The Journal of Chemical Physics

RESEARCH ARTICLE | MAY 03 2023

Analytical approximation to the local softness and hypersoftness and to their applications as reactivity indicators

Piotr Ordon ✉; Jarosław Zaklika; Jerzy Hładyszowski; ... et. al

Check for updates

J. Chem. Phys. 158, 174110 (2023)
https://doi.org/10.1063/5.0142656

CrossMark

View Online

Export Citation

Articles You May Be Interested In

Near plithogenic hypersoft sets

AIP Conference Proceedings (November 2022)

Molecular softness, hypersoftness, infrared absorption, and vibrational Raman scattering: New relations derived from nonlocal polarizability densities

J. Chem. Phys. (December 1995)

Beyond electronegativity and local hardness: Higher-order equalization criteria for determination of a ground-state electron density

J. Chem. Phys. (August 2008)

AIP Publishing

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

Analytical approximation to the local softness and hypersoftness and to their applications as reactivity indicators

Cite as: J. Chem. Phys. 158, 174110 (2023); doi: 10.1063/5.0142656
Submitted: 16 January 2023 • Accepted: 13 April 2023 •
Published Online: 3 May 2023

View Online Export Citation CrossMark

Piotr Ordon,[1,a)] Jarosław Zaklika,[2,b)] Jerzy Hładyszowski,[3,c)] and Ludwik Komorowski[2,d)]

AFFILIATIONS

[1] Department of Physics and Biophysics, Wrocław University of Environmental and Life Sciences, ul. Norwida 25, 50-373 Wrocław, Poland
[2] Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
[3] Department of Physical Chemistry and Biophysics, Wrocław Medical University, ul. Borowska 211 A, 50-556 Wrocław, Poland

[a)] **Author to whom correspondence should be addressed:** piotr.ordon@upwr.edu.pl
[b)] biojarek@gmail.com
[c)] jhladysz@wp.pl
[d)] ludwik.komorowski@pwr.edu.pl

ABSTRACT

Local density functional theory derivatives of the electron density have been calculated analytically for the set of canonical hydrogenic orbitals; original solutions have been obtained using the novel density gradient theorem. Results for the first and second derivatives of electron density over N (number of electrons) and over μ (chemical potential) have been demonstrated. Calculations of the state functions ΔN, ΔE, and $\Delta\mu$ disturbed by an external potential $\Delta v(r)$ have been obtained via the concept of alchemical derivatives. The local softness $s(r)$ and local hypersoftness $[ds(r)/dN]_v$ have been proved to provide crucial chemical information on the sensitivity of orbital density to the disturbance of the external potential $\Delta v(r)$, leading to electron exchange ΔN and the corresponding changes of the state functions ΔE, $\Delta\mu$. The results are fully compatible with the well-understood character of atomic orbitals in chemistry and open a perspective to applications to atoms, free or bonded.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0142656

I. INTRODUCTION

The group of authors active in Conceptual Density Functional Theory (cDFT) has recently reviewed the status and prospects for this field, with a focus on applicability of the existing tools in chemistry. In conclusion, the authors stressed "the need to formulate simple rules so that the non-expert users (both theorists and experimentalists) can reliably and appropriately use cDFT as an interpretational tool, with the ambition that cDFT can segue from its current predominantly interpretative role into more powerful predictive tool."[1] Following these queries, Geerlings and De Proft have reminded in their most recent review paper, the original thoughts by Parr and by Clementi and Coulson: New ideas (e.g., orbital or electronegativity) have found their place in the imagination of chemists not because they enable accurate predictions but allow for rationalization of commonly observed phenomena.[2] This viewpoint is corroborated by any physical chemistry textbook: The role of chemical thermodynamics rests on the conceptual power of the formal analysis, while applications to real systems inevitably require reasonable and well-founded approximations (e.g., activity coefficients).

This present work is based on the newly found relationship of the electron density gradient and the external electric field that we called the electron density gradient theorem.[3] By exploring this theorem, we provide a step in the direction of searching for the coherent, through an idealized mathematical approach to electron density derivatives in a similar manner as we recently have introduced a new approximation for the Fukui function.[4] The near-

Published under an exclusive license by AIP Publishing

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

sightedness principle for electron density[5] justifies the use of the Vela–Gazquez approximation.[6] This way, our localized gradient theorem delivers the electronic softness indices (global and local) for atoms as well as for the orbitals. Analytically obtained results of the global and local softness from the electron density function were presented in our recent work.[4] These results, albeit not exact, have opened a perspective for analytical calculation of the entire group of local density derivatives and for demonstrating their practical role in the description of the response of state functions for an electronic system (ΔE, ΔN, $\Delta\mu$) to a perturbation by an external potential. The goal of our work is not to compete with the existing sophisticated approaches but rather to search for a handy tool that chemists could readily use with understanding of its theoretical background.

According to the fundamental DFT axiom,[7] electron density has been identified as the basic source of functional quantification for any property of molecular systems. This directly corresponds to our density gradient theorem that has recently delivered the Fukui function and local and global softness indices.[4] In order to gain physical and chemical insight into the properties of model entities, in the spirit recently discussed in the work of Ayers *et al.*,[8] we consider the basic components that can be used to form the total density, namely the density of hydrogenic orbitals. This is the case where exact analytical solution is available and the results may then serve as a model for numerical calculation for real systems. Orbitals, fundamental objects of the contemporary chemistry, have won the imagination of chemists as a tool for the interpretation of chemical properties of atoms. The first attempt on this track was encouraging: the relation between the global softness (S) [calculated by integration of the analytical local softness $s(r)$ obtained with the approximation derived from our density gradient theorem] and the atomic number of the nucleus (Z) has been discovered for orbitals as $S \propto Z^{-2}$ as it is expected for atoms due to their positions in the Periodic Table.[4]

II. ENERGY DERIVATIVES FOR CHEMICAL PURPOSES

Derivatives of electronic energy $E[N, v(\boldsymbol{r})]$ have long been recognized as potentially valuable factors for describing the reactivity of molecular entities.[1,9–11] Global derivatives over N have been used as reactivity indicators before the advent of the DFT concept. Electronegativity χ was introduced by Pauling;[12] the quantified measure of electronegativity for atoms proposed by Mulliken[13] was first identified as the energy derivative over the formal charge of an atom[14,15] and later adopted by conceptual Density Functional Theory (cDFT) as the negative chemical potential of electrons $\mu = [\partial E/\partial N]_v = -\chi$.[16] The chemical hardness, originally postulated as a qualitative indicator,[17] has also been identified with the cDFT derivative:[18–21] $\eta = [\partial^2 E/\partial N]_v$. These global indices have also been recalled in relation to the electrophilicity of molecules $\omega = \mu^2/2\eta$,[22,23] once considered an important concept in the DF reactivity theory.[24]

The energy derivatives over the electron number belong to the larger group of response functions defined at the cDFT level, which may potentially help in the prediction of chemical processes.[25] The local energy derivative representing actual electron density function, $\rho(\mathbf{r}) = [\delta E/\delta v(\mathbf{r})]_N$, has served for a qualitative indicator of nucleophilic of electrofilic character of bonded atoms. The second, mixed energy derivative, the Fukui function, $f(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial N]_v = [\delta\mu/\delta v(\mathbf{r})]_N$ was introduced by Parr and Yang[26,27] and proved to represent an extension of the original proposal by the MO theory of reactivity by Fukui.[28,29] Its relation to the alternative second derivative of local character, the local softness, $s(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial N]_\mu$, has been presented by the original authors.[9] The panorama of energy derivatives of the second order has been completed by the two nonlocal derivatives: the linear response function $\omega(\boldsymbol{r}, \boldsymbol{r}') = \left[\delta^2 E/\delta v(\mathbf{r})\delta v(\mathbf{r}')\right]_N$ and the analogous derivative of the grand potential ($\Omega = E - \mu N$), the softness kernel:[30] $s(\mathbf{r}, \mathbf{r}') = \left[\delta^2\Omega/\delta v(\mathbf{r})\delta v(\mathbf{r}')\right]_\mu$. The third-order and higher derivatives have also been considered, though rarely tested.[31] Formally, the route for calculation of the response of the global quantities (e.g., ΔE, $\Delta\mu$, ΔN) to the variation of the external potential $\Delta v(\boldsymbol{r})$ has been opened.

In the early cDFT era, particular attention was given to the global factors supposedly determining the direction of a chemical reaction, on the ground of well-recognized rules: electronegativity equalization[32] and HSAB principle.[17] A number of more or less elegant formulas for ΔE and ΔN prediction for a reaction between atoms have been proposed using the variables χ and η for reactants.[19,33–37] The profound analysis of coupling between equilibrium state variables was elaborated by Nalewajski.[38]

The next stage of efforts to the cDFT platform has been dominated by the exploration of the Fukui function in the direction indicated by Parr and Yang in their fundamental statement: "Of two different sites with generally similar dispositions for reacting with a given reagent, the reagent prefers the one which on the reagent's approach is associated with the maximum response of the system's chemical potential." A variety of approaches to the Fukui functions have been elaborated, with an objective to find rational atomic indices in that matter, which would allow a nonlocal treatment of chemical reactions as an interaction between contact atoms.[27,39–45]

The finite difference method, much in the spirit of the Fukui theory, has typically been used in practical applications leading to the Fukui functions characterizing nucleophilic, electrophilic, and radical attack, respectively: $f^+(\mathbf{r})$, $f^-(\mathbf{r})$, and $f^o(\mathbf{r}) = \frac{1}{2}\left[f^+(\mathbf{r}) + f^-(\mathbf{r})\right]$. The results of this widely used approach are exact at the 0 K limit; however, the characterization of reacting properties of an object with N electrons could not be extracted from its electron density function $\rho_N(\mathbf{r})$ but required additional information on its ionized states $\rho_{N-1}(\mathbf{r})$ and $\rho_{N+1}(\mathbf{r})$. Calculation along these lines have been explored widely,[46–51] leading to practical computational schemes.[52,53] Extensive theoretical work in this matter has been presented in the work of Ayers *et al.*[54–57]

Another promising derivative of the local character was the derivative of the Fukui function $[\partial f(\mathbf{r})/\partial N]_v$ introduced in the work of Fuentealba and Parr[58] through the Maxwell relation as a derivative of the global hardness: $h(\mathbf{r}) = [\delta\eta/\delta v(\mathbf{r})]_N$. The work of Ordon *et al.* has explored this derivative in order to reveal the significance of the derivatives of Hellmann–Feynman forces[59,60] and tested the role of the $h(\mathbf{r})$ function in applications to the reactivity of molecules of energetic materials;[61] it has also been applied in an original formulation of the maximum hardness principle together with a formula for $\gamma = (\partial\eta/\partial N)_v$.[62] The work of Morell *et al.* introduced this derivative under the name of dual descriptor $f^+(\mathbf{r}) - f^-(\mathbf{r}) = f^{(2)}(\mathbf{r})$ as an extension to the Fukui function concept.[63,64] The authors claimed that the dual descriptor could

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

be a remedy, when MO theory fails to correctly predict molecular reactivity.[65] The concept has been further developed for applications as reactivity index[66,67] and alternative operational formulas have also been proposed.[68] The initial hardness response provided by this index has been explored in the theoretical description of the Woodward–Hoffman rules.[69–71]

The nonlocal density derivatives have been a challenge for their potential applications in chemistry due to their multidimensional nature. Initial efforts have been invested in analyzing the potential role of the hardness kernel $\eta(\mathbf{r},\mathbf{r}')$ as an alternative to the softness kernel;[72–75] however, the ambiguities concerning the local hardness $\eta(\mathbf{r})$ prevented its practical use.[76–78] The extensive presentation of the linear response function (LRF) has been provided in the work of Geerlings *et al.*;[79] the concept has been little exploited in chemistry unlike in solid state physics. Berkowitz and Parr first recalled the perturbation formula for the calculation of $\omega(\mathbf{r},\mathbf{r}')$.[30] Senet provided the fundamental analysis of nonlinear electronic responses.[80] The work of Yang *et al.* presented analytical expressions for the real-space linear response function using the Kohn–Sham equations.[81] The direct connection to the dipole polarizability tensor has been demonstrated in the work of Komorowski *et al.*[82,83] $\underline{\underline{\alpha}} = \int\int \mathbf{r}\mathbf{r}'\omega(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'$. The authors also proposed a method for modeling $\omega(\mathbf{r},\mathbf{r}')$ and $s(\mathbf{r},\mathbf{r}')$ functions in 3D space.[84] In the series of papers presented in the works of Boisdenghien *et al.*, the energy expansion to the Taylor series has been used, leading to disturbance of the density formulated as $\Delta\rho(\mathbf{r}) = A\omega(\mathbf{r},0)$. Attractive two- and one-dimensional projections of the LRF $\omega(\mathbf{r},0)$ resulted for atoms.[85,86]

The chemical relevance of the whole body of DFT derivatives of electron density has been discussed in the work of Geerlings and De Proft.[87] Systematic formulas have been collected in the work of Heidar-Zadeh *et al.* for derivatives of any order, with no reference to the actual methods of their computations.[88] The unique mathematical formalism and working equations for the first- and second-order chemical reactivity response functions at finite temperatures has been proposed in the work of Franco-Pérez *et al.*[52,89] The general phenomenological relationships have been demonstrated, all of which reduce to the traditional formulas in the zero-temperature limit.

