Theor Chem Acc (2012) 131:1223
DOI 10.1007/s00214-012-1223-x

REGULAR ARTICLE

Why the traditional concept of local hardness does not work

Tamás Gál

Received: 19 October 2011 / Accepted: 14 April 2012

Abstract Finding a proper local measure of chemical hardness has been a long-standing aim of density functional theory. The traditional approach to defining a local hardness index, by the derivative of the chemical potential μ with respect to the electron density $n(\vec{r})$ subject to the constraint of a fixed external potential $v(\vec{r})$, has raised several questions, and its chemical applicability has proved to be limited. Here, we point out that the only actual possibility to obtain a local hardness measure in the traditional approach emerges if the external potential constraint is dropped; consequently, utilizing the ambiguity of a restricted chemical potential derivative is not an option to gain alternative definitions of local hardness. At the same time, however, the arising local hardness concept turns out to be fatally undermined by its inherent connection with the asymptotic value of the second derivative of the universal density functional. The only other local hardness concept one may deduce from the traditional approach, $\delta\mu[n]/\delta n(\vec{r})\big|_{v(\vec{r})}$, is the one that gives a constant value, the global hardness itself, throughout an electron system in its ground state. Consequently, the traditional approach is *in principle* incapable of delivering a local hardness indicator. The parallel case of defining a local version of the chemical potential itself is also outlined, arriving at similar conclusions.

Keywords Reactivity indices · Restricted derivatives · Local hardness · Local chemical potential

1 Introduction

Chemical reactivity indices [1–9], defined within the framework of density functional theory (DFT) [1], have found successful application in the study of chemical phenomena. The three most well-known reactivity descriptors, the electronegativity [10–13], or in the language of DFT, minus the chemical potential [13], the chemical hardness, and its inverse, the softness [14–17], are basic constituents of essential principles governing chemical reactions—the electronegativity equalization principle [13, 18], the hard/soft acid/base principle [14–17, 19–24], and the maximum hardness principle [25–30]. An important aim of chemical reactivity theory [2–9] is to establish local versions of the global indices, on the basis of which predictions can be made regarding the molecular sites a given reaction happens at.

Defining a local softness can be done in a natural way [31], by replacing the electron number N with the electron density $n(\vec{r})$ in the definition of softness as the derivative of N with respect to the chemical potential μ. However, defining a local counterpart [32, 33] of hardness, the multiplicative inverse of softness, has met essential difficulties [34–40], undermining the applicability of the local hardness concept. This may not seem to be a substantial problem, as the concepts of hardness and softness are simple complementers; however, very recently, even the definition of local softness $s(\vec{r})$ has been found to fail to properly signify the soft sites in the case of hard systems [41, 42], and even before, the interpretation of small $s(\vec{r})$ values as indicators of locally hard sites, preferred in hard–hard interactions [43], had been put into question [44–46]. Therefore, the question of a possible existence of a proper local hardness indicator has a renewed significance.

T. Gál (✉)
Quantum Theory Project, University of Florida,
Gainesville, FL 32611, USA
e-mail: galt@phys.unideb.hu

In this study, we will re-examine the idea of defining a local hardness concept via differentiation of the chemical potential with respect to the density subject to the constraint of a fixed external potential $v(\vec{r})$, in the view of the questions as to (1) why this traditional way of defining a local hardness concept could not yield a (generally) correct local indicator of chemical hardness, and (2) whether there is any possibility at all to gain such a local index from this approach. We will find that the only possibility to obtain a local hardness measure in the traditional approach emerges if the external potential constraint on the differentiation is dropped. The arising local hardness concept, however, will be shown to be fatally undermined by the necessary involvement of the asymptotic fixation of the external potential. At the same time, we will show that the constant local hardness of Ghosh [33] emerges as μ's unique constrained derivative with respect to $n(\vec{r})$ corresponding to the fixed-$v(\vec{r})$ constraint—but this local hardness concept cannot be a local reactivity measure because of its constancy. Our conclusion will be that the traditional approach to defining a local hardness index is, in fact, not capable of delivering a local hardness measure; therefore, an essentially new approach to this problem needs to be applied (like that proposed in [40], which originates a local hardness index via a local chemical potential—a chemical potential density). We will also consider the analogous case of defining a local counterpart of the chemical potential itself, having relevance (1) regarding the definition of a local electronegativity index and (2) serving as a potential basis for an alternative local hardness definition. The results will be similar to the local hardness case—in particular, the idea of defining a local chemical potential through the derivative of the ground-state energy with respect to the density subject to the constraint of a fixed external potential yields the constant local chemical potential concept of Parr et al. [13] as the only feasible option.

