24) and (25) and

$$f^{\text{p}}(\mathbf{r}) = f^{\text{EG}}(\mathbf{r}) \frac{NY(\mathbf{r})}{\int \rho(\mathbf{r})Y(\mathbf{r}) d\mathbf{r}}, \quad (37)$$

where $f^{\text{EG}}(\mathbf{r})=\rho(\mathbf{r})/N$ may be considered to represent the FF for noninteracting electron gas (EG), thus fully nonlocal. The combined local and nonlocal contributions to the FF are fully exposed in Eq. (36). This result represents the FF that warrants the expectations values for two important global quantities: electronic polarizability and softness, with one parameter d . As demonstrated by Chattaraj *et al.*¹² in their fundamental paper, any FF must also conform to the condition:

$$\int \frac{f(\mathbf{r})}{r} d\mathbf{r} \equiv \Delta = - \left(\frac{\partial \mu}{\partial Z} \right)_N. \quad (38)$$

If this is used to normalize the FF resulting in Eq. (36), the single parameter d becomes:

$$d = \frac{\Delta - \Delta^{\rho}}{\Delta^{\text{LA}} - \Delta^{\rho}}, \quad (39)$$

where symbols $\Delta^{\text{LA}}, \Delta^{\rho}$ are defined accordingly by using $f^{\text{LA}}(\mathbf{r})$ and $f^{\text{p}}(\mathbf{r})$ in Eq. (38) (first part). For atoms located at the origin of the nuclear coordination system $\mathbf{M}_e=0$, $\mathbf{M}_e^{(N)}=0$, and the result for the FF becomes much simplified:

$$f^{\text{LA}}(\mathbf{r}) = \frac{\boldsymbol{\alpha}(\mathbf{r}) \cdot \mathbf{r}}{r^2} \frac{1}{S^{\text{LA}}}, \quad f^{\text{p}}(\mathbf{r}) = f^{\text{EG}}(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N}, \quad (40)$$

$$\text{and } d = \frac{\Delta - \Delta^{\text{EG}}}{\Delta^{\text{LA}} - \Delta^{\text{EG}}}. \quad (41)$$

The working formula for the polarization justified FF of atoms becomes attractively simple:

$$f(\mathbf{r}) = d \frac{\boldsymbol{\alpha}(\mathbf{r}) \cdot \mathbf{r}}{r^2} \left[\int \frac{\boldsymbol{\alpha}(\mathbf{r}) \cdot \mathbf{r}}{r^2} d\mathbf{r} \right]^{-1} + (1 - d) \frac{\rho(\mathbf{r})}{N}. \quad (42)$$

IV. RESULTS

A. Computational methods

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.³⁷ The best fit to experimental polarizations of 29 atoms was obtained for the B3LYP method with aug-cc-pvqz basis set (except for five atoms for which the Sadlej basis set pVTZ was adopted^{48,49}), Table I. Calculated as well as experimental hardness data $\eta=I-A$ are also given in Table I. Local polarizability vector $\boldsymbol{\alpha}(\mathbf{r})$ [Eq. (12)] has been calculated by the finite field procedure; results were checked by numerical in-

TABLE I. Calculated electronic dipole polarizability α_e and hardness η of selected atoms explored as input parameters; experimental data are also given.

Atom	α_e (a.u.)		$\eta=I-A$ (eV)	
	Calc.	Expt. ^a	Calc.	Expt. ^b
He	1.50	1.38 ^c	27.3127	24.59 ^d
Li	143.06	164	5.0696	4.77
Be	43.21	37.8	9.1759	8.90
B	22.59	20.4	8.2752	8.02
C	12.72	11.9	10.1637	9.99
N	7.79	7.42	14.4251	14.46
O	5.46	5.41	12.4604	12.16
F	3.82	3.76	14.2319	14.02
Ne	2.74	2.66	26.6106	21.57 ^d
Na	143.32	159.3	4.8492	4.59
Mg	72.08	71.5	7.8017	7.80
Al	64.30	56.3	5.5594	5.53
Si	40.72	36.3	6.7703	6.76
P	27.00	24.5	9.4262	9.75
S	20.51	19.8	8.3514	8.28
Cl	15.27	14.7	9.3936	9.35
Ar	11.55	11.09	18.3572	15.76 ^d
K ^c	276.62	293	3.9784	3.84
Ca ^c	153.31	168	6.1064	7.90
Ga	60.51	54.8	5.5893	5.70
Ge	44.01	41	6.5635	6.70
As	32.46	29.1	8.8521	9.00
Se	27.05	25.4	7.6439	7.73
Br	21.70	20.6	8.4031	8.45
Kr	17.52	16.8	16.1041	14.00 ^d
Rb ^c	325.68	319	3.7716	3.69
Sr ^c	196.61	186	5.6193	7.40
I ^f	33.96	33	7.2547	7.39

^aReference 45.