III. EXPLORING THE GRADIENT THEOREM

Applications of the formal cDFT apparatus to reacting objects not only require the stationary values of the derivatives characterizing these reactants but also call for describing their response to the external electric field. While there is no problem with the formulation of the electrostatic potential of nuclei, the formal relation of energy derivatives to $v(\mathbf{r})$ remains a mystery, as does the fundamental relation between $\rho(\mathbf{r})$ and $v(\mathbf{r})$. The recent discovery of the original gradient theorem provided a fresh starting point[90–93] by presenting the exact relation between the electron density gradient and the electric field,[3,4]

$$\nabla\rho(\mathbf{r}) = \int \omega(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}(\mathbf{r}')d\mathbf{r}' = -\int s(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}(\mathbf{r}')d\mathbf{r}', \tag{1}$$

$\boldsymbol{\varepsilon}(\mathbf{r}) = \sum_B \boldsymbol{\varepsilon}_B(\mathbf{r})$, where $\boldsymbol{\varepsilon}_B(\mathbf{r}) = -\nabla_B v(\mathbf{r})$ represents the electric field vectors, total and atomic, respectively. A brief reminder of the formal derivation of Eq. (1) is enclosed in the Appendix. The very interesting new property has been unveiled by Eq. (1). The linear response function $\omega(\mathbf{r},\mathbf{r}')$ and the softness kernel $s(\mathbf{r},\mathbf{r}')$ are strictly equivalent, even though both functions are by no means identical and their mutual relation has been known as the Berkowitz and Parr equation.[30] Theoretical studies by several authors have focused on the very nature of kernel functions and led to interesting conclusions on their spatial properties. Prodan and Kohn have proposed a principle of nearsightedness of electronic matter (NEM),[94] first introduced by Kohn[95] and later discussed by Bader.[96] According to NEM, "for a given unperturbed system and a given R, the density changes at r_o, $\Delta\rho(r_o)$, due to all admissible $\Delta v(\mathbf{r})$ have a finite maximum magnitude, $\Delta\rho$, which, of course, depends on r_o, R, and the unperturbed system. $(\cdots)$ $\Delta\rho(r_o, R)$ decays monotonically as a function of R." Applications of the NEM principle to chemical systems within the cDFT framework lead to the convincing conclusion that the softness kernel $s(\mathbf{r},\mathbf{r}')$ at constant μ can be characterized as nearsighted in contrast to the linear response function $\omega(\mathbf{r},\mathbf{r}')$ at constant N.[5] By this conclusion, the older, intuitive approach for the softness kernel $s(\mathbf{r},\mathbf{r}')$ has been justified—the local approximation introduced in the work of Vela and Gázquez,[6]

$$s(\mathbf{r},\mathbf{r}') = s(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}'). \tag{2}$$

This approximation arises in the NEM formulation by taking the limit $R \to 0$ and has been explored by several authors.[82,97–99] It has been tested in calculations of the Fukui functions[97,100] and allowed for linking the DFT formalism to the polarization properties of atoms and molecules.[82,98,99] The limitations of the local approximation may be tested by a simple example. At constant μ, the density disturbance due to the external potential is

$$d\rho(\mathbf{r}) = -\int s(\mathbf{r},\mathbf{r}')\delta v(\mathbf{r}')d\mathbf{r}'.$$

With Eq. (2), this is reduced to $d\rho(\mathbf{r}) = -s(\mathbf{r})dv(\mathbf{r})$; the result is nonidentical to the exact one. However, when the global change is calculated by integration, the difference between both vanishes: $dN = \int \rho(\mathbf{r})d\mathbf{r} = -\int s(\mathbf{r})\delta v(\mathbf{r})d\mathbf{r}$.

When combined with the gradient theorem [Eq. (1)], the local approximation [Eq. (2)] opens a straightforward route to the local softness $s(\mathbf{r})$, hence also to the Fukui function $f(\mathbf{r})$. Equation (1) leads to the relation[4]

$$\nabla\rho(\mathbf{r}) = -s(\mathbf{r})\boldsymbol{\varepsilon}(\mathbf{r}). \tag{3a}$$

Consequently,

$$s(\mathbf{r}) = -\frac{\nabla\rho(\mathbf{r})\cdot\boldsymbol{\varepsilon}(\mathbf{r})}{|\boldsymbol{\varepsilon}(\mathbf{r})|^2}. \tag{3b}$$

This equation, though not exact, formally allows for the calculation of the local softness function in any system and provides the global softness $S = \int s(\mathbf{r})d\mathbf{r}$. Consequently, it leads directly to the Fukui function: $f(\mathbf{r}) = s(\mathbf{r})/S$. The above practical solution to the problem of finding the Fukui function was first suggested in the

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

work of Chattaraj *et al.*[101] but has only been applied in practice in the preceding paper by the present authors.[4]

The first application of Eq. (3b) focused on the verification of this approximation for atoms.[4] For an isolated atom, Eq. (3a) is nearly exact, since the gradient vector and electric field vector are indeed antiparallel in every point in space. Moreover, when Eq. (3b) is applied to an atom, the following realistic conclusion is born: $s(\mathbf{r}) \to 0$ at the nucleus since the density gradient at $\mathbf{r} \to 0$ is finite.[91,102] Calculation of the global softness by integration of the local softness for atoms has led to the first approach to the global hardness (inverse softness) resulting analytically from the electron density $\rho(\mathbf{r})$.[4] The results for atoms correlated reasonably with the traditional measure of hardness by the ionization energy (I) and electron affinity (A) $\eta \propto (I - A)$. Fukui functions calculated with Eq. (3) for atoms were based solely on the ground state electron density of neutral atoms. Results for 36 atoms (1–4 rows in the Periodic Table) have been demonstrated to be reasonably close (not identical) to the average value $f^o(\mathbf{r})$, characteristic for a radical attack. These results have opened a broader perspective. It is now possible to explore the formal cDFT apparatus in relation to the analytical description of the response of global state functions of a system to a variable external electric field.

IV. THE LOCAL ELECTRON DENSITY DERIVATIVES

The concise review of the first and second derivatives of local character presented below is aimed at disclosing a minimum group of the derivatives, sufficient to reproduce the entire collection. The derivatives of $\rho(\mathbf{r})$ have been considered in two alternative situations: for a closed system and for an open system.[31] This classification allows for their thermodynamic analysis by the canonical ensemble $E[N, v(\mathbf{r})]$ and grand canonical ensemble $\Omega[\mu, v(\mathbf{r})]$, respectively, with the number of electrons (N) and chemical potential ($\mu = dE/dN$) serving as basic variables, respectively, with the external potential $v(\mathbf{r})$. The density itself is a unique derivative in both systems $\rho(\mathbf{r}) = [\delta E/\delta v(\mathbf{r})]_N = [\delta\Omega/\delta v(\mathbf{r})]_\mu$. The two ensembles also provide Maxwell relations between the derivatives: derivatives of the density in the first order may be alternatively expressed as derivatives of the state function (μ, N) over the external potential,[26]

$$f(\mathbf{r}) = \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_v = \left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right]_N, \tag{4}$$

$$s(\mathbf{r}) = \left[\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right]_v = -\left[\frac{\delta N}{\delta v(\mathbf{r})}\right]_\mu. \tag{5}$$

The information content of the local softness $s(\mathbf{r})$ is considerably richer than that of the Fukui function $f(\mathbf{r})$: The relation $s(\mathbf{r}) \Rightarrow f(\mathbf{r})$ is not reversible since $Sf(\mathbf{r}) = s(\mathbf{r})$ and $S = \int s(\mathbf{r})d\mathbf{r}$. The second mixed derivative of the density over N and μ is

$$\left[\frac{\partial^2\rho(\mathbf{r})}{\partial\mu\partial N}\right]_v = \left[\frac{\partial f(\mathbf{r})}{\partial\mu}\right]_v = \left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v. \tag{6}$$

This may be transformed by using Eq. (5) and the connection between global hardness and softness $(\partial\mu/dN)_v = \eta = 1/S$ given by

$$\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v = \left[\frac{\partial s(\mathbf{r})}{\partial\mu}\right]_v \left(\frac{\partial\mu}{\partial N}\right)_v = -\frac{1}{S}\left[\frac{\delta S}{\delta v(\mathbf{r})}\right]_\mu. \tag{7}$$

The second density derivative over μ is also related to the derivative of global softness over the external potential. Exploring Eq. (5) and the basic relation in the grand canonical ensemble $(\partial N/d\mu)_v = S$ leads to the result in Eq. (7). We have

$$\left[\frac{\partial^2\rho(\mathbf{r})}{\partial\mu^2}\right]_v = \left[\frac{\partial s(\mathbf{r})}{\partial\mu}\right]_v = -\left[\frac{\delta S}{\delta v(\mathbf{r})}\right]_\mu = S\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v. \tag{8}$$

The second density derivative over N (the hardness function or the dual descriptor) does not provide new information,

$$\left[\frac{\partial^2\rho(\mathbf{r})}{\partial N^2}\right]_v = \left[\frac{\partial f(\mathbf{r})}{\partial N}\right]_v = \left[\frac{\delta\eta}{\delta v(\mathbf{r})}\right]_v = -\frac{1}{S^2}\left[\frac{\delta S}{\delta v(\mathbf{r})}\right]_\mu = \frac{1}{S}\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v. \tag{9}$$

Equation (8) represents the derivative in the grand canonical ensemble and it deserves strictly the name of local hypersoftness.[87] Nevertheless, since the three derivatives are redundant, the name hypersoftness may be extended to all three [Eqs. (6), (8) and (9)].

The demonstrated direct connections of the electron density derivatives to the functional derivatives of the global quantities over the external potential $v(\mathbf{r})$ are crucial for potential applications in chemistry since they describe the response of state functions (μ, N, S). An alternative local index, the local hardness, does not appear in this consideration. The well-recognized ambiguity concerning the local hardness parameter[103] has been naturally circumvented by the systematic approach to closed and open systems by means of the canonical and grand canonical ensembles, respectively.

Analysis of the second derivatives of the electron density hints to possible access to their practical calculations, since the basic first derivative $s(\mathbf{r})$ is available [Eq. (3)].[4] Calculation of $[\partial s(\mathbf{r})/\partial N]_v$ by application of the gradient theorem with local approximation has been presented in Sec. V. Practical determination of $s(\mathbf{r})$ and $[\partial s(\mathbf{r})/\partial N]_v$ allows for the exploration of the response of state functions to an external potential; formal analysis follows in Sec. VI, the results are presented in Sec. VII.