2 The traditional concept of local hardness

The chemical concept of hardness has been quantified by Parr and Pearson [15] as

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})}. \tag{1}$$

In contrast with its inverse chemical quantity, the softness,

$$S = \left(\frac{\partial N}{\partial \mu}\right)_{v(\vec{r})}, \tag{2}$$

defining a local counterpart for hardness has met essential difficulties, due to the fact that there is no such obvious way to do this as in the case of Eq. (2). For Eq. (2), a corresponding local quantity can be readily introduced [31]:

$$s(\vec{r}) = \left(\frac{\partial n(\vec{r})}{\partial \mu}\right)_{v(\vec{r})}, \tag{3}$$

which has been termed local softness. This has a direct connection with the Fukui function [47]

$$f(\vec{r}) = \left(\frac{\partial n(\vec{r})}{\partial N}\right)_{v(\vec{r})}, \tag{4}$$

a well-established chemical reactivity index: Applying the chain rule of differentiation, one obtains

$$s(\vec{r}) = \left(\frac{\partial n(\vec{r})}{\partial N}\right)_{v(\vec{r})} \left(\frac{\partial N}{\partial \mu}\right)_{v(\vec{r})} = f(\vec{r})S. \tag{5}$$

$s(\vec{r})$ integrates to S (just as the Fukui function integrates to 1), and it is natural to interpret it as a pointwise, that is, local, softness [31].

A local hardness concept has been introduced by Berkowitz et al. [32], who defined the local hardness as

$$\eta(\vec{r}) = \left(\frac{\delta \mu}{\delta n(\vec{r})}\right)_{v(\vec{r})}. \tag{6}$$

Equation (6) has since been the basis for practically all investigations concerning the local counterpart of hardness; therefore, we will term it the traditional concept of, or (since it actually embraces a class of concrete local hardness concepts, with different concrete quantitative formulae) traditional approach to, local hardness. This local index is not a local quantity in the sense the local softness is, since it does not integrate to the hardness; consequently, its integral over a region in the molecule will not give a regional hardness. In fact, $\eta(\vec{r})$ times the Fukui function is what gives η by integration over the whole space,

$$\int \eta(\vec{r}) f(\vec{r}) d\vec{r} = \eta, \tag{7}$$

which emerges via an application of the chain rule, as can be seen from the definitions (4) and (6).

The biggest difficulty with the local hardness defined by Eq. (6) has been that it is not clear how to understand the fixed external potential $[v(\vec{r})]$ condition on the differentiation in Eq. (6).

If we consider that the hardness is defined by Eq. (1) as the partial derivative of the chemical potential $\mu[N, v]$ (a function(al) of the electron number and the external potential) with respect to N, Eq. (6) suggests that $v(\vec{r})$ *as one of the variables* in $\mu[N, v]$ should be fixed when differentiating with respect to the electron density $n(\vec{r})$. However, this yields

$$\eta(\vec{r}) = \left(\frac{\partial\mu[N,v]}{\partial N}\right)_{v(\vec{r})} \frac{\delta N}{\delta n(\vec{r})} = \eta, \tag{8}$$

that is, the local hardness equals the global hardness at every point in space. If one utilizes the DFT Euler–Lagrange equation

$$\frac{\delta F[n]}{\delta n(\vec{r})} + v(\vec{r}) = \mu, \tag{9}$$

emerging from the minimization principle for the ground-state energy density functional

$$E_v[n] = F[n] + \int n(\vec{r})v(\vec{r})\mathrm{d}\vec{r} \tag{10}$$

for the determination of the ground-state density corresponding to a given $v(\vec{r})$, $\mu[N,v]$ $(\equiv \partial E[N,v]/\partial N)$ can be obtained as

$$\mu[N,v] = \frac{\delta F}{\delta n(\vec{r})}[n[N,v]] + v(\vec{r}). \tag{11}$$

Differentiating this expression with respect to N yields

$$\begin{aligned}\eta = \left(\frac{\partial\mu[N,v]}{\partial N}\right)_v &= \int \frac{\delta^2 F}{\delta n(\vec{r})\delta n(\vec{r}')}\left(\frac{\partial n(\vec{r}')}{\partial N}\right)_v \mathrm{d}\vec{r}' \\ &= \int \frac{\delta^2 F}{\delta n(\vec{r})\delta n(\vec{r}')} f(\vec{r}')\mathrm{d}\vec{r}'.\end{aligned} \tag{12}$$

On the basis of this, then, it is natural to identify the local hardness yielding Eq. (8) with

$$\eta(\vec{r}) = \int \frac{\delta^2 F}{\delta n(\vec{r})\delta n(\vec{r}')} f(\vec{r}')\mathrm{d}\vec{r}'. \tag{13}$$

This local hardness definition was proposed by Ghosh [33] and was discovered to be a constant giving the global hardness everywhere by Harbola et al. [34]. Equation (13) thus cannot be a local counterpart of hardness on the basis of which one could differentiate between molecular sites. However, it still is a useful conceptual and practical tool since a hardness equalization principle can be based on it [48–51], which says that $\eta(\vec{r})$ of Eq. (13) should be constant for the whole system for the ground-state density—but only for that density. This principle is closely related with the long-known chemical potential (or electronegativity) equalization principle [13, 52].

