Modeling the Electron Density Kernels

PAWEŁ SZAREK, LUDWIK KOMOROWSKI
Wrocław University of Technology, Institute of Physical and Theoretical Chemistry, Wybrzeże Wyspiańskiego 27 50-370 Wrocław, Poland

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Abstract: Existing approximation to the softness kernel, successfully explored in earlier work, has been extended; the normal Gauss distribution function has been used instead of the Dirac delta. The softness kernel becomes continuous functions in space and may be used to calculate the linear response function of the electron density. Three-dimensional visualization of the softness kernel and the linear response function are presented for a nitrogen atom as a working example. By using a single parameter of the spatial Gauss distribution, the novel softness kernel has been adjusted to be consistent with the standard form of the hardness kernel, representing the leading fraction of the electronic interactions in the system.

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Introduction

Softness kernels and hardness kernels are important nonlocal quantities in the conceptual density functional theory. The recent works from this laboratory have demonstrated how the approximated softness kernel can be explored in determination of the Fukui function, which is fully consistent with the electronic dipole polarization of the system.[1,2]

The fundamental quantity describing the effect of change of the external potential $v(\mathbf{r})$ on the electron density $\rho(\mathbf{r})$ in a closed system of N electrons is the linear response function[3]:

$$\omega(\mathbf{r},\mathbf{r}') = \left(\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_N \tag{1}$$

This is physically sound, nonlocal function, continuous in space. It contains full information on the electronic polarization of a closed electronic system[1];

$$\boldsymbol{\alpha}_e = -\int\int \omega(\mathbf{r},\mathbf{r}')\mathbf{r}\mathbf{r}'d\mathbf{r}d\mathbf{r}' \tag{2}$$

$\boldsymbol{\alpha}_e$ is the electron dipole polarizability tensor. A similar quantity is the softness kernel defined as[3,4]:

$$s(\mathbf{r},\mathbf{r}') = -\left(\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right)_\mu \tag{3}$$

The constant chemical potential conditions ($\mu = (\partial E/\partial N)_v$) indicate that the effect described by this derivative is polarization of an open system: the density change caused by the electron flow in/out of a system as a result of the change in the external potential. Basic properties of the softness kernel are[3]:

$$\int s(\mathbf{r},\mathbf{r}')d\mathbf{r}' = s(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right)_v = Sf(\mathbf{r}) \tag{4}$$

$$\int\int s(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}' = S = \left(\frac{\partial N}{\partial\mu}\right)_v \tag{5}$$

Here, $f(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial N]_v = [\delta\mu/\delta v(\mathbf{r})]_N$ is the Fukui function[3]; for the purpose of this analysis, the second part of the definition has been explored[1] leading to the single value of the Fukui function. S stands for the global softness (inverse global hardness) of the system. The two kernels are bound by the exact relation[4]:

$$\omega(\mathbf{r},\mathbf{r}') = -s(\mathbf{r},\mathbf{r}') + Sf(\mathbf{r})f(\mathbf{r}') \tag{6}$$

The definition of the hardness kernel results from an alternative view point:

$$\eta(\mathbf{r},\mathbf{r}') = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{7}$$

$F[\rho]$ is Hohenberg and Kohn universal functional. The hardness kernel is functional inverse of the softness kernel[3]:

Correspondence to: L. Komorowski; e-mail: ludwik.komorowski@pwr.wroc.pl.

$$\int\int s(\mathbf{r},\mathbf{r}')\eta(\mathbf{r}',\mathbf{r}'')d\mathbf{r}d\mathbf{r}' = 1 \tag{8}$$

Little is known about the nature of kernels; only some approximations have been examined. The independent perturbation formula has been proposed for the linear response function $\omega(\mathbf{r},\mathbf{r}')$.[4] The hardness kernel has been examined by several authors: Liu et al. proposed complete neglect of the contributions other than the electron–electron repulsion,[5] which leads to:

$$\eta(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{9}$$

Chattaraj et al. studied the Thomas–Fermi model and demonstrated that approximation identical to eq. (9) leads to very reasonable covalent radii for atoms.[6] Torrent-Sucarrat et al. applied the Thomas–Fermi model to the computationally available densities and tested the method by calculation of the global hardness.[7] They proved that this approximation [eq. (9)] represents the major part of the interelectronic interactions and is sufficient to reproduce experimental values of the global hardness known as $\eta = I - A$.

The softness kernel attracted considerable attention following the Vela and Gaquez proposal[8]:

$$s(\mathbf{r},\mathbf{r}') = s(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \tag{10}$$

This conforms to all known requirements for the softness kernel. More elaborate versions have also been proposed by Li and Evans[9] and Garza and Robles.[10] Approximation of this type has recently been explored in the novel method for calculation of the polarization justified Fukui functions.[1,2]

The aim of this study is to investigate properties of kernels, by extending the approximation in the softness kernel [eq. (10)] beyond the Dirac delta, thus, making it in some way nonlocal but still consistent with the widely accepted approximation for the hardness kernel as given by eq. (9).