^bReference 46.

^cReference 47.

^dAssumed $A=0$ in $(I-A)_{\text{exp}}$.

^eReference 48.

^fReference 49.

tegration of $\alpha(\mathbf{r}) \cdot \mathbf{r}$ to the electronic dipole polarizability of atom [Eq. (16)] leading to exact reproduction of the B3LYP calculated values. The derivative Δ has been calculated from the chemical potential of neutral atom and its ions in the finite difference approximation [Eq. (38), second part]. The value was proved to be identical within the numerical accuracy to the integral:

$$\Delta = - \left(\frac{\partial \mu}{\partial Z} \right)_N = \int \frac{\rho^-(\mathbf{r}) - \rho^+(\mathbf{r})}{2r} d\mathbf{r}. \quad (43)$$

$\Delta^{\text{LA}}, \Delta^{\text{EG}}$ have been calculated by numerical integration of $f(\mathbf{r})^{\text{LA}}/r$ and $f(\mathbf{r})^{\text{EG}}/r$ functions accordingly, from Eq. (38) (first part).

B. The hydrogen atom

The hydrogen atom electron field dependent analytical orbital functions³⁸ allow for testing the result:

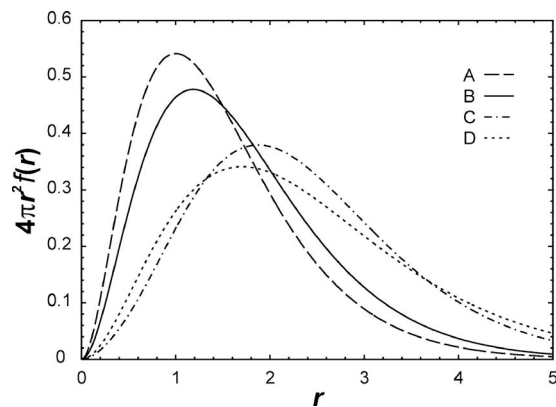


FIG. 1. Radial FF for the hydrogen atom from this work and by other authors (in atomic units). (a) $f(r)=\rho(r)/N$; (b) $f^{\text{LA}}(r)$ [Eq. (48)], this work; (c) $f(r)$ by Garza and Robles (Ref. 32); (d) $f(r)$ by Fuentealba (Ref. 13).

$$\Phi_{1s} = \frac{1}{\sqrt{\pi}} \exp(-r) \left[1 - \varepsilon \left(r + \frac{1}{2} r^2 \right) \cos \theta_{\varepsilon r} \right]. \quad (44)$$

Corresponding local polarization is in the direction r :

$$\alpha(r) = - \left(\frac{\partial \rho(r)}{\partial \varepsilon_r} \right)_N = \frac{2}{\pi} \exp(-2r) \left(r + \frac{1}{2} r^2 \right). \quad (45)$$

The local softness, according to Eq. (23) is:

$$s(r) = \frac{2}{\pi} \exp(-2r) \left(1 + \frac{1}{2} r \right). \quad (46)$$

The global softness obtained by integration is [Eq. (25)]:

$$S^{\text{LA}} = 4\pi \int_0^{+\infty} s(r) r^2 dr = \frac{7}{2} \text{ a.u.} \quad (47)$$

The Li and Evans parameter for hydrogen atom can be calculated from Eq. (28):

$$a = \frac{7}{2} (I - A) = 1.6885.$$

Derivative $\Delta = -(\partial \mu / \partial Z)_N$ could not be determined for hydrogen in the procedure used for other atoms and the only nontrivial result for the FF of hydrogen atoms is the one in the local approximation:

$$f^{\text{LA}}(r) = \frac{4}{7\pi} \left(1 + \frac{1}{2} r \right) \exp(-2r). \quad (48)$$

The radial function $4\pi r^2 f^{\text{LA}}(r)$ for a hydrogen atom shown in Fig. 1 compares favorably with the results by other authors.