To gain other definition for the local hardness than the one giving the global hardness in every point of space, one may consider the fixed-$v(\vec{r})$ constraint in Eq. (6) as a constraint on the differentiation with respect to the density,

$$\eta(\vec{r}) = \left.\frac{\delta\mu[N[n],v[n]]}{\delta n(\vec{r})}\right|_{v(\vec{r})}, \tag{14}$$

instead of a simple fixation of the variable $v(\vec{r})$ of $\mu[N,v]$. That is, the density domain over which the differentiation is carried out is restricted to the domain of densities that yield the given $v(\vec{r})$, through the first Hohenberg–Kohn theorem [1], which constitutes a unique $n(\vec{r}) \to v(\vec{r})$ mapping, that is, a $v(\vec{r})[n]$ functional. The result will be an ambiguous restricted derivative (see Sec.II of [53]), similarly to the case of derivatives restricted to the domain of densities of a given normalization N, which derivatives are determined only up to an arbitrary additive constant [1, 54].

Harbola et al. [34], to characterize the ambiguity of the local hardness concept of Eq. (6), first pointed out by Berkowitz and Parr [55], have given the explicit form

$$\eta(\vec{r}) = \int \frac{\delta^2 F}{\delta n(\vec{r})\delta n(\vec{r}')} u(\vec{r}')\mathrm{d}\vec{r}' \tag{15}$$

for the possible local hardness candidates, where $u(\vec{r})$ is an arbitrary function that integrates to 1. The second derivative of $F[n]$, appearing in Eq. (15), is called the hardness kernel [55], which also serves as a basis for a minimization theorem determining the Fukui function [56]. The choice $u(\vec{r}) = f(\vec{r})$ gives back Eq. (13), while another natural choice is $u(\vec{r}) = n(\vec{r})/N$, which yields the original local hardness formula of Berkowitz et al. [32],

$$\eta(\vec{r}) = \frac{1}{N}\int \frac{\delta^2 F}{\delta n(\vec{r})\delta n(\vec{r}')} n(\vec{r}')\mathrm{d}\vec{r}', \tag{16}$$

who deduced it as an alternative form of Eq. (6).

Besides the above two definitions for $\eta(\vec{r})$, another one, termed the unconstrained local hardness, has been proposed by Ayers and Parr [28, 38]:

$$\eta(\vec{r}) = \frac{\delta\mu[N[n],v[n]]}{\delta n(\vec{r})}, \tag{17}$$

where the fixed-$v(\vec{r})$ constraint on the differentiation with respect to $n(\vec{r})$ is simply dropped. A substantial difficulty with this definition as regards practical use [38] is the explicit appearance of the derivative of $v(\vec{r}')$ with respect to $n(\vec{r})$, as can be seen by

$$\begin{aligned}\eta(\vec{r}) &= \frac{\partial\mu}{\partial N} + \int \frac{\delta\mu[N,v]}{\delta v(\vec{r}')}\frac{\delta v(\vec{r}')}{\delta n(\vec{r})}\mathrm{d}\vec{r}' \\ &= \eta + \int f(\vec{r}')\frac{\delta v(\vec{r}')}{\delta n(\vec{r})}\mathrm{d}\vec{r}',\end{aligned} \tag{18}$$

where the well-known fact

$$\frac{\delta E[N,v]}{\delta v(\vec{r})} = n(\vec{r}) \tag{19}$$

and Eqs. (1) and (4) have been utilized. Note that Eq. (17), too, is embraced by Eq. (14), since for a restricted derivative, a trivial choice is the unrestricted derivative itself (if exists), being valid over the whole functional domain, hence over the restricted domain too. (That $\eta(\vec{r})$ of Eq. (8) [that is, of Eq. (13)] and of Eq. (16), or generally, of Eq. (15), are also embraced by Eq. (14) will be shown at the end of Sect. 3.)

3 Excluding the ambiguity of the local hardness concept of Eq. (14)

A proper local hardness is expected to yield proper regional hardness values, on the basis of which one can predict the molecular region (or site) a reaction with another species happens at. The only plausible way of obtaining regional hardnesses from an $\eta(\vec{r})$ defined by Eq. (14) is

$$\eta_\Omega = \int_\Omega \eta(\vec{r}) \left(\frac{\partial n(\vec{r})}{\partial N} \right)_v \mathrm{d}\vec{r} \equiv \int_\Omega \eta(\vec{r}) f(\vec{r}) \mathrm{d}\vec{r}; \qquad (20)$$

that is, the integral in Eq. (7) is carried out over a given region Ω of space instead of the whole space. Equation (20) has been applied in practical calculations to characterize the hardness of atomic regions or functional groups in molecules (for recent examples, see for instance [57–62]), and as a special case [in the form of Eq. (7)], to evaluate the global (that is, total) hardness itself [63–70]. Equation (20) represents an "extensive" hardness concept: The total hardness of a molecule can be obtained as a sum of its regional hardness corresponding to a given (arbitrary) division of the molecule into regions. That is, roughly saying, a molecule that contains regions having high values of hardness in a majority will have a high global hardness, while a molecule that contains mainly soft regions, with low $\eta(\Omega)$, will have a low global hardness. Of course, in a strict sense, the hardness will not be an extensive property, since for the determination of the hardness of a given region on the basis of Eq. (20), the whole of the electronic system needs to be involved (a change in the electron number induces a change in the electron density distribution as a whole)—however, we cannot expect more in quantum mechanics, since there is no sense in asking how much a given property of a segment of a system changes due to the addition of a fraction dN of electrons to, and only to, that segment.

