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New Link between Conceptual Density Functional Theory and Electron Delocalization

Eduard Matito^{*,†} and Mihai V. Putz^{*,‡}

[†]Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland

[‡]Laboratory of Computational and Structural Physical Chemistry, Chemistry Department, West University of Timisoara, Pestalozzi Str. 16, Timisoara, RO-300115, Romania

ABSTRACT: In this paper we give a new definition of the softness kernel based on the exchange–correlation density. This new kernel is shown to correspond to the change of electron fluctuation upon external perturbation, thus helping to bridge the gap between conceptual density functional theory and some tools describing electron localization in molecules. With the aid of a few computational calculations on diatomics we illustrate the performance of this new computational tool.

A new softness kernel
 $s(\mathbf{r}, \mathbf{r}') = \left(\frac{\partial \rho_{xc}(\mathbf{r}, \mathbf{r}')}{\partial \mu} \right)_v$

1. INTRODUCTION

The premier goal of conceptual DFT (CDFT) is the study of chemical reactivity. Many classical concepts in chemistry have found a solid basis for existence under the umbrella of CDFT,¹ and nowadays the calculation of the chemical potential, the chemical hardness or the softness have become routine practice in the studies of chemical reactivity.^{2,3} On the other side of the coin, the study of chemical bonding has been addressed from many perspectives including atomic populations, bond orders or, more recently, the renowned electron localization function (ELF).⁴ These tools are extremely useful in characterizing the electronic structure of molecules but very rarely can be used to predict chemical reactivity. Both CDFT and the study of chemical bonding have produced an enormous amount of literature and play a prominent role in computational chemistry. In contrast, the number of studies dealing with chemical bonding from a CDFT perspective are scarce. In this paper, we put forward a new quantity, which fulfills some conditions requested to softness kernels and provides the possibility to study chemical bonding upon external perturbation and, thus, could be adequate for the study of chemical reactivity.

2. METHODOLOGY

Parr and Pearson⁵ defined the global hardness as the derivative of the chemical potential, which arises naturally in density functional theory (DFT), and Parr and Yang defined the softness as the inverse of the hardness,⁶

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_v \quad S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu} \right)_v \quad (1)$$

Note that some authors define the latter quantities with an extra factor of 1/2. We have decided to drop it for the sake of clarity. Despite the universality of these quantities, they have been used mainly in DFT,² where μ , the chemical potential, is the Lagrange multiplier in the Euler–Lagrange equation.

These global quantities have accompanying local analogs that can be naturally defined by replacing the global quantity N by a local one, $\rho(\mathbf{r})$, which returns N upon integration. In this way, the local softness is defined as⁶

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_v \quad (2)$$

so that

$$\int s(\mathbf{r}) \, d\mathbf{r} = S \quad (3)$$

Likewise, Ghosh and Berkowitz⁷ define the local hardness as

$$\eta(\mathbf{r}) = \left(\frac{\delta \mu}{\delta \rho(\mathbf{r})} \right)_v \quad (4)$$

Within DFT, the latter can be also written in terms of Hohenberg–Kohn functional,⁸

$$\eta(\mathbf{r}) = \frac{1}{N} \int \frac{\delta^2 F_{\text{HK}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \rho(\mathbf{r}') \, d\mathbf{r}' \quad (5)$$

from which the hardness kernel is defined as⁷

$$\eta(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 F_{\text{HK}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = - \frac{\delta u(\mathbf{r})}{\delta \rho(\mathbf{r}')} \quad (6)$$

where the intrinsic potential is given by the external potential

$$u(\mathbf{r}) = v(\mathbf{r}) - \mu \quad (7)$$

Special Issue: Richard F. W. Bader Festschrift

Received: January 24, 2011

Revised: April 15, 2011

Published: May 11, 2011

and

$$\frac{1}{N} \int \eta(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}' = \eta(\mathbf{r}) \quad (8)$$

While the hardness kernel has a particular clear definition within DFT, the softness kernel is defined as the reciprocal of the latter⁹

$$s(\mathbf{r}, \mathbf{r}') = -\frac{\delta \rho(\mathbf{r})}{\delta u(\mathbf{r}')} \quad (9)$$

giving the well-known equation

$$\int s(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = s(\mathbf{r}) \quad (10)$$

In the framework of DFT, the hardness kernel is also the integrand entering to second-order in the Taylor expansion of the energy functional in terms of the density.^{10,11} This guarantees the existence of these derivatives within DFT and provides the usual way to construct hardness kernels from which to obtain all the other quantities.^{12–17}