C. Results for other atoms

An example of the result for local polarization is given in Fig. 2 for halogen atoms.

Radial FF for three example atoms are given in Fig. 3 as compared to the widely used FF by common definitions. Polarization justified FF resulting from this work shows negative regions, which is not unexpected (cf. Ref. 10). The accuracy of calculation may not be equal for atoms and may be

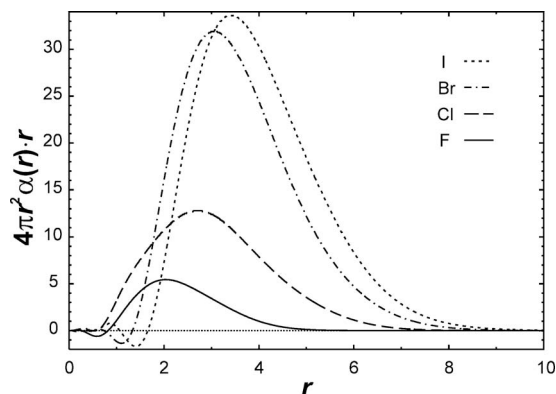


FIG. 2. The radial values of local electronic dipolar polarizability as calculated for the halogen atoms (atomic units).

readily checked by comparing the global polarizabilities to expected experimental results (Table I); it is good for N, F, poor for Li.

The suitable test for the resulting atomic FF is by calculation of the global hardness, well established experimental quantity $I-A$. This will be done as to expose the role of the FF derivative $f'(\mathbf{r}) = (\partial f(\mathbf{r}) / \partial N)_{v(\mathbf{r})}$, implicit in this approach. Standard expressions for the potential energy $V[\rho]$ and electronic coulomb term $J[\rho]$ are:

$$V[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = -Z \int \rho(\mathbf{r})/|\mathbf{r}|d\mathbf{r} \text{ and}$$

$$J[\rho] = \frac{1}{2} \int \int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}d\mathbf{r}';$$

$K[\rho]$ contains a sum of the exchange and correlation interactions. Using the virial theorem, the unknown and large kinetic energy term $T[\rho]$ can be eliminated:

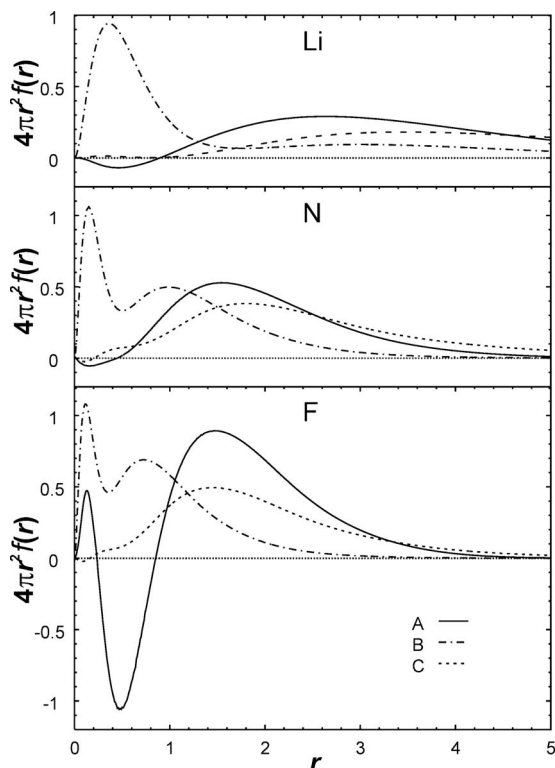


FIG. 3. The radial FF for Li, N, and F atoms (atomic units). (a) This work [Eq. (42)]; (b) $f^{\text{EG}}(r) = \rho(r)/N$; (c) $f^{+-}(r) = 1/2[\rho^-(r) - \rho^+(r)]$.