A problem with this local hardness/regional hardness scheme is that if η is extensive, with regional hardnesses given by Eq. (20), the quantity $\eta(\vec{r})f(\vec{r})$ should be considered to be the local hardness instead of $\eta(\vec{r})$ [of Eq. (14)]. A local quantity $\rho(\vec{r})$ corresponding to a given extensive global quantity Θ emerges as $\rho(\vec{r}) = \lim_{\Delta V \to \vec{r}} \frac{\Delta\Theta}{\Delta V}$, implying $\Theta(\Omega) = \int_\Omega \rho(\vec{r}) \mathrm{d}\vec{r}$. At the same time, however, it seems plausible to take $\eta(\vec{r})$ of Eq. (14) as the local hardness since it characterizes the change of the chemical potential induced by a small (infinitesimal) change of the electron density $n(\vec{r})$ at a given point of space in a given external potential—this seems to be a proper local counterpart of the hardness, given by Eq. (1). Although this view is intuitively appealing, one should be careful with such an approach, because then we may argue that a change (even if infinitesimal) of the density at a single $\vec{r}$ will yield a discontinuous density, so why should one bother himself with chemical potential changes corresponding to unphysical density changes? This point is just to show the dangerous side of intuitive arguing regarding a functional derivative—but there is a physical/real argument against the above interpretation of Eq. (14) as the local counterpart of hardness. If we add a small fraction dN of number of electrons to a molecule, it will be distributed over the whole molecule, no matter "where we added" that dN of electrons. Consequently, only a change of μ that is induced by a density change that is caused by a dN makes sense directly. $\frac{\delta\mu}{\delta n(\vec{r})}$ is only an intermediate quantity that delivers the infinitesimal change in μ due to an infinitesimal change of N or some other quantity determining the given electron system and hence $n(\vec{r})$, through

$$\left(\frac{\partial\mu}{\partial N} \right)_v = \int \frac{\delta\mu}{\delta n(\vec{r})}\bigg|_v \left(\frac{\partial n(\vec{r})}{\partial N} \right)_v \mathrm{d}\vec{r}, \qquad (21)$$

or

$$\left(\frac{\delta\mu}{\delta v(\vec{r})} \right)_N = \int \frac{\delta\mu}{\delta n(\vec{r}\,')}\bigg|_N \left(\frac{\delta n(\vec{r}\,')}{\delta v(\vec{r})} \right)_N \mathrm{d}\vec{r}\,', \qquad (22)$$

for example. (Provided it exists, an unrestricted derivative of μ with respect to $n(\vec{r})$, $\frac{\delta\mu}{\delta n(\vec{r})}$, may be used in both of the above equations in the place of the restricted derivatives). Thus, instead of $\delta\mu/\delta n(\vec{r})|_v$, and $\delta\mu/\delta n(\vec{r})|_N$, alone, the whole of the integrands in the above equations should be considered the local quantities corresponding to the quantities on the left-hand sides. It may then be more appropriate to term Eq. (14), for example, as "local hardness factor," instead of "local hardness," which indicates its role in delivering the actual local hardness $\eta(\vec{r})f(\vec{r})$ and regional hardnesses. Of course, this is just a matter of terminology (and why should we change a name nearly 30 years old?); however, the relevant point here is that one should not expect $\eta(\vec{r})$ of Eq. (14) itself to be a measure of local hardness. The question of considering $\eta(\vec{r})f(\vec{r})$ a local hardness measure instead of $\eta(\vec{r})$ was first raised by Langenaeker et al. [71] (to get a proper complementer quantity of local softness $s(\vec{r})$), who called $\eta(\vec{r})f(\vec{r})$ "hardness density." The latter term, of course, is an appropriate name for $\eta(\vec{r})f(\vec{r})$ as this integrates to the hardness and even more appropriate if η is indeed extensive. However, if $\eta(\vec{r})f(\vec{r})$ proved to be a proper hardness density distribution indeed (with larger values in harder regions), it should be termed also "local hardness," since it would then be a local measure of hardness. But if (some choice of) $\eta(\vec{r})$ of Eq. (14) *itself* turned out to be a proper local hardness measure, it would be $\eta(\vec{r})$ what should be termed "local hardness" (but in this case, even terming $\eta(\vec{r})f(\vec{r})$ "hardness density," just because it integrates to the hardness, would become strongly questionable). $\eta(\vec{r})$ and $\eta(\vec{r})f(\vec{r})$ simultaneously cannot be a correct measure of local hardness. We note that a local hardness index does not *have to* be a property density [72]—but if Eq. (20) is to deliver regional hardnesses, then it does have to be, and the local hardness cannot be $\eta(\vec{r})$ of Eq. (14) itself.