The Softness Kernel and $\omega(\mathbf{r},\mathbf{r}')$

The softness kernel given by eq. (10) may be modeled by replacing the Dirac delta with a function $P(x - x')$, such that $\int P(x - x')dx = 1$. This is a property of the normal (Gauss) distribution in one dimension:

$$P(x-x') = \frac{1}{\sigma(2\pi)^{1/2}}\exp\left[-\frac{(x-x')^2}{2\sigma^2}\right] \tag{11}$$

For any parameter σ[distance] and for every point in space x this is integrated to unity. In three dimensions, with $\sigma_x = \sigma_y = \sigma_z = \sigma$, the normal distribution becomes:

$$P_\sigma(\mathbf{r}-\mathbf{r}') = \frac{1}{\sigma^3(2\pi)^{3/2}}\exp\left[-\frac{1}{2\sigma^2}(\mathbf{r}-\mathbf{r}')^2\right] \tag{12}$$

Although other functions may be proposed to replace the Dirac delta, exploring the three-dimensional (3D) Gauss distribution greatly simplifies the analysis. Using eq. (12) instead of the Dirac delta in eq. (10) gives the simple equation where the parameter σ must be independently determined:

$$s(\mathbf{r},\mathbf{r}') = s(\mathbf{r})P_\sigma(\mathbf{r}-\mathbf{r}') = f(\mathbf{r})SP_\sigma(\mathbf{r}-\mathbf{r}') \tag{13}$$

Such softness kernel is not fully symmetric in $(\mathbf{r},\mathbf{r}')$ and care must be taken to keep the order of integration: first over $\mathbf{r}'$, then over $\mathbf{r}$; it gives proper result (S) by double integration. This softness kernel must be verified by confronting with a measurable physical quantity The analysis that has led to the polarization justified Fukui functions[1,2] proved that approximation by eq. (10), leads to accurate reproduction of the electronic dipole polarizability for atoms. The analysis must now be repeated with eq. (13).

At the basic level (the local approximation, LA) the local polarization vector has been defined as the vector derivative of the density over the electron field ε in the symbolic notation[1]:

$$\vec{\alpha}(\mathbf{r}) = -\left(\frac{\partial\rho(\mathbf{r})}{\partial\boldsymbol{\varepsilon}}\right)_N = -\int \omega(\mathbf{r},\mathbf{r}')\mathbf{r}'d\mathbf{r}' \tag{14}$$

Using eq. (6) and exploring eq. (13) for the softness kernel of an atom produces the result identical to the one obtained originally with eq. (10):

$$f^{LA}(\mathbf{r}) = \frac{\vec{\alpha}(\mathbf{r})\cdot\mathbf{r}}{r^2}\left[\int\frac{\vec{\alpha}(\mathbf{r})\cdot\mathbf{r}}{r^2}d\mathbf{r}\right]^{-1} \tag{15}$$

This Fukui function is computable and may serve for the purpose of modeling the softness kernel itself through eq. (13) [with eq. (4)]. However, such a LA provided rather crude results even for atoms (cf. ref. 1). The more realistic approximation for the FF has been obtained with the more elaborated version of the softness kernel instead of eq. (10)[1]:

$$s(\mathbf{r},\mathbf{r}') = k(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + b\rho(\mathbf{r})\rho(\mathbf{r}') + cSf(\mathbf{r})f(\mathbf{r}') \tag{16}$$

where $k(\mathbf{r})$, b, and c are arbitrary parameters. Using the Gauss function instead of the Dirac delta in eq. (16) and eliminating parameters leads to the Fukui function identical to the one in ref. 1.

$$f(\mathbf{r}) = df^{LA}(\mathbf{r}) + (1-d)f^{EG}(\mathbf{r}) \tag{17}$$

Here, $f^{EG}(\mathbf{r}) = \rho(\mathbf{r})/N$ and parameter d is independently established for atoms.[1,2] This result may be used in eq. (13) leading to the explicit equation for the softness kernel. Equation (17) has only been proved for atoms; extension to molecules is nontrivial as the spherical symmetry of atom greatly simplified the analysis.[11] The linear response function is then obtained via eq. (6).