V. THE LOCAL HYPERSOFTNESS $[\partial s(\mathbf{r})/\partial N]_v$

The straightforward route to the local softness $s(\mathbf{r})$ has been opened, when the local approximation [Eq. (2)] was applied to softness kernel in the gradient theorem [Eq. (1)]. The operating formula for the local softness index is provided by Eq. (3b), since the electric field from all nuclei $\boldsymbol{\varepsilon}(\mathbf{r})$ and the density gradient $\nabla\rho(\mathbf{r})$ are readily computable. Extension of that calculation scheme to the second density derivative is straightforward, by taking the d/dN derivative of Eq. (3b). Since the electric field is independent of N, the result is

$$\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v = -\frac{\nabla f(\mathbf{r})\cdot\boldsymbol{\varepsilon}(\mathbf{r})}{|\boldsymbol{\varepsilon}(\mathbf{r})|^2}, \tag{10}$$

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

where $\nabla f(\mathbf{r})$ is found by taking a divergence from Eq. (3a). By the Laplace law, $\nabla \cdot \left(\frac{\hat{\mathbf{r}}}{r^2}\right) = 4\pi\delta(\mathbf{r})$, where $\hat{\mathbf{r}}$ is a unit vector in the direction $\mathbf{r}$ and $\delta(\mathbf{r})$ is the Dirac delta function.[92] Thus, for a system with many nuclei,

$$\nabla \cdot \boldsymbol{\varepsilon}(\mathbf{r}) = -4\pi \sum_A Z_A \delta(\mathbf{r} - \mathbf{R}_A). \tag{11}$$

Using this with Eq. (3a) leads to

$$\nabla^2 \rho(\mathbf{r}) = -S\nabla f(\mathbf{r}) \cdot \boldsymbol{\varepsilon}(\mathbf{r}) + 4\pi s(\mathbf{r}) \sum_A Z_A \delta(\mathbf{r} - \mathbf{R}_A). \tag{12}$$

The sum in the second term in Eq. (12) vanishes except at the nuclei $\mathbf{r} = \mathbf{R}_A$. On the other hand, by Eq. (3b), $s(\mathbf{r}) \to 0$ when $\mathbf{r} \to \mathbf{R}_A$ at each nucleus under the local approximation. The second term in Eq. (12) may be omitted entirely. We have

$$\nabla^2 \rho(\mathbf{r}) = -S\nabla f(\mathbf{r}) \cdot \boldsymbol{\varepsilon}(\mathbf{r}). \tag{13}$$

By using this in Eq. (10), the required result for the derivative of local softness is obtained,

$$\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v = \frac{1}{S}\frac{\nabla^2 \rho(\mathbf{r})}{|\boldsymbol{\varepsilon}(\mathbf{r})|^2}. \tag{14}$$

Considering the relation $Sf(\mathbf{r}) = s(\mathbf{r})$, we also have

$$\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v = \left[\frac{\partial f(\mathbf{r})}{\partial N}\right]_v S + f(\mathbf{r})\left[\frac{\partial S}{\partial N}\right]_v. \tag{15}$$

By combining this with Eq. (14) and using Eq. (3b), the result for another second derivative of electron density is obtained (the dual descriptor),

$$f^{(2)}(\mathbf{r}) = \left[\frac{\partial f(\mathbf{r})}{\partial N}\right]_v = \frac{1}{S^2|\boldsymbol{\varepsilon}(\mathbf{r})|^2}\left[\nabla^2 \rho(\mathbf{r}) + \nabla\rho(\mathbf{r}) \cdot \boldsymbol{\varepsilon}(\mathbf{r})\left(\frac{\partial S}{\partial N}\right)_v\right]. \tag{16}$$

The above results have all been formulated in the Cartesian coordinates. Considering atomic orbitals, Eqs. (14) and (16) may be anchored to the exact formulas for the electron density function $\rho(\mathbf{r})$ for these orbitals in spherical coordinates.[104] The solutions will be expressed by the radial part of the density function $R(r)$. The spherical symmetry of the electron density in a free atom allows for the transformation of the above into a simplified form: The distance r from the nucleus is the sole variable and $v(r) = Z_A/r$. The global softness S and the atomic number Z_A serve as the parameters for the result. The radial distributions function of the local hyperhardness $[ds(r)/dN]_v$ and dual descriptor $[df(r)/dN]_v$ are

$$\left[\frac{ds(r)}{dN}\right]_v = \frac{r^4}{SZ_A^2}\left[\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR(r)}{dr}\right], \tag{17}$$

$$\left[\frac{df(r)}{dN}\right]_v = \frac{r^4}{S^2Z_A^2}\left\{r^2\frac{d^2R(r)}{dr^2} + \left[\frac{dR(r)}{dr}\right]\left(2r + Z\frac{dS}{dN}\right)\right\}. \tag{18}$$

$[dS/dN]_v$ is obtained by integrating Eq. (17), integration of Eq. (18) is zero by definition, this condition served as a simple test for the results.

VI. THE RESPONSE OF THE STATE FUNCTIONS TO A VARIATION OF THE EXTERNAL POTENTIAL

The available local derivatives: softness $s(\mathbf{r})$ and hypersoftness $[\partial s(\mathbf{r})/\partial N]_v$ allow access to the calculation of the state functions of an electronic system, modified by an external field $v(\mathbf{r})$. On the ground of the canonical ensemble the appropriate functions are energy ΔE_N and the chemical potential $\Delta\mu_N$ calculated at constant number of electrons N; they describe an initial polarization effect due to the external field. Corresponding functions in the grand canonical ensemble are grand potential $\Omega = E - \mu N$ and the electron flow ΔN_μ calculated at constant chemical potential μ, thus describing a potential exchange of electrons with a reservoir, induced by the external field.

Since the changes in global quantities ($\Delta E_N, \Delta\mu_N$ and also $\Delta\Omega_\mu, \Delta N_\mu$) result as a sole consequence of variable $\Delta v(\mathbf{r})$, they all may be calculated by the Taylor expansion to the second order, where only the local external field appears as a variable, the associated global parameter marked with each of the calculated values is kept constant. The local approximation has been applied where necessary to eliminate the nonlocal derivatives $s(\mathbf{r}, \mathbf{r}')$ by Eq. (2) and $\omega(\mathbf{r}, \mathbf{r}')$ via the Berkowitz and Parr relation.[30]

A. The electron flow at $\mu = const.$ ΔN_μ

$$\Delta N_\mu = \int \left[\frac{\delta N}{\delta v(\mathbf{r})}\right]_\mu \Delta v(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\iint \left[\frac{\delta^2 N}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right]_\mu \Delta v(\mathbf{r})\Delta v(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \tag{19a}$$

By using Eq. (5),

$$\Delta N_\mu = -\int s(\mathbf{r})\Delta v(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\iint \left[\frac{\delta s(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_\mu \Delta v(\mathbf{r})\Delta v(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \tag{19b}$$

Since $s(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial\mu]_v$ and $[\delta\rho(\mathbf{r})/\delta v(\mathbf{r}')]_\mu = -s(\mathbf{r}, \mathbf{r}')$, Eq. (19b) is transformed,

$$\Delta N_\mu = -\int s(\mathbf{r})\Delta v(\mathbf{r}) d\mathbf{r} - \frac{1}{2}\iint \left[\frac{\delta s(\mathbf{r}, \mathbf{r}')}{\delta\mu}\right]_v \Delta v(\mathbf{r})\Delta v(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \tag{19c}$$

The local approximation [Eq. (2)] leads to

$$\Delta N_\mu = -\int s(\mathbf{r})\Delta v(\mathbf{r}) d\mathbf{r} - \frac{1}{2}\int \left[\frac{\partial s(\mathbf{r})}{\partial\mu}\right]_v [\Delta v(\mathbf{r})]^2 d\mathbf{r}. \tag{19d}$$

Considering $\left[\frac{\partial s(\mathbf{r})}{\partial\mu}\right]_v = S\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v$, the result is

$$\Delta N_\mu = -\int s(\mathbf{r})\Delta v(\mathbf{r}) d\mathbf{r} - \frac{S}{2}\int \left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v [\Delta v(\mathbf{r})]^2 d\mathbf{r}. \tag{19e}$$

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

B. The chemical potential at $N = const.$ $\Delta\mu_N$

$$\Delta\mu_N = \int \left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right]_N \Delta v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int\int\left[\frac{\delta^2\mu}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right]_N \Delta v(\mathbf{r})\Delta v(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{20a}$$

Using the definitions $f(\mathbf{r}) = [\partial\rho(\mathbf{r})/\partial N]_v$, $\mu = [\partial E/\partial N]_v$ allows for transformation of Eq. (20a),

$$\Delta\mu_N = \int f(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int\int\left[\frac{\partial\omega(\mathbf{r},\mathbf{r}')}{\partial N}\right]_v \Delta v(\mathbf{r})\Delta v(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{20b}$$

With the Berkowitz and Parr relation and the local approximation [Eq. (2)], Eq. (20b) becomes

$$\Delta\mu_N = \eta\int s(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\left\{\begin{array}{l} -\int\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_\mu [\Delta v(\mathbf{r})]^2 d\mathbf{r} \\ +\gamma\left[\int s(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r}\right]^2 \\ +2\eta\int\left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_\mu \Delta v(\mathbf{r})d\mathbf{r}\int s(\mathbf{r}')\Delta v(\mathbf{r}')d\mathbf{r}' \end{array}\right\}. \tag{20c}$$

In Eq. (20c), the replacement of dumb variables was used. Moreover, the hyperhardness parameter $\gamma = [\partial\eta/\partial N]_v$ has been introduced and the Fukui function has been replaced by the local softness $f(\mathbf{r}) = s(\mathbf{r})/S = \eta s(\mathbf{r})$.

C. The energy at $N = const.$ ΔE_N

$$\Delta E_N = \int\left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_N \Delta v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int\int\left[\frac{\delta^2 E}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right]_N \times \Delta v(\mathbf{r})\Delta v(\mathbf{r}')d\mathbf{r}d\mathbf{r}' = \int\rho(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int\int\omega(\mathbf{r},\mathbf{r}')\Delta v(\mathbf{r})\Delta v(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{21a}$$

After using the Berkowitz and Parr relation, the local approximation [Eq. (2)], and replacing the dumb variables, the result reads as follows:

$$\Delta E_N = \int\rho(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} - \frac{1}{2}\left\{\int s(\mathbf{r})[\Delta v(\mathbf{r})]^2 d\mathbf{r} - \eta\left[\int s(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r}\right]^2\right\}. \tag{21b}$$

D. The grand potential at $\mu = const.$ $\Delta\Omega_\mu$

$$\Delta\Omega_\mu = \int\left[\frac{\delta\Omega}{\delta v(\mathbf{r})}\right]_\mu \Delta v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int\int\left[\frac{\delta^2\Omega}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right]_\mu \times \Delta v(\mathbf{r})\Delta v(\mathbf{r}')d\mathbf{r}d\mathbf{r}' = \int\rho(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} - \frac{1}{2}\int\int s(\mathbf{r},\mathbf{r}')\Delta v(\mathbf{r})\Delta v(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{22a}$$

Using the local approximation [Eq. (2)],

$$\Delta\Omega_\mu = \int\rho(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} - \frac{1}{2}\int s(\mathbf{r})[\Delta v(\mathbf{r})]^2 d\mathbf{r}. \tag{22b}$$

The analytical results presented above allow for the calculation of the state functions with only three basic entries: electron density $\rho(\mathbf{r})$, local softness $s(\mathbf{r})$, and the local hypersoftness $[\partial s(\mathbf{r})/\partial N]_v$. Analytical results are available for the hydrogenic orbitals.

VII. RESULTS

A. Local derivatives of electron density for the hydrogenic orbitals

The derivatives in Eqs. (17) and (18) have been calculated analytically for the radial part of the same set of atomic orbitals that has been used in our preceding work:[4] 1*s*, 2*s*. 2*p*, 3*s*, 3*p*, 3*d*; the radial parts of the wave function for an orbital $R(r)$ fully determines the gradient and Laplacian of the electron density.[104] The quality of the results has been controlled by the natural critical tests: $\int f(r)dr = 1$ and $\int f^{(2)}(r)dr = 0$.