Now, the question is as to which of the choices of Eq. (14), that is, which way of fixing the external potential while differentiating with respect to the density, is (are) the proper one(s) to obtain a local quantity $\eta(\vec{r})f(\vec{r})$ that may correctly deliver regional hardnesses. As we will see, the only possible concrete choice of Eq. (14) is the unconstrained local hardness (factor) of Ayers and Parr. Consider Eqs. (21) and (22) with the integrals taken only over a given region of space. We are interested (directly) only in the case of Eq. (21), but by the example of Eq. (22), some more insight may be gained; therefore, it is worth considering it, too, in parallel with Eq. (21). Thus, we have, on one hand, Eq. (20), and on the other hand,

$$f_\Omega(\vec{r}) = \int\limits_\Omega \left.\frac{\delta\mu}{\delta n(\vec{r}\,')}\right|_N \left(\frac{\delta n(\vec{r}\,')}{\delta v(\vec{r})}\right)_N \mathrm{d}\vec{r}\,', \tag{23}$$

which is a "regional Fukui function," as the left-hand side of Eq. (22) is just the Fukui function,

$$\left(\frac{\delta\mu}{\delta v(\vec{r})}\right)_N = f(\vec{r}), \tag{24}$$

due to Eq. (19). What do these regional integrals tell us? They can be viewed as entities that give the contributions, to the infinitesimal change of μ, that come from the change of the density over the given region Ω due to an increment of N and $v(\vec{r})$, respectively. To ease understanding, compare this with the finite-dimensional example of a function $g(x(t), y(t))$ (with a derivative $\dot{g} = \frac{\partial g}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{\partial g}{\partial y}\frac{\mathrm{d}y}{\mathrm{d}t}$, with respect to t), for which a "regional integral," or partial sum, means $\dot{g}_x = \frac{\partial g}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}t}$—that is, the part of $\dot{g}$ that is due to the x part of the full change of $g(x(t), y(t))$ with respect to t. Thus, an infinitesimal change of N, or $v(\vec{r})$, induces a density change $\delta n(\vec{r})$, and then the regional integral Eq. (20), or Eq. (23), tells us how much the part of $\delta n(\vec{r})$ that falls on the given domain Ω contributes to the whole change $\partial\mu$ of μ due to $\delta n(\vec{r})$, via $(\partial\mu)_\Omega = \int_\Omega \frac{\delta\mu}{\delta n(\vec{r})}\delta n(\vec{r})\mathrm{d}\vec{r}$ (multiply Eq. (20) and Eq. (23) by ∂N and $\int d\vec{r}\,\delta v(\vec{r})$, respectively). This shows that Eq. (20) is indeed a plausible way to obtain a regional hardness measure—but *only* if the unrestricted derivative of μ is applied, as will be pointed out below. Note that Eq. (23) gives a natural decomposition of the Fukui function $f(\vec{r})$, $\sum_i f_{\Omega_i}(\vec{r}) = f(\vec{r})$. It gives how much contribution to $f(\vec{r})$, at any given $\vec{r}$, can be attributed to a given region Ω of the molecule (which does not necessarily include $\vec{r}$!).

To understand why the unrestricted derivative $\frac{\delta\mu}{\delta n(\vec{r})}$ is the only possible choice in Eqs. (20) and (23) to obtain proper regional measures, it is important to see where the ambiguity of restricted derivatives emerges from. The derivative of a functional $A[\rho]$, as used in physics, is defined by

$$\int \frac{\delta A[\rho]}{\delta\rho(x')}\Delta\rho(x')\mathrm{d}x' = D(A)[\rho;\Delta\rho], \tag{25a}$$

which has to hold for any $\Delta\rho(x)$, and where $D(A)[\rho;\Delta\rho]$ denotes the Fréchet, or Gâteaux, differential of $A[\rho]$ for $\Delta\rho(x)$; see for example [53] for details. Equation (25a) may be written less rigorously as

$$\int \frac{\delta A[\rho]}{\delta\rho(x')}\delta\rho(x')\mathrm{d}x' = A[\rho+\delta\rho] - A[\rho], \tag{25b}$$

where $\delta\rho(x)$ denotes a first-order, that is, "infinitesimal," increment of $\rho(x)$. Now, if we restrict the functional domain by the requirement that the $\rho(x)$'s of the domain have to satisfy some constraint $C[\rho] = C$ (i.e., we are not expecting the functional derivative to be valid over the whole domain of $\rho(x)$'s), more than one function $\frac{\delta A[\rho]}{\delta\rho(x)}$ will be capable of delivering $D(A)[\rho;\Delta\rho]$ for any $\Delta\rho(x)$ [that is in accordance with the constraint, $\Delta_C\rho(x)$]. Namely, if $\frac{\delta A[\rho]}{\delta\rho(x)}$ fulfills Eq. (25), any other $\frac{\delta A[\rho]}{\delta\rho(x)} + \lambda\frac{\delta C[\rho]}{\delta\rho(x)}$ will fulfill it, too, over the given restricted domain, since