$$E[\rho] = V[\rho] + T[\rho] + J[\rho] + K[\rho]$$

$$= 1/2(V[\rho] + J[\rho] + K[\rho]).$$

First derivatives of the energy terms $V[\rho]$ and $J[\rho]$ are simply:

$$\left(\frac{\partial V[\rho]}{\partial N}\right)_v = \int v(\mathbf{r})f(\mathbf{r})d\mathbf{r},$$

$$\begin{aligned} \left(\frac{\partial J[\rho]}{\partial N}\right)_v &= \frac{1}{2} \int \int d\mathbf{r}'d\mathbf{r} \left[\frac{f(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{f(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \right] \\ &= \int \int \frac{\rho(\mathbf{r}')f(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \end{aligned} \quad (49)$$

Using $f'(\mathbf{r}) = (\partial^2 \rho(\mathbf{r}) / \partial N^2)_{v(\mathbf{r})}$ the second derivatives are

$$\begin{aligned} \eta_V &= \left(\frac{\partial^2 V[\rho]}{\partial N^2}\right) = \int v(\mathbf{r}) \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial N^2}\right) d\mathbf{r} = -Z \int \frac{f'(\mathbf{r})}{|\mathbf{r}|} d\mathbf{r}, \\ \eta_J &= \left(\frac{\partial^2 J[\rho]}{\partial N^2}\right) = \int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\ &\quad + \int \int \frac{\rho(\mathbf{r})f'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \end{aligned} \quad (50)$$

The global hardness takes the form:

$$\begin{aligned} \eta &= \frac{1}{2} \left\{ \int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int \int \frac{\rho(\mathbf{r})f'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \right. \\ &\quad \left. - Z \int \frac{f'(\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} + \frac{\partial^2 K}{\partial N^2} \right\} \end{aligned} \quad (51)$$

Substituting

$$P = \left(\int \int \frac{\rho(\mathbf{r})f'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \right) / \left(\int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \right)$$

and

$$R = \frac{1}{2} \left\{ -Z \int \frac{f'(\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} + \frac{\partial^2 K}{\partial N^2} \right\}.$$

The relation between the $I-A$ quantity and integrated hardness kernel is then expected as:

$$\eta = I - A = \left(\frac{1+P}{2} \right) \int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + R. \quad (52)$$

The test for Eq. (52) is shown in Fig. 4. The linear relation is indeed found for the group of 29 atoms in the consideration, a single notable exceptions being the noble gases. The value of resulting constant $P=1.2162$ contains an indirect hint to the value of the derivative $f'(\mathbf{r})$. Standard deviation between the two sets of data, as given by $r^2=0.8957$, is remarkable, comparing to the study by Liu *et al.*,³⁹ where the results for a selection of 20 main group elements is reported (the authors arbitrarily excluded groups IIA, VA, and noble gases). The small value of constant $R=-1.1422$ eV compares favorably with the one reported by Liu *et al.*³⁹ (-1.39766 eV), in their linear correlation between the experimental hardness and integrated hardness kernel (modi-

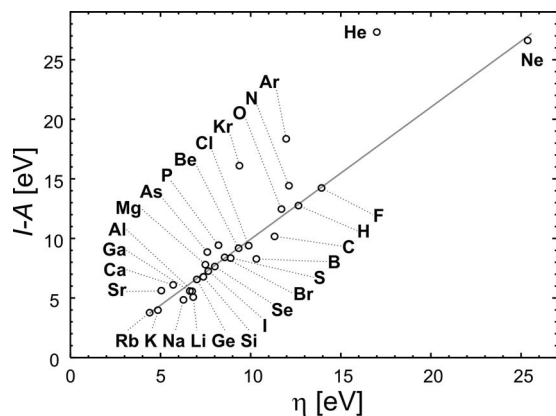


FIG. 4. Correlation between the global hardness $I-A$ resulting from B3LYP calculations and the integrated hardness kernel [Eq. 60]: $(I-A)=1.1081 \cdot \eta - 1.1422$ [eV]; $r^2=0.8957$ (excluding group 8: He, Ne, Ar, and Kr).

fied model). The linear correlation becomes exact when it is studied within the main groups I-VIIA, i.e., for equal number of valence electrons, then for each group $r^2 \geq 0.99$. In such case, however, P and R constants vary between main groups of the periodic table, with the extreme values for group IA: $P_I=0.1116$, $R_I=1.3142$ eV and group VIA: $P_{VI}=1.6838$, $R_{VI}=-3.2652$ eV.