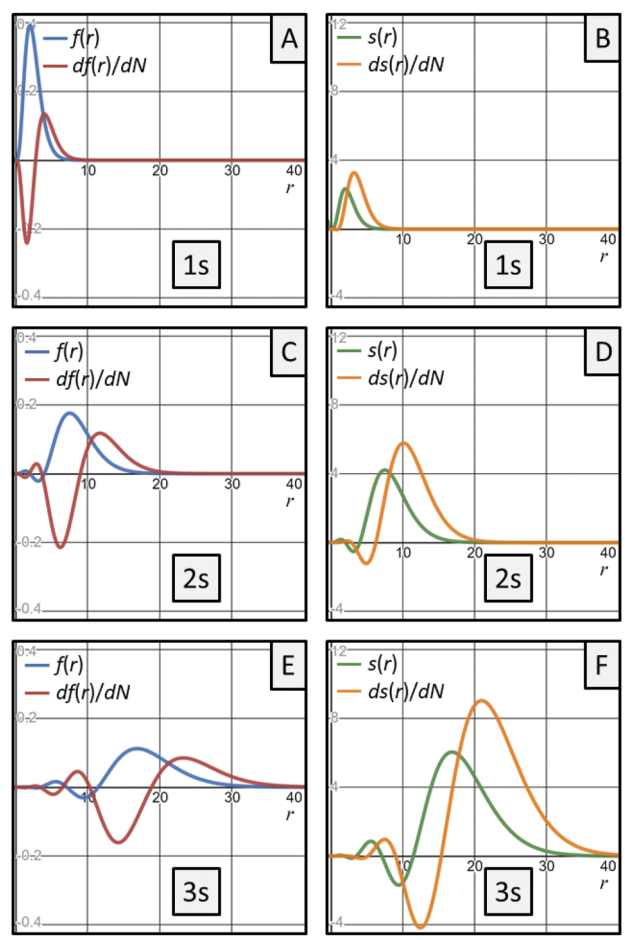

FIG. 1. Radial distribution for the derivatives of *s*-type orbitals: 1*s*: (a) and (b), 2*s*: (c) and (d) and 3*s*: (e) and (f); axes in a.u.

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

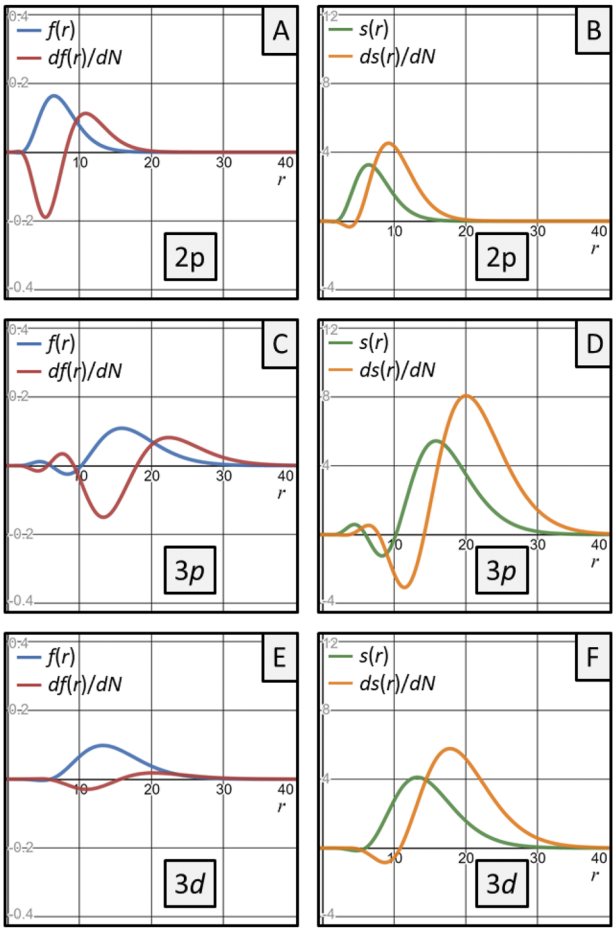

FIG. 2. Radial distribution for the derivatives of the *p*-type and *d*-type orbitals, 2*p*: (a) and (b), 3*p*: (c) and (d) and 3*d*: (e) and (f); axes in a.u.

Graphical presentations of the local hypersoftness $[\partial s(r)/\partial N]_v$ and the dual descriptor $[\partial f(r)/\partial N]_v$ representing the important result of this work are shown in Fig. 1 for *s*-type orbitals and in Fig. 2 for *p*- and *d*-type orbitals. For the sake of completeness, the radial distribution functions for the original first derivatives $s(r)$ and $f(r)$ have also been included in Figs. 1 and 2.[4] Global $[\partial S/\partial N]_v$ derivatives have been collected in Table I along with the formerly calculated global softness S results for the chosen set of orbitals (see Sec. VI C). New analytic results [Eqs. (17) and (18)] for the above hydrogenic orbitals have all been collected in the Appendix (Table IV). Graphical presentation of the Z-dependence of the radial distribution function for the chosen group of orbitals (3*s*, 3*p*, 3*d*) has additionally been presented in the supplementary material (Figs. S1–S4) for the complete set of derivatives discussed hereby.

The analysis presented in this work can be readily implemented in numerical computations of the cDFT derivatives for free atoms. It is also applicable to molecules, by standard techniques of visualization for the Fukui functions. By focusing on the hydrogenic orbitals only, the authors aim to reach an understanding of the meaning of the newly accessible electron density derivatives and especially their relation to the radial electron density distribution itself, available for hydrogenic orbitals by a textbook exercise (cf. the supplementary material, Figs. S5, S6, and S7).

B. Testing the spatial properties of the local energy derivatives

As demonstrated in Sec. III, numerical results for the calculated DFT electron density derivatives allow access to the important local derivatives of the global values characterizing the electronic system: chemical potential μ [Eq. (4)], number of electrons N [Eq. (5)], and hardness/softness η/S [Eqs. (6)–(9)] of the electronic system. In order to assess the potential utility of the calculated complete set of electron density derivatives, the radial distribution of each derivative has been confronted with the radial distribution of the density itself. The numerical data for the characteristic points of each radial density function (maxima, minima, and zero point) have been collected in Tables S1–S3 in the supplementary material. Concise information has been extracted from this collection in Fig. 3. For each orbital, only the outermost maximum of the function (electron density, first and second derivatives over N) has been selected and their positions and heights have been marked in the diagrams, separately presented for the electron density and two pairs of the density derivatives. Expressions linking each derivative to the specific global quantity have also been recalled with these diagrams. Notable differences between the characteristics of the derivatives have been unveiled in the diagrams, they will be discussed in Sec. VIII.

C. Global hypersoftness and hyperhardness

Global softness $S = (\partial N/\partial \mu)_v$, the inverse of hardness $\eta = (\partial \mu/\partial N)_v = (\partial^2 E/\partial N^2)_v$, has already been demonstrated as the natural quantity to describe the character of orbitals and atoms by the present method.[4] Its derivative $(dS/dN)_v$ is related to the hyperhardness defined in CDFT as $\gamma = (\partial \eta/\partial N)_v = (\partial^3 E/\partial N^3)_v$.[58,60] However, there is no unique definition for the

TABLE I. Global softness S (Ref. 4), global hypersoftness $(dS/dN)_v$ [Eq. (24)], and global hyperhardness γ [Eq. (23)] calculated for hydrogenic orbitals.

Orbital	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*
S (a.u.)	$\frac{6}{Z^2}$	$\frac{24}{Z^2}$	$\frac{20}{Z^2}$	$\frac{54}{Z^2}$	$\frac{50}{Z^2}$	$\frac{42}{Z^2}$
$(dS/dN)_v$ (a.u.)	$\frac{10}{Z^2}$	$\frac{35}{Z^2}$	$\frac{30}{Z^2}$	$\frac{230}{3Z^2}$	$\frac{72}{Z^2}$	$\frac{60}{Z^2}$
$\gamma = (d\eta/dN)_v$ (a.u.)	$-\frac{5}{18}Z^2$	$-\frac{35}{576}Z^2$	$-\frac{3}{40}Z^2$	$-\frac{115}{4374}Z^2$	$-\frac{18}{625}Z^2$	$-\frac{5}{147}Z^2$

Published under an exclusive license by AIP Publishing

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

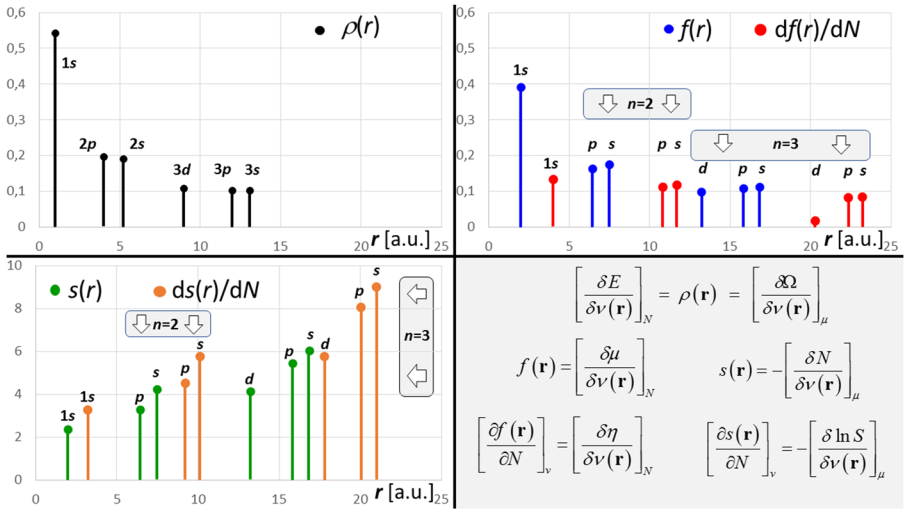

FIG. 3. Positions and heights of the outermost maxima (in a.u.) for the radial distributions of the electron density derivatives for the canonical hydrogenic orbitals (Z = 1): Fukui function $f(r)$, dual descriptor $[df(r)/dN]_v$, local softness $s(r)$, and local hypersoftness $[ds(r)/dN]_v$. For the sake of comparison, analogous data for the density function have been added (upper row left). The derivatives of energy and other global quantities natural in the closed system {canonical ensemble: $E[N, v(r)]$, μ, η} and the open system {grand canonical ensemble: $\Omega[\mu, v(r)], N, S$} have also been recalled along with rigorous definitions of all derivatives (lower row right).

corresponding hypersoftness.[60] Since $\eta = 1/S$, the hyperhardness parameter γ may be directly linked to the global hypersoftness understood as $(dS/dN)_v$,

$$\gamma = \left[\frac{\partial \eta}{\partial N}\right]_v = -\frac{1}{S^2}\left[\frac{\partial S}{\partial N}\right]_v. \tag{23}$$

The global hypersoftness is readily calculated by integration of its local counterpart,

$$\left[\frac{\partial S}{\partial N}\right]_v = \int \left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_v d\mathbf{r}. \tag{24}$$

Once the way to calculation of S and $(\partial S/\partial N)_v$ has been opened, the hyperhardness parameter γ also becomes available from the unique data of the electron density [Eq. (23)]. Calculated results have been collected in Table I.

For the purpose of this work, only $(\partial s(\mathbf{r})/\partial N)_v$ has been explored as the local hypersoftness and the global hypersoftness by its integration [Eq. (24)]. This provides the most natural relation with the already defined hyperhardness parameter [Eq. (23)]. However, it is possible to explore another derivative natural for the open system: $(\partial S/\partial \mu)_v = S(\partial S/\partial N)_v$ as an alternative choice for the definition of global hypersoftness as has been proposed by the group of authors in their systematic work.[87,105]

D. Calculation of the state functions variable with $\Delta v(\mathbf{r})$

Testing the above results for hydrogenic orbitals in atoms is most natural via the concept of alchemical derivatives over the atomic number$(d^n E/dZ^n)_N$.[106,107] The idea has been earlier demonstrated by March for atomic ions with $\Delta v(\mathbf{r}) = \Delta Z/r$ proving for the energy derivative in the first order,[108,109]

$$\left(\frac{\partial E}{\partial Z}\right)_N = -\int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} \quad \text{hence} \quad \Delta E_N = -\Delta Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r}. \tag{25}$$

When this is consequently applied to calculation of the integrals required in the results exposed in Eqs. (19e), (20c), (21b), and (22b), the collection of integrals presented in Table II is obtained.