$$\int \frac{\delta C[\rho]}{\delta\rho(x')}\delta_C\rho(x')\mathrm{d}x' = 0, \tag{26}$$

emerging from $C[\rho+\delta_C\rho] - C[\rho] = 0$. Denoting a restricted derivative by $\left.\frac{\delta A[\rho]}{\delta\rho(x)}\right|_C$, while reserving the notation $\frac{\delta A[\rho]}{\delta\rho(x)}$ for the unrestricted derivative (valid over the unrestricted domain), this ambiguity can be expressed as

$$\left.\frac{\delta A[\rho]}{\delta\rho(x)}\right|_C = \frac{\delta A[\rho]}{\delta\rho(x)} + \lambda\frac{\delta C[\rho]}{\delta\rho(x)} \tag{27}$$

(with λ being an arbitrary constant), provided, of course, that the unrestricted derivative exists. As has been proved in the Appendix of [53], in the chain rule of differentiation of a composite functional $A[\rho[q]]$, the full derivative $\frac{\delta A[\rho]}{\delta\rho(x)}$ may be replaced by any choice of the restricted derivative $\left.\frac{\delta A[\rho]}{\delta\rho(x)}\right|_C$,

$$\frac{\delta A[\rho[q]]}{\delta q(x)} = \int \left.\frac{\delta A[\rho]}{\delta\rho(x')}\right|_C \frac{\delta\rho(x')[q]}{\delta q(x)}\mathrm{d}x', \tag{28}$$

in the case $\rho(x)[q]$ is such that it satisfies the given constraint $C[\rho] = C$ for all $q(x)$'s—which is the case for Eqs. (21) and (22). It is crucial for both of the above cancellations of the ambiguity of restricted derivatives (yielding a unique $A[\rho + \delta_C\rho] - A[\rho]$ and a unique $\frac{\delta A[\rho[q]]}{\delta q(x)}$) that the integrals [in Eqs. (25a) and (28)] are taken over the whole space. In the case of applications of a derivative $\frac{\delta A[\rho]}{\delta\rho(x)}$ where the ambiguity of the corresponding restricted derivative under a given constraint does not cancel [like in the case of Eqs. (20) and (23)], the unrestricted derivative *cannot* be replaced by another choice $\left.\frac{\delta A[\rho]}{\delta\rho(x)}\right|_C$. We should keep in mind that only the unrestricted derivative is capable of delivering the correct change of $A[\rho]$ due to a change of its variable at a given point x' induced by a change of a function $q(x)$ that $\rho(x')$ depends on—either $\rho(x')[q]$ obeys some constraint or not. An additional term $+\lambda\frac{\delta C[\rho]}{\delta\rho(x)}$ just unnecessarily, and incorrectly, modifies the result given by $\frac{\delta A[\rho]}{\delta\rho(x)}$. To gain more insight into this, one may consider again the example of a composite function $g(x(t), y(t))$, with $(x(t), y(t))$ now obeying the constraint $x^2(t) + y^2(t) = c$, for example. Under this constraint on g's variables, the ambiguous restricted derivative $\left(\frac{\partial g(x,y)}{\partial x}, \frac{\partial g(x,y)}{\partial y}\right) + \lambda(2x, 2y)$, with any choice of λ, will correctly deliver the full first-order change of g due to a change in (x, y) that is in accordance with the constraint—but *not* a partial first-order change, such as $\frac{\partial g}{\partial x}\frac{\mathrm{d}x(t)}{\mathrm{d}t}\mathrm{d}t$.

We have pointed out above that (1) it is $\eta(\vec{r})f(\vec{r})$ what may deliver a correct local hardness measure instead of $\eta(\vec{r})$ of Eq. (14) alone, and (2) $\eta(\vec{r})$ should be an unrestricted derivative in order to correctly obtain regional hardnesses by integration of $\eta(\vec{r})f(\vec{r})$ over molecular regions. Thus, we conclude that a correct local hardness measure may be delivered only by

$$\eta(\vec{r}) = \frac{\delta\mu[N[n], v[n]]}{\delta n(\vec{r})} f(\vec{r}). \tag{29}$$

However, there is an inherent problem with $\frac{\delta\mu}{\delta n(\vec{r})}$, as will be pointed out in the following section. We should add here that the above local quantity may not quite be a local counterpart of *hardness*, since $v(\vec{r})$ in $\mu[N, v]$ is explicitly fixed when obtaining $\eta[N, v]$. However, the unrestricted derivative of μ with respect to $n(\vec{r})$ that keeps $v(\vec{r})$ explicitly fixed is the derivative $\frac{\delta\mu[N[n],v]}{\delta n(\vec{r})}$, that is, the derivative in Eq. (8). Hence, it is not capable of giving a local measure of hardness. It would only yield a local quantity that is proportional to the Fukui function itself, $\eta(\vec{r}) = \eta f(\vec{r})$, which would therefore measure regional *softnesses* by integration over molecular regions for soft molecules. (We note that this is precisely the reason for the numerical observations of Torrent-Sucarrat et al. [41, 42], who found that the regional integrals calculated with Eq. (8) used in Eq. (20) predict high regional hardness for actually soft regions—in the case of globally soft systems. This is then not surprising, since this is just what is expected from the Fukui function. The interesting fact, which gives the findings of Torrent-Sucarrat et al. high significance, is that this "local hardness" expression works well for hard systems [41, 42], which implies that the Fukui function actually indicates local hardness instead of softness in the case of globally hard systems. Therefore, the interpretation of the Fukui function as a general local softness measure has to be reconsidered. But it is clear that $\eta(\vec{r}) = \eta f(\vec{r})$ also cannot be a local hardness measure.)