The kernels described in this section are physical functions in 3D space; examples have been provided in the last section of

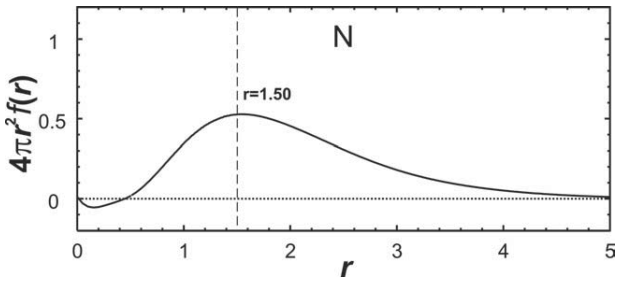

Figure 1. Radial Fukui function for the nitrogen atom as presented in previous work[1,2]; the choice of $\mathbf{r} = 1.50$a.u. has been indicated (a.u. on axes).

this article. The unknown parameter σ, the half width of the Gauss distribution, must be resolved first. This will be done by the analysis of the hardness kernel given by eq. (9).

The Hardness Kernel

The widely used form of the hardness kernel [eq. (9)] is motivated by the electron repulsion formula; this interaction is deemed to have a major contribution to this kernel. The global hardness results by integrations of the hardness kernel:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v} = \int\int \eta(\mathbf{r},\mathbf{r}')f(\mathbf{r})f(\mathbf{r}')d\mathbf{r}d\mathbf{r}' = I - A \qquad (18)$$

It has been demonstrated for a collection of more than 50 atoms and atomic ions[1,2] that the polarization justified Fukui functions [eq. (17)] and the basic hardness kernel [eq. (9)] reproduce the global hardness for this group by eq. (18) with impressive accuracy (except for the noble gases and the fluorine anion), better than any other approach.[5] This result suggests that the polarization justified Fukui functions represent an implicit, well-balanced approximation for the density derivatives. Hence, the basic identity [eq. (8)] will be explored to identify the parameter σ. Equations (9) and (13) with eq. (8) lead to:

$$S\int\int \frac{f(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}''|}P_\sigma(\mathbf{r}-\mathbf{r}')d\mathbf{r}d\mathbf{r}' = 1 \qquad (19)$$

The left hand side might be a function of $\mathbf{r}''$, depending on the quality of approximations explored. With $\sigma \to 0$ the Gauss distribution tends to $\delta(\mathbf{r}-\mathbf{r}')$ and the integral becomes

$$\int \frac{f(\mathbf{r})}{|\mathbf{r}-\mathbf{r}''|}d\mathbf{r} = \eta(\mathbf{r}'') \qquad (20)$$

This result has been known as the electrostatic potential of the Fukui function or the local hardness, first calculated for atoms by Chattaraj et al.[6] $\eta(\mathbf{r}'') \approx \eta$ but contains only weak dependence on $\mathbf{r}''$ at reasonable distances from a nucleus. As σ is an arbitrary parameter only, it may be most reasonably identified for the point of maximum density, hence at $\mathbf{r}'' = 0$ assuming $\eta(\mathbf{r}''=0) = \eta = I - A$. This produces the computable result directly dependent on the single parameter σ:

$$\sigma^{-3}(2\pi)^{-3/2}\int f(\mathbf{r})d\mathbf{r}\int\frac{1}{|\mathbf{r}'|}\exp\left[-\frac{(\mathbf{r}-\mathbf{r}')^2}{2\sigma^2}\right]d\mathbf{r}' = I - A \qquad (21)$$

Results and Discussion

The Fukui function calculated in previous work for a nitrogen atom has been explored as a test in this present work.[1,2] It resulted from calculations with the Gaussian 03 code[12] by the B3LYP method with aug-cc-pvqz basis set. Calculated data are:

- Global hardness $= \eta = I - A = 14.4251$ *a.u.* (experiment: 14.46, ref. 13).
- Electron dipole polarizability $= \langle\alpha_e\rangle = 7.79$ *a.u.* (experiment: 7.42, ref. 14).
- Parameter in eq. (16) (dimensionless) $= d = 1.066$, ref. 1.
- Parameter σ (length) $= \sigma = 0.775$ *a.u.*, eq. (21), this work.

Determination of the σ parameter opens the way to inspection of the spatial properties of the kernels. To visualize the nonlocal function in the 3D space, one of the points must be fixed. The arbitrary choice was to fix the reference point at $\mathbf{r} = 1.50$ a.u. from the nucleus at the point of the maximum of the radial Fukui function, as presented in Figure 1 and locate the reference point at z axis. With this choice, spatial pictures of $\omega(\mathbf{r},\mathbf{r}')$ and $s(\mathbf{r},\mathbf{r}')$ have been shown in Figures 2 and 3, respectively.