All integrals in Table II have been found to be functions of the ratio $\alpha = \Delta Z/Z$, hence the α factor has been introduced throughout the formalism, for the sake of clarity. Application of these data to the

TABLE II. Integrals calculated from the radial distribution functions for the local softness $s(r)$, its derivative $ds(r)/dN$, and the electron density $\rho(r)$. S is the global softness of an orbital, Z is the atomic number, n stands for the principal quantum number of an orbital.

Equivalence of the alchemical integrals	Calculated integrals for hydrogenic orbitals $\alpha = \Delta Z/Z$, n – principal quantum number
$\int s(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} = -\Delta Z \int \frac{s(r)}{r} dr$	-3α
$\int s(\mathbf{r})[\Delta v(\mathbf{r})]^2 d\mathbf{r} = -[\Delta Z]^2 \int \frac{s(r)}{r^2} dr$	$-2\frac{Z^2}{n^2}\alpha^2$
$\int \left[\frac{ds(\mathbf{r})}{dN}\right]_\mu \Delta v(\mathbf{r})d\mathbf{r} = -\Delta Z \int \left[\frac{ds(r)}{dN}\right]_\mu \frac{1}{r} dr$	-3α
$\int \left[\frac{\partial s(\mathbf{r})}{\partial N}\right]_\mu [\Delta v(\mathbf{r})]^2 d\mathbf{r} = -[\Delta Z]^2 \int \left[\frac{ds(r)}{dN}\right]_\mu \frac{1}{r^2} dr$	$-\frac{6}{S}\alpha^2$
$\int \rho(\mathbf{r})\Delta v(\mathbf{r})d\mathbf{r} = -\Delta Z \int \frac{\rho(r)}{r} dr$	$-\frac{Z^2}{n^2}\alpha$

Published under an exclusive license by AIP Publishing

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

TABLE III. Calculated changes in state functions induced by the variation of the external potential as a result of change in Z by ΔZ for hydrogenic orbitals. Substitution $\alpha = \Delta Z/Z$ has been used. S stands for the global softness, γ is the hyperhardness of an orbital (cf. Table I), and n is the principal quantum number of an orbital. E_n^o stands for the basic energy term for an orbital of the quantum number n.

State functions calculated by the alchemical method for $\alpha = \Delta Z/Z$	Slope of the ΔN_μ, $\Delta\Omega_\mu$, ΔE_μ, $\Delta\mu_N$, ΔE_N vs α at $\alpha = 0$
$\Delta N_\mu = 3\alpha(1+\alpha)$	3
$\Delta\Omega_\mu = \frac{Z^2}{n^2}\cdot\alpha(\alpha-1)$	$-\frac{Z^2}{n^2} = -2E_n^o$
$\Delta E_\mu = \frac{Z^2}{n^2}\cdot\frac{\alpha}{4}(\alpha-7)$	$-\frac{7}{4}\frac{Z^2}{n^2} = -\frac{7}{2}E_n^o$
$\Delta\mu_N = -\frac{3\alpha}{S}\left[1+\alpha\left(\frac{3}{2}\gamma S+2\right)\right]$	$-\frac{3}{S} = -3\eta$
$\Delta E_N = \frac{Z^2}{n^2}\cdot\alpha\left[\alpha\left(1-\frac{9n^2}{2SZ^2}\right)-1\right]$	$-\frac{Z^2}{n^2} = -2E_n^o$

working equations in Sec. VI leads the results for the state functions presented in Table III.

Given the input data in Table I (S, γ for orbitals), it should be noted that the γS term and SZ^2 term are numbers characteristic for an orbital but not dependent on the variable factors (Z, ΔZ, or α). The energy measures in Table III are explicit functions of the Z^2/n^2 term in the same manner as are the electron energy terms in the Bohr atom. The following substitution has been introduced for the ground state energy of the singly occupied orbital with the quantum number n: $E_n^o = Ry\frac{Z^2}{n^2} = \frac{Z^2}{2n^2}[a\cdot u.]$, where $Ry = 1/2$ a.u. is the Rydberg constant.

An additional, supplementary energy parameter ΔE_μ, has also been included in Table III. It has been obtained by exploring the relation between $\Delta\Omega_\mu$ and ΔN_μ at constant chemical potential,

$$\Delta\Omega_\mu = \Delta E_\mu - \mu\Delta N_\mu. \tag{26}$$

The chemical potential for any orbital may be approximated by $\mu = -\frac{1}{2}I = \frac{1}{2}E_n^o = -Z^2/4n^2$, leading to the general function for the relative energy of orbitals at constant chemical potential $\Delta E_\mu(\alpha)$ included in Table III.

VIII. DISCUSSION

The condensed results for the electron density and its derivatives collected in Fig. 3 allow for a rational quantification of the effects of variable external electric field on the electron density described by any chosen hydrogenic orbital. These effects are clearly divided into two separate systems: closed system ($N = const.$) described by $f(r)$, $[df(r)/dN]_v$ and open system ($\mu = const.$) characterized by $s(r)$ and $[ds(r)/dN]_v$. The closed system derivatives describe the effect of polarization (no electron exchange); the open system derivatives describe the true chemical effect by some electron exchange between an object (here merely an orbital) and a neighbor, possibly responsible for the disturbance in question. Exploration of these derivatives is built on a tacit assumption: that the whole process may be divided into little steps, all of which represent a system in an electronic equilibrium, hence an equalized chemical potential μ. That corresponds to a typical analysis of a reaction path.

The ΔN_μ value calculated by the alchemical approach (Table III) contains a hint of the profound physical meaning: To keep constant chemical potential while increasing the electric field, an increase of N by exchanging electrons with some "reservoir" is required $\Delta N_\mu(\alpha)$ that leads to the energy change $\Delta E_\mu(\alpha)$. Interestingly, the tendency to exchange electrons measured in the limit of infinitely small disturbance $\Delta N_\mu(\alpha\to 0)$ is uniform for all orbitals. However, the associated energy change, $\Delta E_\mu(\alpha\to 0)$, remarkably decreases with increase in the principal quantum number of an orbital $\left(|\Delta E_\mu| \propto Z^2/n^2\right)$. The $\Delta E_\mu(\alpha)$ and $\Delta N_\mu(\alpha)$ functions may then be explored for modeling the response of atoms to the external electric field with the electron density derivatives $s(r)$ and $[ds(r)/dN]_v$ now available by the local approximation. The specific conditions of the exchange process applied in the above analysis, constant chemical potential, is crucial from the chemical point of view, when the response of an atom bonded to some molecular entity is considered.

Individual derivatives $s(r)$ and $[ds(r)/dN]_v$ fully describe the effect of change in the state functions ($\Delta\mu$, ΔN) and the inherent property of the system (ΔS or $\Delta\eta$). The range of observation provided by each derivative is different, an instructive comparison has been illustrated in Fig. 3 by the position and height of the last, outermost maximum for the corresponding derivatives for each orbital (cf. Figs 1 and 2). This has been intentionally compared to the range and height of the electron density function itself for each type of orbital; its range increases gradually, and the height of the outermost maximum systematically decreases with increase in the principal quantum number n (cf. Fig. S5 in the supplementary material). Within the group of orbitals chosen for this study, the last maximum on the radial distribution of the density appears at distances well below 15 a.u.; however, the density function does not fall to zero until at distances twice as large.

The local softness and hypersoftness functions, $s(r)$ and $[ds(r)/dN]_v$, are dominated by the outermost maximum peak for all orbitals, as demonstrated in diagrams (Figs. 1 and 2). Positions of the last maximum on the radial distribution for these density derivatives typically falls beyond the last density peak (Fig. 3). This observation is vital: The response effect described by the derivatives (ΔN) comes largely from the outer part of the electron density around an atomic center. Additional information available in the supplementary material completes the panorama of derivatives for chosen orbitals: They have been calculated analytically also for $Z = 2$ and $Z = 3$ to confirm the effect of change in the density function for orbitals and of its derivatives with increasing charge at a nucleus.

Additional information available directly on Fig. 3 is the notable difference between derivatives in both systems: values of

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

$f(r)$ and $[df(r)/dN]_v$ span a range over an order of magnitude smaller than values of $s(r)$ and $[ds(r)/dN]_v$. Moreover, the last outermost maxima for functions $s(r)$ and $[ds(r)/dN]_v$ systematically increase with the principal quantum number n, indicating realistically the dominant role of the outer range of the density for a chemical change. This is not the case for $f(r)$ and $[df(r)/dN]_v$ derivatives, which show only weak dependence on n, except the very inner part of the orbital system (1s).

The second derivatives characterize an object rather than a process: the change introduced to the global hardness η [Eq. (9)] or to the global softness S [Eq. (6)]. Since both quantities are not independent, the choice of equation for characterization of the effect is dictated by the nature of the elementary process chosen as appropriate by an observer. As demonstrated in Sec. IV, Eqs. (6), (8) and (9) are redundant, providing similar information on ΔS once the global softness itself (S) has been determined for an unperturbed system. As a consequence, the local hypersoftness $[ds(r)/dN]_v$ appears to be the only second electron density derivative sufficient to characterize an evolution of a reacting species; neither $[df(r)/dN]_v$ nor $[ds(r)/d\mu]_v$ derivatives are needed for practical calculation of the response of an object to the variation of the external potential disturbing an electronic equilibrium.

The hyperhardness γ has been investigated in early efforts for the expansion of the $E(N)$ function beyond the second order.[58,62] The available data for atoms indicate that hyperhardness is negative and small as compared to other global quantities: hardness (η) and electronegativity ($-\mu$). The results for orbital hyperhardness are all negative and rather small, as expected. The discovered uniform relation of γ to the nuclear charge is intriguing; it comes from the uniform dependence on Z^2 both by S and $(dS/dN)_v$ (Table I). The relation $S(Z^2)$ for atoms has been confirmed in our study of global softness by confronting with available hardness data of atoms.[4] Relation between the hyperhardness data and the nuclear charge, shown in Table I, could only be roughly estimated by the method used at the time of its early observations.[58] The orbital hyperhardness data in Table I call for extending this study to atoms.

IX. CONCLUSION

The analytical calculation scheme first tested for the Fukui function and the local softness has been proved successful also for the second electron density derivatives over N. The results present a complete picture of the electron density derivatives allowing, at least formally, for a calculation of the change in state functions induced with a disturbance by a variable external electrostatic potential.

Although the pilot results for the hydrogenic orbitals, as described by this work, cannot be directly transferred to real systems, the results do provide valuable hints to the vital characteristics of the density derivatives and also to the extension of the method to molecules. For symmetry reasons, the basic relations [Eqs. (3a) and (14)] may rather safely be transferred to free atoms, if $\nabla\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$, fundamental for the method, are calculated with sufficient accuracy. The radial functions $s(r)$ and $[ds(r)/dN]_v$ for atoms, when considered jointly with the spatial density shapes, provide qualitative hints for the sensitivity of atoms toward an electron exchange, coherent with the familiar pictures of the orbitals. The characteristics of each type of derivative as demonstrated by Fig. 3 may also be taken as a rough guide for their use: The commonly explored $f(r)$ and $f^{(2)}(r)$ functions appear to be less sensitive a guide than the local softness and hypersoftness. Quite technically, the basic relations [Eqs. (3a) and (14)] also hold for any molecular system and may be solved by standard method except the unique point where $\boldsymbol{\varepsilon}(r) = 0$. Calculation of the local softness and hypersoftness in molecules requires a solution of the topological dilemma, as the $\nabla\rho(\mathbf{r})$ and $\boldsymbol{\varepsilon}(\mathbf{r})$ vectors may not be parallel and the local softness must be considered a tensor. Nevertheless, the additive character of both canonical equations of the method [since $\boldsymbol{\varepsilon}(\mathbf{r}) = \sum_A \boldsymbol{\varepsilon}_A(\mathbf{r})$] opens the door for the calculation of atomic indices with no need for a spatial division of the density between atoms. The Kohn–Sham method appears to be preferential for these considerations, as the electron density function provides a firm ground for application of the presented formalism.