To close this section, it is worth exhibiting the ambiguity of the regional integrals Eqs. (20) and (23) that would be caused by the ambiguity of $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_v$ and $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_N$, respectively, if the use of those restricted derivatives, instead of the unrestricted derivative $\frac{\delta\mu}{\delta n(\vec{r})}$, was actually allowed in the case of integrals not covering the whole space. In the case of Eq. (23), the ambiguity of the restricted derivative appears in the form of a simple additive constant; that is, in the place of a given $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_N$, any other $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_N + \lambda$ can be taken as a choice for the chemical potential derivative over the N-restricted domain of $n(\vec{r})$'s. We may exhibit this ambiguity as

$$\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_N = \frac{\delta\mu}{\delta n(\vec{r})} + \lambda. \tag{30}$$

This ambiguity then leads to an ambiguity of $+\lambda\left(\frac{\delta N_\Omega}{\delta v(\vec{r})}\right)_N$ in $f_\Omega(\vec{r})$. The ambiguity Eq. (30) may be expressed with other particular choices of $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_N$ replacing $\frac{\delta\mu}{\delta n(\vec{r})}$ in Eq. (30). Such a choice is

$$\left(\frac{\delta\mu[N, v[n]]}{\delta n(\vec{r})}\right)_N = \int \left(\frac{\delta\mu[N, v]}{\delta v(\vec{r}\,')}\right)_N \frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,'$$
$$= \int f(\vec{r}\,')\frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,', \tag{31}$$

which is the analogue of Eq. (8). With this, then, we may also write

$$\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_N = \int f(\vec{r}\,')\frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,' + \lambda \tag{32}$$

(emphasizing that λ denotes an arbitrary constant throughout, not to be taken to be identical when appearing in different equations). By inserting Eq. (32) in Eq. (23), we obtain

$$f_\Omega(\vec{r}) = \int f(\vec{r}\,'')\int_\Omega \frac{\delta v(\vec{r}\,'')}{\delta n(\vec{r}\,')}\left(\frac{\delta n(\vec{r}\,')}{\delta v(\vec{r})}\right)_N \mathrm{d}\vec{r}\,'\mathrm{d}\vec{r}\,'' + \lambda\left(\frac{\delta N_\Omega}{\delta v(\vec{r})}\right)_N . \tag{33}$$

(It can be seen that if Ω is chosen to be the whole space, Eq. (33) gives back the Fukui function). As regards $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_v$, it is determined only up to a term $+\int\lambda(\vec{r}\,')\frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,'$ (with $\lambda(\vec{r})$ arbitrary), emerging from the fixed-$v(\vec{r})$ constraint, $v(\vec{r}\,')[n(\vec{r})] = v(\vec{r}\,')$—which can be considered as an infinite number of constraints ("numbered" by $\vec{r}\,'$) on the $n(\vec{r})$-domain. This ambiguity may be exhibited as

$$\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_v = \frac{\delta\mu}{\delta n(\vec{r})} + \int\lambda(\vec{r}\,')\frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,', \tag{34}$$

or with the particular choice Eq. (8) instead of $\frac{\delta\mu}{\delta n(\vec{r})}$, as

$$\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_v = \eta + \int\lambda(\vec{r}\,')\frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,'. \tag{35}$$

With Eq. (35), for example, the ambiguity of Eq. (20) may then be given as

$$\eta_\Omega = \eta\int_\Omega f(\vec{r}\,')\mathrm{d}\vec{r}\,' + \int\lambda(\vec{r}\,'')\int_\Omega\frac{\delta v(\vec{r}\,'')}{\delta n(\vec{r}\,')}f(\vec{r}\,')\mathrm{d}\vec{r}\,'\mathrm{d}\vec{r}\,''. \tag{36}$$

Equation (35) gives back Eq. (17) with the choice $\lambda(\vec{r}) = f(\vec{r})$, as can be seen from Eq. (18). From Eq. (34), one can get back Eq. (15) if $-\lambda(\vec{r})$ is chosen to be a function $u(\vec{r})$ that integrates to 1, utilizing $\frac{\delta\mu}{\delta n(\vec{r})} = \int u(\vec{r}\,')\frac{\delta\mu}{\delta n(\vec{r})}\mathrm{d}\vec{r}\,'$ and Eq. (9). This then shows that the possible choices of Eq. (14) are even more numerous than has been believed on the basis of Eq. (15).