V. DISCUSSION

FFs resulting from this work are polarization justified in the sense that they reproduce accurately both the global softness and the electronic dipole polarizability of the system. The polarization justified FF also reproduce properly the $(\partial\mu/\partial Z)_N$ derivative given by Eq. (38) [this is automatically true for $f_{+/-}$ (see Sec. IV A) but does not hold for $\rho(\mathbf{r})/N$]. It is remarkable to see that only one experimental parameter d is sufficient to warrant these properties of the polarization justified FF. Moreover, in most cases studied, parameter d is close to 1.0 (Table II). This indicates that the sole LA is reasonably good for most atoms (exceptions: He, N, O, F, Ne, and Ar). Other experimental parameters listed in Table II corroborate this conclusion; parameter b [Eqs. (31), (32), and (34)] is very close to 0 for all atoms but H, He, Li, and Be. Parameters of the linear correlation as given in Fig. 4 obtained with the f^{LA} FFs [Eq. (24)] are very close to the result in Fig. 4:

$$(I-A) = 1.0529 \cdot \eta - 0.8218 \text{ [eV]}, \quad r^2 = 0.8951.$$

Special position of noble gases can be attributed to the ambiguity concerning their calculated and experimental hardness ($I-A$) as indicated in Table I, the source of ambiguity is in large and negative values of their electron affinity, as compared to $A=0$ assumed for experimental data.

The proposed FF offers a unique opportunity to study the role of derivative $f'(\mathbf{r})=(\partial f(\mathbf{r})/\partial N)_{v(\mathbf{r})}$ in the conceptual DFT. It has recently attracted some attention; Morell *et al.*^{40,41} introduced it as an intuitive dual descriptor for chemical reactivity; Ayers *et al.*^{42,43} presented formal definition and interesting applications thereof. $f'(\mathbf{r})$ appears naturally in calculation of the global hardness as the derivative of the chemical potential:

TABLE II. Calculated derivative $\Delta=-(\partial\mu/\partial Z)_N$ and dimensionless parameters a, c, d explored in calculations of the polarization justified FFs.

Atom	Δ (a.u.) [Eq. (38)]	a [Eq. (28)]	c [Eq. (33)]	d [Eq. (46)]
He	0.8199	2.324	-0.087	2.138
Li	0.2614	4.717	-4.000	0.943
Be	0.3050	4.730	-3.903	0.965
B	0.3243	2.654	-1.615	1.015
C	0.4593	2.310	-1.282	1.012
N	0.4932	2.485	-1.332	1.066
O	0.5477	1.546	-0.320	1.172
F	0.5113	1.272	0.053	1.343
Ne	0.5670	1.794	-0.165	1.539
Na	0.2363	4.069	-2.997	1.018
Mg	0.2300	4.783	-3.609	1.038
Al	0.2203	2.409	-1.334	1.032
Si	0.3291	2.298	-1.284	1.006
P	0.3399	2.637	-1.560	1.030
S	0.3740	1.933	-0.892	1.022
Cl	0.3431	1.883	-0.801	1.045
Ar	0.3752	3.193	-1.885	1.107
K	0.1876	3.820	-2.747	1.019
Ca	0.1840	4.623	-3.516	1.024
Ga	0.2206	2.193	-1.133	1.028
Ge	0.3141	2.185	-1.185	1.000
As	0.3160	2.570	-1.554	1.006
Se	0.3399	1.974	-1.025	0.975
Br	0.3029	1.981	-0.975	1.003
Kr	0.3248	3.426	-2.401	1.007
Rb	0.1764	3.644	-2.554	1.025
Sr	0.1644	4.418	-3.285	1.031
I	0.3219	2.139	-1.242	0.954

$$\begin{aligned} \mu &= \left(\frac{\partial E}{\partial N} \right)_v = \int d\mathbf{r} f(\mathbf{r}) \left[v(\mathbf{r}) + \left(\frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} \right)_v \right. \\ &\quad \left. + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \left(\frac{\delta K[\rho]}{\delta \rho(\mathbf{r})} \right)_v \right] \\ &= \int d\mathbf{r} f(\mathbf{r}) \mu(\mathbf{r}). \end{aligned} \quad (53)$$