Exploration of the gradient theorem has opened a new field for assessing the role of the linear response function $\omega(\mathbf{r},\mathbf{r}')$, widely considered as the cornerstone for chemical applications in cDFT. With both the gradient of the density and the electric field available independently, Eq. (1) may well be used for testing the exactness of any working approximation to $\omega(\mathbf{r},\mathbf{r}')$. On the other hand, since both basic kernels $\omega(\mathbf{r},\mathbf{r}')$ and $s(\mathbf{r},\mathbf{r}')$ can be used alternatively in Eq. (1), and the local approximation can be applied to the softness kernel, the linear response function has been eliminated from calculations of the response functions (cf. Sec VI); the results involve the local softness and hypersoftness $s(r)$ and $[ds(r)/dN]_v$, exclusively.

Practical application of the local approximation to the softness kernel only leads to interesting consequences: The softness kernel seems to disappear for the formalism. The local softness may be attributed to atoms, e.g., by the method proposed in the work of Fias *et al.*;[5] however, no interatomic terms can be defined. This is justified by the nearsightedness of this derivative (at constant μ) and reflects the specific property of that kernel. The physics of electron density is specifically described by the linear density function, leading to the alternative picture where interatomic relation may still be exposed. This may be illustrated by Eq. (1) directly combined with the local approximation [Eq. (2)],

$$\nabla\rho(\mathbf{r}) = \int \omega(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}(\mathbf{r}')d\mathbf{r}' = -s(\mathbf{r})\boldsymbol{\varepsilon}(\mathbf{r}). \tag{27}$$

The atom condensed approximations for the linear response function can still be explored, if necessary; however, a more specific and exact method has recently been available.

The role of $\omega(\mathbf{r},\mathbf{r}')$ has been most naturally exposed on the new platform beyond the local approximation as demonstrated by our former works. It is the inherent component of the elements of the density functional connectivity matrix [Eq. (A9)].[3,90] The elements of this matrix provide an adequate description of every contact between well-defined atoms, with no need to artificially define borderlines between them. Moreover, the exact C_{AB} elements are readily obtained from the Hessian matrix, with no need to specify the $\omega(\mathbf{r},\mathbf{r}')$ function itself. Moreover, tracing their evolution along a reaction path provides the reaction fragility spectra, a handy tool for computational studies of transformation along an IRC.[92]

The alchemical approach has been applied; it is a very instructive method for systematic analysis of chemical objects, well in line

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

with its most recent applications.[110] An interesting result of the analysis was the response of the electronic cloud of an atom to ΔZ being limited to the relative change in the external field measured by the ratio $\Delta Z/Z$, exclusively. This observation provides a hint as to the role of a nucleus in deformations of the electronic density by interactions with an external field. Politzer and Murray have recently presented a refreshing analysis of the effects of the electric field of nuclei on electron density (generally underestimated, according to these experienced authors).[111]

The responses of the state functions, to the disturbance $\Delta v(\boldsymbol{r}) \propto \Delta Z/r$, are all scaled down by the charge of the nucleus, with the $\Delta Z/Z$ factor playing a unique role, as demonstrated by the results shown in Table III. Calculated responses of the state functions for an electronic system (ΔE, ΔN, $\Delta\mu$) provide indications reaching beyond the narrow orbital picture. Both ΔN_μ and $\Delta\mu_N$ in the limit $(\frac{\Delta Z}{Z}) \to 0$ reach unique values. The limiting value $\Delta N_\mu = 3$ a.u. appears to represent the general property of atoms, while the result $\Delta\mu_N = -3\eta$, clearly dependent on the global hardness of an atom, is well in accord with the meaning of this quantity and the DFT fundamentals.

It is also possible to comment on the local hardness, a quantity once intuitively considered for a much-needed measure of the local tendency to exchange electrons. The group of CDFT experts suggested a defiant, far-reaching conclusion: "The discussion of the local hardness should either converge toward a widely accepted and broadly useful definition or else this quantity should be discarded.[1]" A publication by other authors has tried to save the "raison d'être of a local hardness function,[112]" even though the very authors admit: "the ambiguity that underlines attempts at a formal definition of a local hardness."

The results of this work hint at a possible resolution: The local softness providing the subtle characteristics of the electron density may replace the idea of the local hardness as a local measure of site sensitivity, bypassing the ambiguities concerning the local hardness.[103] The set of two derivatives, local softness and local hypersoftness calculated at the level of local approximation as presented in this work, has been demonstrated to provide a complete and formally sufficient measure for the site reactivity.

This contribution has been limited to classic hydrogenic orbitals to test the potential utility of this method with the available analytic apparatus. As confirmed in recent applications, focusing on orbitals allows for a general treatment of phenomena in accord with the documented properties of density functions[113] and beyond specific features of interacting objects.[114–116] Results of this present work call for extending the proposed method to calculation of the hypersoftness for atoms, as derivative has been proved hereby to be non-negligible in characterization of reactive properties (Fig. 3). The newly accessible derivatives may also contribute to understanding the wider effects of external field on a chemical reaction, since also mechanistic and confinement effects focused upon in recent studies[2] occur via the electric field interaction on the density function.

SUPPLEMENTARY MATERIAL

The supplementary material provided with this work contains detailed results for the (i) radial distribution functions of the density derivatives in 3s, 3p, and 3d orbitals with the nuclear charges $Z = 1$, $Z = 2$ and $Z = 3$; (ii) radial distribution functions for the electron density in 1s, 2s, 2p, 3s, 3p, and 3d orbitals with nuclear charges $Z = 1$, $Z = 2$, and $Z = 3$; and (iii) a collection of the extreme points in the radial density functions $\rho(r)$ and its derivatives under consideration in this work $f(r)$, $\frac{df(r)}{dN}$, $s(r)$, and $\frac{ds(r)}{dN}$ for orbitals with nuclear charges $Z = 1$, $Z = 2$, and $Z = 3$.

ACKNOWLEDGMENTS

J.Z. acknowledges his friendly cooperation with Mr. Mateusz Jędrzejewski. The use of resources of Wrocław Center for Networking and Supercomputing in these projects is acknowledged (WCSS Grant Nos. 249 and GW 036). P.O. was supported by the Wrocław University of Environmental and Life Science (Poland) under the Project POMOST, Grant No. N110/0004/21.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Piotr Ordon: Conceptualization (lead); Formal analysis (lead); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jarosław Zaklika**: Data curation (equal); Software (equal); Visualization (equal). **Jerzy Hładyszowski**: Data curation (equal); Investigation (equal); Validation (equal); Visualization (equal). **Ludwik Komorowski**: Conceptualization (lead); Data curation (equal); Formal analysis (lead); Investigation (equal); Methodology (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

APPENDIX: PROOF OF THE GRADIENT THEOREM [EQ. (10)]

For a system of n atoms, the divergences of Hellmann–Feynman (H–F) forces in a molecule form the $(n \times n)$ DF connectivity matrix.[90] Considering the properties of this matrix leads directly to the gradient theorem [Eq. (1)].

The elements of this symmetric matrix represent the electronic energy only and are exactly[91,92]

$$C_{AA} = \nabla_A \cdot \mathbf{F}_A = \int \boldsymbol{\varepsilon}_A(\mathbf{r}) \cdot [\nabla\rho(\mathbf{r}) + \nabla_A\rho(\mathbf{r})]d\mathbf{r}, \tag{A1}$$

$$C_{A\neq B} = \nabla_{B\neq A} \cdot \mathbf{F}_A = \int \boldsymbol{\varepsilon}_A(\mathbf{r}) \cdot [\nabla_{B\neq A}\rho(\mathbf{r})]d\mathbf{r}. \tag{A2}$$

The sum rule has been proved: $C_{AA} = -\sum_{B\neq A} C_{BA}$. By combining this with Eqs. (A1) and (A2),[3,4]

Published under an exclusive license by AIP Publishing

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

TABLE IV. Radial distribution of *df(r)/dN* and *ds(r)/dN* functions for the hydrogenic orbitals.

1*s*	$\frac{ds(r)}{dN} = \frac{8}{3}Z^4r^5(rZ-1)\exp(-2Zr)$ $\frac{df(r)}{dN} = \frac{2Z^5r^4}{9}\left[Z^2r^2 - Zr - 5\right]\exp(-2Zr)$
2*s*	$\frac{ds(r)}{dN} = \frac{1}{3\cdot 2^6}Z^4r^5\left[Z^3r^3 - 10Z^2r^2 + 26Zr - 16\right]\exp(-Zr)$ $\frac{df(r)}{dN} = \frac{Z^5r^4}{9\cdot 2^9}\left[Z^4r^4 - 10Z^3r^3 - 9Z^2r^2 + 194Zr - 280\right]\exp(-Zr)$
3*s*	$\frac{ds(r)}{dN} = \frac{8Z^4r^5}{3^{14}}(Zx-9)(2Zx(Zx-18)+81)(2Zx(Zx-6)+9)\exp(-\frac{2}{3}Zr)$ $\frac{df(r)}{dN} = \frac{4Z^5r^4}{3^{17}}\left[\begin{array}{c} Zr(Zx-9)(2Zx(Zx-18)+81)(2Zx(Zx-6)+9) \\ -345(27-18Zr+2Z^2r^2)(27-10Zr+\frac{2}{3}Z^2r^2) \end{array}\right]\exp(-\frac{2}{3}Zr)$
2*p*	$\frac{ds(r)}{dN} = \frac{Z^5r^6}{480}\exp(-Zr)\left[Z^2r^2 - 6Zr + 6\right]$ $\frac{df(r)}{dN} = \frac{Z^6r^5}{75\cdot 2^7}\left[Z^3r^3 - 6Z^2r^2 - 24Zr + 60)\right]\exp(-Zr)$
3*p*	$\frac{ds(r)}{dN} = \frac{16Z^5r^6}{25\cdot 3^{11}}\exp(-\frac{2}{3}Zr)\left[Z^4r^4 - 27Z^3r^3 + 225Z^2r^2 - 648Zr + 486\right]$ $\frac{df(r)}{dN} = \frac{8Z^6r^5}{5^4\cdot 3^{11}}\left[\begin{array}{c} Z^5r^5 - 27Z^4r^4 + 117Z^3r^3 + 1296Z^2r^2 - \\ -9234Zr + 11\,664 \end{array}\right]\exp(-\frac{2}{3}Zr)$
3*d*	$\frac{ds(r)}{dN} = \frac{16Z^7r^8}{35\cdot 3^{12}}\exp(-\frac{2}{3}Zr)\left[Z^2r^2 - 15Zr + 45\right]$ $\frac{df(r)}{dN} = \frac{8Z^8r^7}{945\cdot 3^{13}}\left[Z^3r^3 - 15Z^2r^2 - 45Zr + 540)\right]\exp(-\frac{2}{3}Zr)$

$$\int \boldsymbol{\varepsilon}_A(\mathbf{r})\cdot\left[\nabla\rho(\mathbf{r}) + \textstyle\sum_B \nabla_B\rho(\mathbf{r})\right]d\mathbf{r} = 0. \tag{A3}$$

$\nabla\rho(\mathbf{r})$ must be unique and Eq. (A3) holds separately for every atom (B) in a system. Hence,

$$\nabla\rho(\mathbf{r}) = -\textstyle\sum_B \nabla_B\rho(\mathbf{r}). \tag{A4}$$

The electric field from all nuclei is $\boldsymbol{\varepsilon}(\mathbf{r}) = \sum_B \boldsymbol{\varepsilon}_B(\mathbf{r})$. In the canonical ensemble,

$$[\nabla_B\rho(\mathbf{r})]_N = -\int \omega(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}_B(\mathbf{r}')d\mathbf{r}'. \tag{A5}$$

Hence,

$$\nabla\rho(\mathbf{r}) = \int \omega(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}(\mathbf{r}')d\mathbf{r}'. \tag{A6}$$

In the grand canonical ensemble,

$$[\nabla_B\rho(\mathbf{r})]_\mu = \int s(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}_B(\mathbf{r}')d\mathbf{r}'. \tag{A7}$$

The alternative for (A6) reads as follows:

$$\nabla\rho(\mathbf{r}) = -\int s(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}_B(\mathbf{r}')d\mathbf{r}'. \tag{A8}$$

The results shown in Eqs. (A6) and (A8) are identical; this is proved by using the Berkowitz and Parr relation and considering the sum of Hellmann–Feynman forces acting on the nuclei,[3]

$$\textstyle\sum_B \mathbf{F}_B = 0.$$

The DF connectivity matrix also provides insight into the specific role of the linear response function in describing the interatomic interactions by an original formula,

$$C_{AB} = [\nabla_A\cdot\mathbf{F}_B]_N = -\int\int \omega(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}_A(\mathbf{r}')\cdot\boldsymbol{\varepsilon}_B(\mathbf{r})d\mathbf{r}'d\mathbf{r}. \tag{A9}$$

REFERENCES

[1] P. Geerlings, E. Chamorro, P. K. Chattaraj, F. De Proft, J. L. Gázquez, S. Liu, C. Morell, A. Toro-Labbé, A. Vela, and P. Ayers, "Conceptual density functional theory: Status, prospects, issues," Theor. Chem. Acc. **139**, 36 (2020).