On the other hand, the exchange–correlation density (XCD),¹⁸

$$\rho_{xc}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) \rho(\mathbf{r}') - \rho_2(\mathbf{r}, \mathbf{r}') \quad (11)$$

where $\rho_2(\mathbf{r}, \mathbf{r}')$ is the second-order density matrix, is the workhorse for the methods that account for electron localization. The XCD has been used to define many popular tools in bonding analysis, such as the electron-sharing indices (or bond orders),¹⁹ the domain-averaged Fermi holes,^{20,21} and the electron localization function.^{4,22} Upon integration of the XCD we obtain the density,

$$\int \rho_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \rho(\mathbf{r}) \quad (12)$$

taking the derivative with respect to μ at each side, we obtain

$$\int \left(\frac{\partial \rho_{xc}(\mathbf{r}, \mathbf{r}')}{\partial \mu} \right) d\mathbf{r}' = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right) = s(\mathbf{r}) \quad (13)$$

which gives a natural alternative definition of the softness kernel

$$s(\mathbf{r}, \mathbf{r}') = \left(\frac{\partial \rho_{xc}(\mathbf{r}, \mathbf{r}')}{\partial \mu} \right) \quad (14)$$

Equation 13 proves that this new definition of the softness kernel fulfills eq 10 and thus is adequate to obtain the local softness. It uses the exchange–correlation function, which is not defined in the DFT framework, thus limiting its applicability to wave function methods. However, as we shall see, this definition connects very well with another conceptual tool used to describe the electronic structure of molecules. In the last part of the manuscript we give a version of this softness kernel which can be used in DFT.

3. CONNECTION WITH ELECTRON DELOCALIZATION DESCRIPTORS

The characterization of chemical bonding has gone a long way since Lewis' first attempt to put it on a firm basis.²³ In the past years, several tools have been designed to this aim, many of them using in one way or another the exchange–correlation density.¹⁸ In particular, the exchange–correlation density has been used to characterize the amount of electron sharing between two atoms

A and B through^{19,24}

$$D(A, B) = 2 \int_A \int_B \rho_{xc}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' d\mathbf{r} \quad (15)$$

as was first suggested in the seminal work of Bader.^{25,26} $D(A, B)$ corresponds to the covariance of the electron atomic populations of A and B,^{24,27} thus giving a measure between the correlation of these two populations but, unlike quantities in conceptual DFT, it has no predictive power about how the electron sharing may change upon external perturbation.

From this analysis we deduce that the new softness kernel, eq 14, corresponds to the change in the electron fluctuation between two regions of the space upon modification of the chemical potential. In particular, one may calculate the new kernel integrated into two atomic regions, A and B,

$$s(A, B) = \frac{1}{2} \left(\frac{\partial D(A, B)}{\partial \mu} \right)_{\nu} = \int_A \int_B \left(\frac{\partial \rho_{xc}(\mathbf{r}, \mathbf{r}')}{\partial \mu} \right)_{\nu} d\mathbf{r}' d\mathbf{r} \quad (16)$$

which would correspond to the change in the electron sharing between two atoms due the change in the chemical potential. This new definition opens the way to study the variation of electron delocalization (essentially a nonlocal effect) upon external perturbation, providing a promising tool for the study of chemical reactivity.

4. CALCULATIONS ON SIMPLE MOLECULAR SYSTEMS

The linear response kernel has been related to the polarizability of molecules. The connection between this concept and the softness kernel is given by the Berkowitz–Parr relationship⁹

$$s(\mathbf{r}, \mathbf{r}') = -\alpha(\mathbf{r}, \mathbf{r}') + \frac{s(\mathbf{r}) s(\mathbf{r}')}{S} \quad (17)$$

where $\alpha(\mathbf{r}, \mathbf{r}')$ is the linear response kernel. This new softness kernel integrated over two atomic regions measures the influence of the chemical potential on the bonding between these atoms. It is thus reasonable to link this concept to the polarizability of the bond. Indeed, some authors have studied the connection between the global softness and the static dipole polarizability in the past.^{28,29} We have investigated this relationship by computing the isotropic polarizability of the molecule for the series of molecules studied and compared it to the absolute value of the softness kernel. To this aim, we have used the finite difference approximation, which gives rise to three forms:

$$s^+(A, B) = \frac{1}{2} S [D^+(A, B) - D(A, B)] \quad (18)$$

$$s^-(A, B) = \frac{1}{2} S [D(A, B) - D^-(A, B)] \quad (19)$$

$$s^0(A, B) = \frac{1}{2} [s^+(A, B) + s^-(A, B)] \quad (20)$$

Within finite difference approximation, these formulas are straightforwardly related to the second-order atomic Fukui indices of Fradera and Solà.³⁰ The latter were used as a complement to the Fukui function, which helped to assess whether the electrons added/removed are more or less localized over the molecule. One should note here that Fradera's indices were calculated for relaxed wave functions (while we used frozen orbitals), and thus they are not directly comparable to our results.

Table 1. Electron Sharing Indices (ESI), Softness Kernels Integrated into Different Atomic Regions, Global Softness (*S*), and Polarizability (α) for the Molecules Taken into Study

molecule	$D(A,B)$	$s^-(A,B)$	$s^+(A,B)$	$s^0(A,B)$	<i>S</i>	α
CO	1.54	0.00	0.08	0.04	0.72	10.72
NO ⁺	2.30	0.07	0.03	0.05	0.57	10.05
N ₂	3.04	0.18	0.08	0.13	0.62	9.36
CN ⁻	2.15	0.06	0.03	0.05	0.78	16.91
LiH	0.19	0.03	0.16	0.10	1.66	23.24
LiF	0.18	0.00	0.17	0.09	1.06	6.43
NaH	0.37	0.06	0.03	0.04	1.86	33.61
HF	0.39	0.00	0.14	0.07	0.63	3.29

We are aware of the conceptual problems of taking derivatives with respect to the number of electrons;^{1,31} however, just for the sake of illustration, we have computed these quantities. Future research will attempt the calculation of $s(A,B)$ without the recourse of *N*-derivatives.