The sum in brackets equal $\mu(\mathbf{r})$ is identical to the chemical potential μ and constant everywhere for exact functionals $T[\rho], K[\rho]$ and the exact density $\rho(\mathbf{r})$ [hence also for appropriate $f(\mathbf{r})$]. Using arbitrarily calculated $f(\mathbf{r})$ [and the density $\rho(\mathbf{r})$] this should not be assumed *a priori*, and then the global hardness comes out as the derivative containing $f'(\mathbf{r})$:

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_v = \int d\mathbf{r} f(\mathbf{r}) \left(\frac{\delta \mu(\mathbf{r})}{\delta \rho(\mathbf{r})} \right)_v + \int d\mathbf{r} f'(\mathbf{r}) \mu(\mathbf{r}). \quad (54)$$

When the relation given by Torrent-Sucarrat *et al.*⁴⁴ is used in integration of the first term,

$$\left(\frac{\delta^2 \{T[\rho] + K[\rho]\}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right)_v = \left(\frac{\delta^2 \{T[\rho] + K[\rho]\}}{\delta \rho^2} \right)_v \delta(\mathbf{r}-\mathbf{r}'), \quad (55)$$

the resulting equation is an alternative to Eq. (51):

$$\eta = \int d\mathbf{r} f^2(\mathbf{r}) \left(\frac{\partial^2 \{T[\rho] + K[\rho]\}}{\partial \rho^2} \right)_v + \int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int d\mathbf{r} f'(\mathbf{r}) \mu(\mathbf{r}). \quad (56)$$

The first term contains hidden dependence on $\rho(\mathbf{r})$ and its derivatives while the last term is expected to be zero. Equation (51) is still better since all but $K[\rho]$ dependence is exposed and contribution to global hardness introduced by $(\partial^2 K[\rho]/\partial N^2)_v$ may be small, as demonstrated by Torrent-Sucarrat *et al.*⁴⁴ However, Eq. (56) is interesting when the demonstrated linear correlation between $\eta = I - A$ and $\int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$ is recalled (Fig. 4). Apparently, with the proposed polarization justified FFs and the B3LYP densities explored, the last term is constant and reasonably close to 0 for atoms under study, as compared to the average global hardness in this group of atoms, 10.03 eV (calculated),

$$\int d\mathbf{r} f'(\mathbf{r}) \mu(\mathbf{r}) = R = -1.1422 \text{ eV}.$$

Also, the first term is rather small, as indicated by the coefficient of the linear dependence in Fig. 4:

$$\int d\mathbf{r} f^2(\mathbf{r}) \left(\frac{\partial \{T[\rho] + K[\rho]\}}{\partial \rho(\mathbf{r})} \right)_v = 0,1081 \cdot \int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (57)$$

If these results are combined with satisfactory value of $r^2 = 0.8957$ for the linear correlation, it is clear that the polarization justified FFs for atoms very reasonably meet the expected general relation between the hardness kernel and the global hardness:

$$\eta \cong \int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (58)$$

The two classical approximations for the FFs have also been tested in the same way, looking for the correlation between $(I - A)$ and the integrated hardness kernel [Eq. (58)]. The result was discouragingly poor for $\rho(\mathbf{r})/N$ (no correlation); it was quite reasonable for $f_{+/-}$: $(I - A) = 1.0411 \cdot \eta + 1.1837$ [eV]; $r^2 = 0.7968$ (groups 1–7 as in Fig. 4). Both approximations allow also for rough estimate of the role of the derivative $f'(\mathbf{r})$ in Eq. (56). For $\rho(\mathbf{r})/N$ approximation, $f' = 0$ and the last term in Eq. (56) is identically zero. For the $f_{+/-}$ approximation corresponding derivative may be found by taking the Taylor expansion to the second order for the density:

$$\begin{aligned} \rho(N) &= \rho_o + \rho'(N)\Delta N + \frac{1}{2}\rho''(N)\Delta N^2 + \dots \\ &= \rho_o + f\Delta N + \frac{1}{2}f'\Delta N^2 + \dots \end{aligned}$$

The density derivatives are:

$$f \cong \frac{1}{2}(\rho_- - \rho_+) = f_{+/-} > 0,$$

$$f' \cong (\rho_- + \rho_+ - 2\rho_o) = f'_{+/-}.$$

Using $f'_{+/-}$ in calculation of the last term in Eq. (56) gives rather poor result: 0.35 ± 1.96 eV for the group of atoms under study.