The general feature of the $\omega(\mathbf{r},\mathbf{r}')$ and $s(\mathbf{r},\mathbf{r}')$ functions at the reference point (maximum effect) is symmetric, which has been expected from their binding equation (eq. 6), considering rather small contributions from the last FF term (cf. Fig. 1). However, in the region close to the nucleus, both $\omega(\mathbf{r},\mathbf{r}')$ and $s(\mathbf{r},\mathbf{r}')$ show

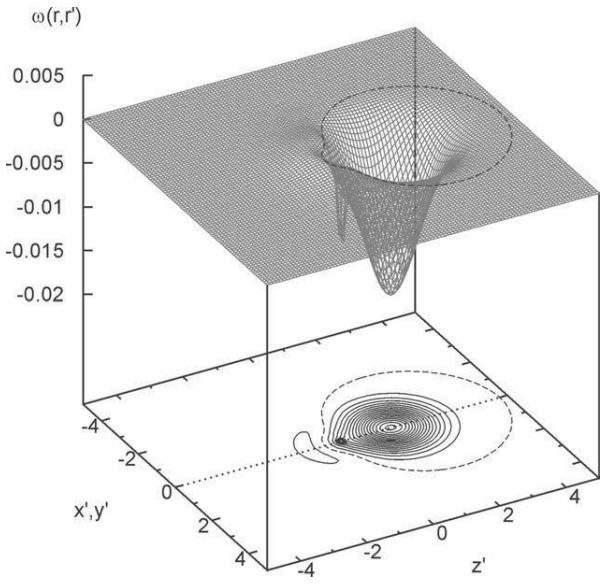

Figure 2. The linear response function for the nitrogen atom located at the origin, drawn at the reference point at the z axis $\mathbf{r}$ [0,0,1.50]. (a.u. on axes).

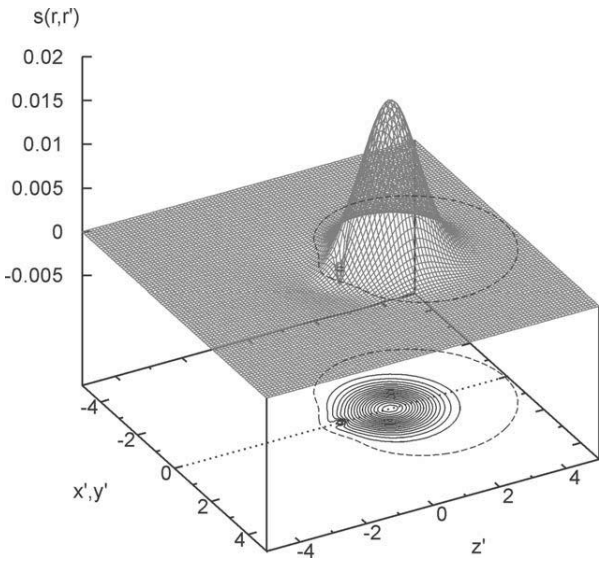

Figure 3. The softness kernel for the nitrogen atom located at the origin, drawn at the reference point at the z axis **r**[0,0,1.50]. (a.u. on axes).

the same negative effect: It comes directly from the negative sign of the FF function $f(\mathbf{r})$ in this region.

Parameter σ has been found by interpolation between a series of computed values for the left hand side of the eq. (21) to match the computed global hardness. It is interesting to see this parameter to be within the range of interelectron distances for an atom. This value has been used to depict the shape of the softness kernel and the linear response function. Parameter σ (and the normal Gauss distribution itself) appears to represent an effective correction to the original Vela and Gazques proposal [eq. (10)], compensating the arbitrary use of the approximated hardness kernel [eq. (9)] in otherwise exact eq. (8). The polarization justified Fukui function used in eq. (21) has been obtained from the electron density calculated at the DFT level, then differentiated over the external field to yield the local polarization vector $\vec{\alpha}(\mathbf{r})$, eq. (14). This requires considerably high computational accuracy necessary to reproduce the electron dipole polarizability [eqs. (14) and (2)], quite sensitive to the choice of the basis set. Thus, $f(\mathbf{r})$ properly contains all contributions to the electron energy, including the electron correlation term. On the other hand, the hardness kernel [eq. (9)] has been known to contain nothing but the effect of interelectronic repulsion; the problem has been discussed in detail in the preceding work.[1] Forcing the eq. (8) to be at least approximately fulfilled brings the two kernels to a harmony.

Conclusions

Replacing the Dirac delta with the 3D Gauss distribution in the working formula for the softness kernel has led to the identical Fukui function for atoms as originally obtained. By making the kernel continuous in space, it allows to visualize the softness kernel for the first time. The novel softness kernel [eq. (13)] with the optimized half width of the Gauss distribution σ is tailored to be coherent with the hardness kernel in its simple and widely accepted form [eq. (9)]. The resulting radius hides the correlation effects and thus may well be considered an effective average correlation radius for the electronic system.

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