All the calculations (including geometry optimization) were done at the HF/cc-pVTZ level³² with the aid of AIMPAC³³ and ESI-3D³⁴ collection of programs. The atomic partition chosen is the well-known quantum theory of atoms in molecules (QTAIM) partition due to Bader,^{35,36} which we have found the most reliable partition of molecular space in several contexts.^{24,37–39} Table 1 collects these results for a few diatomic molecules. There is no straight relation between the polarizability and the condensed softness kernel in any of three forms computed, eqs 18–20. In spite of that, it is significant that $s^-(A,B)$ is small for LiF, HF, and CO, which exhibit small polarizabilities, and that NaH and CN⁻ show the largest polarizabilities and fairly large values for $s^-(A,B)$. On the other hand, N₂ and LiH escape to this general trend. Obviously, the polarizability assesses the ability to distort the electronic cloud in the *whole* molecule, while these softness kernel values focus on the electrons shared by these two atoms; thus one should not overemphasize this finding.

5. DISCUSSION

Yang and Parr demonstrated^{6,40} the connection between the local softness and the variance of the electron density in the grand canonical ensemble. The present work puts forward the relationship at the nonlocal level, by finding a connection between electron population covariance with a new proposal of the softness kernel.

Such a relationship was investigated in the past by Ángyán, who found an analytical expression between the softness kernel and the ESI using the Unsold approximation in the second-order perturbation expansion of the linear response kernel⁴¹ as well as an approximate proportionality between the static polarizability and the XCD.⁴² On the other hand, Cioslowski et al.⁴³ defined an atomic softness matrix that was actually a generalization of the atom–atom polarizability matrix defined in Hückel theory. Interestingly, the condensed version of our definition of the softness kernel correlates with polarizabilities for diatomic molecules. Among the few attempts to define a new softness kernel, one should also mention the recent work of Komorowski.⁴⁴

In addition, a work by Sablon et al.⁴⁵ suggesting the linear response kernel as a measure of electron delocalization has been recently published. Because of the direct connection between the linear response kernel and the local softness (through

Berkowitz–Parr relation), these results suggest also a tight connection between electron delocalization and the softness kernel.

Therefore, it makes sense to investigate the present ansatz as a new softness kernel in DFT. To avoid the conceptual problems of the calculation the XCD within DFT, one could define the new softness kernel in terms of the Kohn–Sham first-order density matrix

$$s(\mathbf{r},\mathbf{r}') = \frac{\partial \rho_s^2(\mathbf{r},\mathbf{r}')}{\partial \mu} \quad (21)$$

as was done for the softness kernel suggested by Fuentealba.⁴⁶ Unlike Fuentealba's kernel, this expression has the advantage of leading to the correct local softness upon integration and in contrast to previous definitions, this formula does not rely on the Dirac delta function. The properties of this kernel, and the possibilities to construct a new hardness kernel from it, will be the subject of future research.

Very recently, a connection between $[4n+2]$ Hückel's rule and electron delocalization in aromatic species has been found.⁴⁷ Namely, the second derivative of the electron fluctuation with respect to the number of electrons is shown to correlate very well with aromaticity. This derivative was approached by finite differences thus far. However, this new formulation of the softness kernel opens a way to calculate the latter quantity analytically by using the tools available in CDFT. It thus prompts the construction of the first aromaticity index based on electron-delocalization that would take into account the reactivity of the molecules.

6. CONCLUSIONS

We give a new definition of the softness kernel based on the exchange–correlation density and show the relationship with the change of electron fluctuation upon external perturbation. We perform a few numerical tests on diatomics, which suggest some relationship between this new softness kernel integrated into two atomic regions and the bond polarizability. This new tool helps in bridging the gap between conceptual density functional theory and electron localization measures in molecules.

During the revision of this manuscript the recent work of Bultinck⁴⁸ came to our attention, which suggests the definition of the Fukui matrix as the *N*-derivative of the first-order density matrix. Our definition of the softness kernel can be expressed in terms of this Fukui matrix and the first-order density matrix.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ematito@gmail.com (E.M.), mvputz@cbg.uvt.ro (M.V.P.).

ACKNOWLEDGMENT

This work has been supported by Marie Curie IntraEuropean Fellowship, Seventh Framework Programme (FP7/2007-2013), under grant agreement PIEF-GA-2008-221734 (E.M.), the Romanian Ministry of Education and Research (CNCS-UEFISCDI, the former CNCSIS-UEFISCSU agency, project number PN II-RU TE16/2010-2011, granted to M.V.P.), and the Polish Ministry of Science and Higher Education (Project No. N N204 215634). We thank Pedro Salvador, Miquel Torrent, and Miquel Solà for helpful comments.

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