If Eq. (56) is consequently applied within the above two widely used approximations, and if the Thomas–Fermi model is applied to determine the derivative $\partial^2 \{T[\rho] + K[\rho]\}/\partial \rho^2$, the correlation found between $(I - A)$ and the integrated hardness kernel [Eq. (56)] was significantly deteriorated for $f_{+/-}$ and not improved for $\rho(\mathbf{r})/N$. Using the same scheme with the polarization justified FFs still gives reasonable linear correlation, with lower r^2 [0.72 for $f(\mathbf{r})$ and 0.78 for $f^{LA}(\mathbf{r})$]. Apparently, Thomas–Fermi model is not suitable to combine with the polarization justified FFs. In fact, they alone provide better accuracy in calculating the global hardness of atoms than any other FFs proposed from *a priori* calculations.

VI. CONCLUSION

Formal analysis of the FFs presented in this work explored two separate regions of modern molecular chemical physics. The conceptual DFT, where the very notion of the FF stems from, offers still growing understanding how the molecular properties could possibly be quantified to describe their “chemistry”—structural changes occurring at short distances. Conceptual DFT is becoming an important branch of theoretical chemistry that aims at understanding the molecular properties and interactions, as opposed to computational chemistry (where the DFT methods themselves are much valuable) providing numerical results sometimes difficult to generalize. The second field involved is the rich body of molecular physics inasmuch as it describes the molecular polarization. There is a vast space to explore here, as interaction of molecules with external fields have recently gained much interest with the nonlinear effects in laser beams being extensively explored. The first step on this way made by this present work is promising: FFs have been linked to the local polarization of the electron density, resulting in FF that are superior to many others, as was demonstrated in calculation of the global hardness. Moreover, an internal test for the quality of results has been indicated at computational level: the method (and the basis set) must correctly reproduce the molecular polarizability in routine calculations first.

Polarization justified FF introduced in this work are conveniently calculated for atoms by the routine quantum chemical tools; extension to molecules does not present computational problems. Properties of this FFs make them a promising target in further studies on molecular reactivity.

ACKNOWLEDGMENTS

This work has been partially financed under the statutory funds of the Faculty of Chemistry, Wrocław University of Technology. The use of resources of Wrocław Center for

Networking and Supercomputing (WCSS) is gratefully acknowledged. Authors are indebted to a referee for a number of valuable advices.