[2] P. Geerlings and F. De Proft, "External fields in conceptual density functional theory," J. Comput. Chem. **44**, 442 (2022).

[3] P. Ordon and L. Komorowski, "Monitoring evolution of the electron density in atoms and bonds on a reaction path by the reaction fragility method," in *Chemical reactivity, Theories and Principles*, edited by S. Kaya, L. von Szentpaly, G. Serdaroglu, and L. Guo (Elsevier, 2023), Vol. **1**, ISBN: 978-032390257X (in press).

[4] J. Zaklika, J. Hładyszowski, P. Ordon, and L. Komorowski, "From the electron density gradient to the quantitative reactivity indicators: Local softness and the Fukui function," ACS Omega **7**, 7745–7758 (2022).

[5] S. Fias, F. Heidar-Zadeh, P. Geerlings, and P. W. Ayers, "Chemical transferability of functional groups follows from the nearsightedness of electronic matter," Proc. Natl. Acad. Sci. U. S. A. **114**, 11633–11638 (2017).

[6] A. Vela and J. L. Gazquez, "A relationship between the static dipole polarizability, the global softness, and the Fukui function," J. Am. Chem. Soc. **112**, 1490–1492 (1990).

[7] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," Phys. Rev. **136**, 8864–8871 (1964).

[8] P. W. Ayers, S. Fias, and F. Heidar-Zadeh, "The axiomatic approach to chemical concepts," Comput. Theor. Chem. **1142**, 83–87 (2018).

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

[9]R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
[10]P. Geerlings, F. De Proft, and W. Langenaeker, "Conceptual density functional theory," Chem. Rev. **103**, 1793–1874 (2003).
[11]H. Chermette, "Chemical reactivity indexes in density functional theory," J. Comput. Chem. **20**, 129–154 (1999).
[12]L. Pauling, "The nature of the chemical bond. IV. The energy of single bonds and the relative electronegativity of atoms," J. Am. Chem. Soc. **54**, 3570–3582 (1932).
[13]R. S. Mulliken, "New electroaffinity scale; together with data on valence states and on valence ionization potentials and electron affinities," J. Chem. Phys. **2**, 782–793 (1934).
[14]R. P. Iczkowski and J. L. Margrave, "Electronegativity," J. Am. Chem. Soc. **83**, 3547–3551 (1961).
[15]J. Hinze, M. A. Whitehead, and H. H. Jaffé, "Electronegativity. II. Bond and orbital electronegativities," J. Am. Chem. Soc. **85**, 148–154 (1962).
[16]R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, "Electronegativity: The density functional viewpoint," J. Chem. Phys. **68**, 3801–3808 (1978).
[17]R. G. Pearson, "Hard and soft acids and bases," J. Am. Chem. Soc. **85**, 3533–3539 (1963).
[18]P. K. Chattaraj and R. G. Parr, "Density functional theory of chemical hardness," in *Chemical Hardness*, *Structure Bonding*, edited by K. D. Sen (Springer-Verlag, 1993), Vol. 80, pp. 11–25.
[19]R. G. Parr and R. G. Pearson, "Absolute hardness: Companion parameter to absolute electronegativity," J. Am. Chem. Soc. **105**, 7512–7516 (1983).
[20]R. G. Pearson, "Absolute electronegativity, and hardness: Application to inorganic chemistry," Inorg. Chem. **27**, 734–740 (1988).
[21]R. G. Pearson, *Chemical Hardness. Applications from Molecules to Solids* (Wiley VCH, 1997).
[22]R. G. Parr, L. v. Szentpály, and S. Liu, "Electrophilicity index," J. Am. Chem. Soc. **121**, 1922–1924 (1999).
[23]P. K. Chattaraj, U. Sarkar, and D. R. Roy, "Electrophilicity index," Chem. Rev. **106**, 2065–2091 (2006).
[24]S. Liu, T. Li, and P. W. Ayers, "Potentialphilicity and potentialphobicity: Reactivity indicators for external potential changes from density functional theory," J. Chem. Phys. **131**, 114106 (2009).
[25]D. Chakraborty and P. K. Chattaraj, "Conceptual density functional theory based electronic structure principles," Chem. Sci. **12**, 6264–6279 (2021).
[26]R. G. Parr and W. Yang, "Density functional approach to the Frontier-electron theory of chemical reactivity," J. Am. Chem. Soc. **106**, 4049–4050 (1984).
[27]P. W. Ayers, W. T. Yang, and L. J. Bartolotti, "Fukui function," in *Chemical Reactivity Theory: A Density Functional View*, edited by P. K. Chattaraj (CRC Press, Boca Raton, 2009), pp. 255–267.
[28]K. Fukui, T. Yonezawa, and H. Shingu, "A molecular orbital theory of reactivity in aromatic hydrocarbons," J. Chem. Phys. **20**, 722–725 (1952).
[29]K. Fukui, "Role of Frontier orbitals in chemical reactions," Science **218**(4574), 747–754 (1982).
[30]M. Berkowitz and R. G. Parr, "Molecular hardness and softness, local hardness and softness, hardness and softness kernels, and relations among these quantities," J. Chem. Phys. **88**, 2554–2557 (1988).
[31]C. Cárdenas, E. Echegaray, D. Chakraborty, J. S. M. Anderson, and P. W. Ayers, "Relationships between the third-order reactivity indicators in chemical density-functional theory," J. Chem. Phys. **130**, 244105 (2009).
[32]R. T. Sanderson, *Chemical Periodicity* (Reinhold Publishing Corp., New York, 1960).
[33]R. G. Pearson, "Absolute electronegativity and absolute hardness of Lewis acids and bases," J. Am. Chem. Soc. **107**, 6801–6806 (1985).
[34]R. F. Nalewajski, "Electrostatic effects in interactions between hard (soft) acids and bases," J. Am. Chem. Soc. **106**, 944–945 (1984).
[35]G. Klopman, "Semiempirical treatment of molecular structures. II. Molecular terms and application to diatomic molecules," J. Am. Chem. Soc. **86**, 4550–4555 (1964).
[36]L. Komorowski, "Chemical hardness and L. Pauling's scale of electronegativity," Z. Naturforsch. **42**, 767–773 (1987).
[37]L. Komorowski, "Hardness indices for free and bonded atoms," in *Structure and Bonding*, edited by K. D. Sen (Springer-Verlag, 1993), Vol. **80**, pp. 46–69.
[38]R. F. Nalewajski, "A coupling between the equilibrium state variables of open molecular and reactive systems," Phys. Chem. Chem. Phys. **1**, 1037–1049 (1999).
[39]A. C. Chandra and M. T. Nguyen, "Fukui function and local softness as reactivity descriptors," in *Chemical Reactivity Theory. A Density Functional View*, edited by P. K. Chattaraj (CRC Press, Boca Raton, 2009), pp. 255–267.
[40]R. Kinkar Roy, K. Hirao, S. Krishnamurty, and S. Pal, "Mulliken population analysis-based evaluation of condensed Fukui function indices using fractional molecular charge," J. Chem. Phys. **115**, 2901–2907 (2001).
[41]A. Michalak, F. De Proft, P. Geerlings, and R. F. Nalewajski, "Fukui functions from the relaxed Kohn–Sham orbitals," J. Phys. Chem. **103**, 762–771 (1999).
[42]P. W. Ayers and J. Melin, "Computing the Fukui function from *ab initio* quantum chemistry: Approaches based on the extended Koopmans' theorem," Theor. Chem. Acc. **117**, 371–381 (2007).
[43]R. Balawender and L. Komorowski, "Atomic Fukui function indices and local softness *ab initio*," J. Chem. Phys. **109**, 5203–5211 (1998).
[44]L. Komorowski, "Electronegativity and hardness in the chemical approximation," Chem. Phys. **114**, 55–71 (1987).
[45]L. Komorowski and J. Lipiński, "Quantum chemical electronegativity and hardness indices for bonded atoms," Chem. Phys. **157**, 45–60 (1991).
[46]J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, "Density-functional theory for fractional particle number: Derivative discontinuities of the energy," Phys. Rev. Lett. **49**, 1691–1694 (1982).
[47]Y. Zhang and W. Yang, "Perspective on 'Density-functional theory for fractional particle number: Derivative discontinuities of the energy,'" Theor. Chem. Acc. **103**, 346–348 (2000).
[48]T. Fievez, N. Sablon, F. De Proft, P. W. Ayers, and P. Geerlings, "Calculation of Fukui functions without differentiating to the number of electrons. III. Local Fukui function and dual descriptor," J. Chem. Theor. Comput. **4**, 1065–1072 (2008).
[49]N. Sablon, F. De Proft, P. W. Ayers, and P. Geerlings, "Computing Fukui functions without differentiating with respect to electron number. II," J. Chem. Phys. **126**, 224108 (2007).
[50]P. W. Ayers, F. De Proft, A. Borgoo, and P. Geerlings, "Computing Fukui functions without differentiating with respect to electron number. I," J. Chem. Phys. **126**, 224107 (2007).
[51]P. W. Ayers, "The dependence on and continuity of the energy and other molecular properties with respect to the number of electrons," J. Math. Chem. **43**, 285 (2008).
[52]M. Franco-Pérez, P. W. Ayers, J. L. Gázquez, and A. Vela, "Local and linear chemical reactivity response functions at finite temperatures in density functional theory," J. Chem. Phys. **144**, 244117 (2015).
[53]R. Flores-Moreno, J. Melin, J. V. Ortiz, and G. Merino, "Efficient evaluation of analytic Fukui functions," J. Chem. Phys. **129**, 224105 (2008).
[54]P. W. Ayers, J. S. M. Anderson, and L. J. Bartolotti, "Perturbative perspectives of the chemical reaction prediction problem," Int. J. Quantum Chem. **101**, 520–534 (2005).
[55]P. W. Ayers, "Strategies for computing chemical reactivity indices," Theor. Chem. Acc. **106**, 271–279 (2001).
[56]P. W. Ayers and M. Levy, "Perspective on 'Density functional approach to the frontier-electron theory of chemical reactivity,'" Theor. Chem. Acc. **103**, 353–360 (2000).
[57]P. W. Ayers and R. G. Parr, "Variational principles for describing chemical reactions: The Fukui function and chemical hardness revisited," J. Am. Chem. Soc. **122**, 2010–2018 (2000).
[58]P. Fuentealba and R. G. Parr, "Higher-order derivatives in density functional theory, especially the hardness derivative $\partial\eta/\partial N$," J. Chem. Phys. **94**, 5559–5564 (1991).
[59]P. Ordon and L. Komorowski, "Nuclear reactivity and nuclear stiffness in density functional theory," Chem. Phys. Lett. **292**, 22–27 (1998).
[60]P. Ordon, "The impact of molecular deformations on the chemical reactivity indices," Ph. D. thesis, Wrocław University of Technology, 2003.
[61]T. Luty, P. Ordon, and C. J. Eckhardt, "A model for mechanochemical transformations: Applications to molecular hardness, instabilities, and shock initiation of reaction," J. Chem. Phys. **117**, 1775–1785 (2002).