- ¹R. G. Parr and W. Yang, *J. Am. Chem. Soc.* **106**, 4049 (1984).
- ²R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ³K. Fukui, in *Frontier Orbitals and Reaction Paths*, edited by K. Fukui and H. Fujimoto (World Scientific, Singapore, 1997), pp. 125–149.
- ⁴H. Chermette, *J. Comput. Chem.* **20**, 129 (1999).
- ⁵P. Geerlings, F. De Proft, and W. Langenaeker, *Chem. Rev. (Washington, D.C.)* **103**, 1793 (2003).
- ⁶P. K. Chattaraj, U. Sakar, and D. R. Roy, *Chem. Rev. (Washington, D.C.)* **106**, 2065 (2006).
- ⁷P. W. Ayers and M. Levy, *Theor. Chem. Acc.* **103**, 353 (2000).
- ⁸P. W. Ayers, J. S. M. Anderson, and L. Bartolotti, *Int. J. Quantum Chem.* **101**, 520 (2005).
- ⁹W. Yang and W. Mortier, *J. Am. Chem. Soc.* **108**, 5708 (1986).
- ¹⁰P. W. Ayers, R. C. Morrison, and R. K. Roy, *J. Chem. Phys.* **116**, 8731 (2002).
- ¹¹P. Bultinck, S. Fias, C. Van Alsenoy, P. W. Ayers, and R. Carbó-Dorca, *J. Chem. Phys.* **127**, 034102 (2007).
- ¹²P. Chattaraj, A. Cedillo, and R. G. Parr, *J. Chem. Phys.* **103**, 10621 (1995).
- ¹³P. Fuentealba, *J. Chem. Phys.* **103**, 6571 (1995).
- ¹⁴L. F. Pacios and P. C. Gomes, *J. Comput. Chem.* **19**, 488 (1998).
- ¹⁵P. W. Ayers, F. De Proft, A. Borgoo, and P. Geerlings, *J. Chem. Phys.* **126**, 224107 (2007).
- ¹⁶N. Sablon, F. De Proft, P. W. Ayers, and P. Geerlings, *J. Chem. Phys.* **126**, 224108 (2007).
- ¹⁷P. W. Ayers, *Theor. Chem. Acc.* **118**, 371 (2007).
- ¹⁸J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., *Phys. Rev. Lett.* **49**, 1691 (1982).
- ¹⁹L. Komorowski and J. Lipiński, *Chem. Phys.* **157**, 45 (1991).
- ²⁰R. Balawender and L. Komorowski, *J. Chem. Phys.* **109**, 5203 (1998).
- ²¹R. F. W. Bader, *Atoms in Molecules. A Quantum Theory* (Clarendon, Oxford, 1990).
- ²²L. Komorowski, S. L. Boyd, and R. J. Boyd, *J. Phys. Chem.* **100**, 3448 (1996).
- ²³R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.* **105**, 7512 (1983).
- ²⁴R. G. Pearson, *Coord. Chem. Rev.* **100**, 403 (1990).
- ²⁵R. G. Pearson, *J. Am. Chem. Soc.* **85**, 3533 (1963).
- ²⁶L. Komorowski in *Chemical Hardness, Structure and Bonding*, edited by K. D. Sen (Springer-Verlag, Berlin, 1993), Vol. 80. See also other contributions in this volume.
- ²⁷L. Komorowski, *Chem. Phys.* **114**, 55 (1987).
- ²⁸Y. Simon-Manso and P. Fuentealba, *J. Phys. Chem. A* **102**, 2029 (1998) (and references therein).
- ²⁹P. W. Ayers, *Faraday Discuss.* **135**, 161 (2007).
- ³⁰L. Komorowski, *Chem. Phys. Lett.* **134**, 536 (1987).
- ³¹A. Vela and J. L. Gazquez, *J. Am. Chem. Soc.* **112**, 1490 (1990).
- ³²J. Garza and J. Robles, *Phys. Rev.* **47**, 2680 (1993).
- ³³Y. Li and N. S. Evans, *J. Am. Chem. Soc.* **117**, 7756 (1995).
- ³⁴C. J. Jameson and A. D. Buckingham, *J. Chem. Phys.* **73**, 5684 (1980).
- ³⁵A. J. Stone, *Mol. Phys.* **56**, 1065 (1985).
- ³⁶M. Berkowitz and R. G. Parr, *J. Chem. Phys.* **88**, 2554 (1988).
- ³⁷M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.01, Gaussian, Inc., Wallingford CT, 2004.
- ³⁸L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968).
- ³⁹S. Liu, F. De Proft, and R. G. Parr, *J. Phys. Chem. A* **101**, 6991 (1997).
- ⁴⁰C. Morell, A. Grand, and A. Toro-Labbe, *J. Phys. Chem. A* **109**, 205 (2005).
- ⁴¹C. Morell, A. Grand, and A. Toro-Labbe, *Chem. Phys. Lett.* **425**, 342 (2006).
- ⁴²P. W. Ayers, C. Morell, F. De Proft, and P. Geerlings, *Chem.-Eur. J.* **13**, 8240 (2007).
- ⁴³F. De Proft, P. W. Ayers, S. Fijas, and P. Geerlings, *J. Chem. Phys.* **125**, 214101 (2006).
- ⁴⁴M. Torrent-Sucarrat, P. Salvador, P. Geerlings, and M. Sola, *J. Comput. Chem.* **28**, 574 (2007).
- ⁴⁵T. H. Miller and B. Bederson, *Adv. At. Mol. Phys.* **13**, 1 (1978).
- ⁴⁶R. G. Pearson, *Inorg. Chem.* **27**, 734 (1988).
- ⁴⁷R. R. Teachout and R. T. Pack, *At. Data* **3**, 195 (1971).
- ⁴⁸Basis Set: pVTZ v1.2.2, A. J. Sadlej and M. Urban, *J. Mol. Struct.: (THEOCHEM)* **234**, 147 (1991).
- ⁴⁹Basis Set: pVTZ v1.2.2, A. J. Sadlej, *Theor. Chim. Acta* **81**, 339 (1992).