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

[62]P. Ordon and A. Tachibana, "Use of nuclear stiffness in search for a maximum hardness principle and for the softest states along the chemical reaction path: A new formula for the energy third derivative gamma," J. Chem. Phys. **126**, 234115 (2007).
[63]C. Morell, A. Grand, and A. Toro-Labbé, "New dual descriptor for chemical reactivity," J. Phys. Chem. A **109**, 205–212 (2005).
[64]C. Morell, A. Grand, and A. Toro-Labbé, "Theoretical support for using the descriptor," Chem. Phys. Lett. **425**, 342–346 (2006).
[65]V. Tognetti, C. Morell, P. W. Ayers, L. Joubert, and H. Chermette, "A proposal for an extended dual descriptor: A possible solution when Frontier molecular orbital theory fails," Phys. Chem. Chem. Phys. **15**, 14465–14475 (2013).
[66]J. I. Martínez-Araya, "A generalized operational formula based of total electronic densities to obtain 3D pictures of the dual descriptor to reveal nucleophilic and electrophilic sites accurately on closed-shell molecules," J. Comput. Chem. **37**, 2279–2303 (2016).
[67]J. I. Martínez-Araya, "Why is the dual descriptor a more accurate local reactivity descriptor than Fukui functions?," J. Math. Chem. **53**, 451–465 (2015).
[68]J. Sánchez-Márquez, "New advances in conceptual-DFT: An alternative way to calculate the Fukui function and dual descriptor," J. Mol. Model. **25**, 123 (2019).
[69]F. De Proft, P. W. Ayers, S. Fias, and P. Geerlings, "Woodward-Hoffmann rules in density functional theory: Initial hardness response," J. Chem. Phys. **125**, 214101 (2006).
[70]P. W. Ayers, C. Morell, F. De Proft, and P. Geerlings, "Understanding the Woodward-Hoffmann rules by using changes in electron density," Chem. Eur. J. **13**, 8240 (2007).
[71]P. Geerlings, P. W. Ayers, A. Toro-Labbe, P. K. Chattaraj, and F. De Proft, "The Woodward-Hoffmann rules reinterpreted by conceptual density functional theory," Acc. Chem. Res. **45**(5), 683 (2012).
[72]P. Fuentealba, "A local model for the hardness kernel and related reactivity parameters in density functional theory," J. Chem. Phys. **103**, 6571–6575 (1995).
[73]F. De Proft, S. Liu, and R. G. Parr, "Chemical potential, hardness, hardness and softness kernel and local hardness in the isomorphic ensemble of density functional theory," J. Chem. Phys. **107**, 3000–3006 (1997).
[74]S. Liu, F. De Proft, and R. G. Parr, "Simplified models for hardness kernel and calculation of global hardness," J. Phys. Chem. A **101**, 6991–6997 (1997).
[75]C. A. Polanco-Ramirez, M. Franco-Perez, J. Carmona-Espindola, J. L. Gazquez, and P. W. Ayers, "Revisiting the definition of local hardness and hardness kernel," Phys. Chem. Chem. Phys. **19**, 12355 (2017).
[76]P. W. Ayers and R. G. Parr, "Local hardness equalization: Exploiting the ambiguity," J. Chem. Phys. **128**, 184108 (2008).
[77]T. Gál, P. Geerlings, F. De Proft, and M. Torrent-Sucarrat, "A new approach to local hardness," Phys. Chem. Chem. Phys. **13**, 15003 (2011).
[78]T. Gal, "Why the traditional concept of local hardness does not work," Theor. Chem. Acc. **131**, 7 (2012).
[79]P. Geerlings, S. Fias, Z. Boisdenghien, and F. De Proft, "Conceptual DFT: Chemistry from the linear response function," Chem. Soc. Rev. **43**, 4989–5008 (2014).
[80]P. Senet, "Nonlinear electronic responses, Fukui functions and hardness of functionals of the ground-state electron density," J. Chem. Phys. **105**, 6471–6489 (1996).
[81]W. Yang, A. J. Cohen, F. De Proft, and P. Geerlings, "Analytical evaluation of Fukui functions and real-space linear response function," J. Chem. Phys. **136**, 144110 (2012).
[82]L. Komorowski, J. Lipiński, and P. Szarek, "Polarization justified Fukui functions," J. Chem. Phys. **131**, 124120 (2009).
[83]L. Komorowski, J. Lipiński, P. Szarek, and P. Ordon, "Polarization justified Fukui functions: The theory and applications for molecules," J. Chem. Phys. **135**, 014109 (2011).
[84]P. Szarek and L. Komorowski, "Modeling the electron density kernels," J. Comput. Chem. **32**, 1721–1724 (2011).
[85]Z. Boisdenghien, C. Van Alsenoy, F. De Proft, and P. Geerlings, "Evaluating and interpreting the chemical relevance of the linear response kernel for atoms," J. Chem. Theor. Comput. **9**, 1007–1015 (2013).
[86]Z. Boisdenghien, S. Fias, C. Van Alsenoy, F. De Proft, and P. Geerlings, "Evaluating and interpreting the chemical relevance of the linear response kernel for atoms II: Open shell," Phys. Chem. Chem. Phys. **16**, 14614 (2014).
[87]P. Geerlings and F. De Proft, "Conceptual DFT: The chemical relevance of higher response functions," Phys. Chem. Chem. Phys. **10**, 3028–3042 (2008).
[88]F. Heidar-Zadeh, M. Richer, S. Fias, R. A. Miranda-Quintana, M. Chan, M. Franco-Pérez, C. E. González-Espinoza, T. D. Kim, C. Lanssens, A. H. G. Patel, X. D. Yang, E. Vöhringer-Martinez, C. Cárdenas, T. Verstraelen, and P. W. Ayers, "An explicit approach to conceptual density functional theory descriptors of arbitrary order," Chem. Phys. Lett. **660**, 307–312 (2016).
[89]M. Franco-Pérez, J. L. Gázquez, P. W. Ayers, and A. Vela, "Revisiting the definition of the electronic chemical potential, chemical hardness and softness at finite temperatures," J. Chem. Phys. **143**, 154103 (2015).
[90]P. Ordon, L. Komorowski, M. Jędrzejewski, and J. Zaklika, "The connectivity matrix: A toolbox for monitoring bonded atoms and bonds," J. Phys. Chem. A **124**(6), 1076–1086 (2020).
[91]S. Liu, R. G. Parr, and A. Nagy, "Cusp relations for local strongly decaying properties in electronic systems," Phys. Rev. A **52**, 2645–2651 (1995).
[92]P. Ordon, L. Komorowski, and M. Jedrzejewski, "Conceptual DFT analysis of the fragility spectra of atoms along the minimum energy reaction coordinate," J. Chem. Phys. **147**, 134109 (2017).
[93]R. F. W. Bader, in *Atoms in Molecules. A Quantum Theory*, *International Series of Monographs in Chemistry* (A Clarendon Press Publication, 1994), Vol. **22**.
[94]E. Prodan and W. Kohn, "Nearsightedness of electronic matter," Proc. Natl. Acad. Sci. U. S. A. **102**, 11635–11638 (2005).
[95]W. Kohn, "Density functional and density matrix method scaling linearly with the number of atoms," Phys. Rev. Lett. **76**, 3168–3171 (1996).
[96]R. F. W. Bader, "Nearsightedness of electronic matter as seen by a physicist and a chemist," J. Phys. Chem. A **112**, 13717–13728 (2008).
[97]J. Garza and J. Robles, "Density-functional-theory softness kernel," Phys. Rev. A **47**, 2680–2685 (1993).
[98]W. Beker, P. Szarek, L. Komorowski, and J. Lipiński, "Reactivity patterns of imidazole, oxazole, and thiazole as reflected by the polarization justified Fukui functions," J. Phys. Chem. A **117**, 1596–1600 (2013).
[99]W. Beker, A. Stachowicz-Kuśnierz, J. Zaklika, A. Ziobro, P. Ordon, and L. Komorowski, "Atomic polarization justified Fukui indices and the affinity indicators in aromatic heterocycles and nucleobases," Comput. Theor. Chem. **1065**, 42–49 (2015).
[100]Y. Li and J. N. S. Evans, "The Fukui function: A key concept linking frontier molecular orbital theory and the hard-soft-acid-base principle," J. Am. Chem. Soc. **117**, 7756–7759 (1995).
[101]P. K. Chattaraj, A. Cedillo, and R. G. Parr, "Variational method for determining the Fukui function and chemical hardness of an electronic system," J. Chem. Phys. **103**, 7645–7646 (1995).
[102]P. K. Chattaraj, A. Cedillo, and R. G. Parr, "Fukui function from a gradient expansion formula, and estimate of hardness and covalent radius for an atom," J. Chem. Phys. **103**, 10621–10626 (1995).
[103]M. K. Harbola, P. K. Chattaraj, and R. G. Parr, "Aspects of softness and hardness concepts of density-functional theory," Isr. J. Chem. **31**, 395–402 (1991).
[104]https://winter.group.shef.ac.uk/orbitron/; see also D. F. Shriver and P. W. Atkins, *Inorganic Chemistry*, 3rd ed. (Oxford University Press, Oxford, 1999), p. 15.
[105]C. Cárdenas, N. Rabi, P. W. Ayers, C. Morell, P. Jaramillo, and P. Fuentealba, "Chemical reactivity descriptors for amphiphilic reagents: Dual descriptor, local hypersoftness, and electrostatic potential," J. Phys. Chem. A **113**, 8660–8667 (2009).
[106]M. Lesiuk, R. Balawender, and J. Zachara, "Higher order alchemical derivatives from coupled perturbed self-consistent field theory," J. Chem. Phys. **136**, 034104 (2012).
[107]R. Balawender, M. Lesiuk, F. De Proft, C. van Alsenoy, and P. Geerlings, "Exploring chemical space with alchemical derivatives: Alchemical transformations of H through Ar and their ions as a proof of concept," Phys. Chem. Chem. Phys. **21**, 23865 (2019).
[108]N. H. March, "Relation between electrostatic potential of electron cloud at nucleus and chemical potential in atomic ions," Phys. Lett. A **82**, 73–74 (1981).

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing

[109]N. H. March, "The ground state energy of atomic ions and its variation with the number of electrons," in *Structure and Bonding*, edited by K. D. Sen (Springer-Verlag, 1993), Vol. 80, pp. 71–86.
[110]Y. Khalak, G. Tresadern, D. F. Hahn, B. L. de Groot, and V. Gapsys, "Chemical space exploration with active learning and alchemical free energies," J. Chem. Theory Comput. **18**, 6259 (2022).
[111]P. Politzer and J. S. Murray, "The neglected nuclei," Molecules **26**, 2982 (2021).
[112]T. Gómez, P. Fuentealba, A. Robles-Navarro, and C. Cárdenas, "Links among the Fukui potential, the alchemical hardness, and the local hardness of an atom in a molecule," J. Comput. Chem. **42**, 1681–1688 (2021).
[113]S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and T. Østergaard Sørensen, "Analyticity of the density of electronic wavefunctions," Ark. Mat. **42**, 87–106 (2004).
[114]Y. Li and C. Li, "Exact analytical form of diatomic molecular orbitals," ACS Omega **7**, 22594 (2022).
[115]T. Giovannini and H. Koch, "Fragment localized molecular orbitals," J. Chem. Theory Comput. **18**, 4806 (2022).
[116]J. Sánchez-Márquez, D. Zorrilla Cuenca, M. Fernández Núñez, and V. J. García Hernández, "Introducing a new model based on electronegativity equalization principle for the analysis of the neutral bond orbital reactivity in the c-DFT background," J. Quantum Chem. **122**, e26993 (2022).

Downloaded from http://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0142656/17302793/174110_1_5.0142656.pdf

Published under an exclusive license by AIP Publishing