4 Ill-definedness of the chemical potential's derivative with respect to the density

For any possible application of Eq. (29), a proper method to evaluate the derivative of $v(\vec{r})$ with respect to the density is necessary, as revealed by Eq. (18). $v(\vec{r})$ is given as a functional of $n(\vec{r})$ by Eq. (9) itself; namely,

$$v(\vec{r}\,')[n] = \mu[n] - \frac{\delta F[n]}{\delta n(\vec{r}\,')}. \tag{37}$$

That is, in order to obtain the derivative of Eq. (37) with respect to $n(\vec{r})$ to determine $\frac{\delta\mu}{\delta n(\vec{r})}$ through Eq. (18), we already need to have $\frac{\delta\mu}{\delta n(\vec{r})}$! We cannot determine $\frac{\delta\mu}{\delta n(\vec{r})}$ without further information on $\mu[n]$, since from Eqs. (18) and (37),

$$\begin{aligned}\frac{\delta\mu[n]}{\delta n(\vec{r})} &= \eta + \int f(\vec{r}\,')\frac{\delta}{\delta n(\vec{r})}\left(\mu[n] - \frac{\delta F[n]}{\delta n(\vec{r}\,')}\right)\mathrm{d}\vec{r}\,' \\ &= \eta + \frac{\delta\mu[n]}{\delta n(\vec{r})} - \int f(\vec{r}\,')\frac{\delta^2 F[n]}{\delta n(\vec{r})\delta n(\vec{r}\,')}\mathrm{d}\vec{r}\,',\end{aligned} \tag{38}$$

which is an identity, involving Eq. (12).

μ is determined as a functional of the density by a boundary condition in Eq. (37). In the case of potentials bounded at infinity, this will be according to the asymptotic condition $v(\infty) = 0$ on the external potentials, yielding

$$\mu[n] = \frac{\delta F[n]}{\delta n(\infty)}. \tag{39}$$

(Note that $n(\vec{r}\to\infty)$ is taken along one given direction, just as $v(\infty)$ needs to be fixed only along one direction—which then allows the extension to an even wider domain of external potentials.) We emphasize that there is no other way to determine μ as a functional of $n(\vec{r})$ than the above, since μ [either as the chemical potential, that is, the derivative of $E[N,v]$ with respect to N, or as the Lagrange multiplier in Eq. (9)] emerges directly as $\mu[N,v]$, which leaves $\mu[N[n],v[n]]$ undetermined, as seen above. With Eq. (39), then, we obtain

$$\frac{\delta\mu[n]}{\delta n(\vec{r})} = \frac{\delta^2 F[n]}{\delta n(\vec{r})\delta n(\infty)}. \tag{40}$$

It is worth observing that Eq. (40) corresponds to the choice $u(\vec{r}\,') = \delta(\vec{r}\,' - \infty)$ in Eq. (15).

Equation (40) seems to offer an easy way to evaluate $\frac{\delta\mu}{\delta n(\vec{r})}$: Just take the hardness kernel and consider its limit as (any) one of its variables approaches infinity. However, a problem immediately arises. With using approximations for $F[n]$ that construct $F[n]$ simply in a form $F[n] = \int g(n(\vec{r}),\nabla n(\vec{r}),\nabla^2 n(\vec{r}),\ldots)\mathrm{d}\vec{r}$ (which is common in practical calculations), delta functions $\delta(\vec{r}-\infty)$ appear as multipliers of constant components on the right of Eq. (40), which cannot yield a useful local index. One may argue that this is only an issue of the quality of approximation for

$F[n]$. For example, as has been pointed out by Tozer et al. [73–75], a proper density functional $F[n]$ (if continuously differentiable) should yield an exchange–correlation potential that has a nonvanishing asymptotic value, in contrast with the commonly used $E_{\mathrm{xc}}[n]$'s, with the above construction. The problem, however, is more fundamental.

Consider the (exact) one-electron version of the DFT Euler–Lagrange equation Eq. (9),

$$\frac{\delta T_W[n]}{\delta n(\vec{r})} + v(\vec{r}) = -I, \tag{41}$$

where $T_W[n]$ is the Weizsäcker functional $T_W[n] = \frac{1}{8}\int \frac{|\nabla n(\vec{r})|^2}{n(\vec{r})} \mathrm{d}\vec{r}$, exactly valid as $F[n]$ for one-particle densities, while I denotes the ionization potential, which is just minus the ground-state energy for one-particle systems. It is important that $T_W[n]$ is not only an exact functional for one-particle densities, in which case its derivative would possibly differ from the generally valid $\frac{\delta F[n]}{\delta n(\vec{r})}$ by a ($n(\vec{r})$-dependent) constant, but in the zero-temperature grand canonical ensemble extension of the energy for fractional electron numbers [76] (see [77] for the spin-polarized generalization), it is the exact F functional for densities with $N \le 1$ [78], implying

$$\frac{\delta T_W[n_1]}{\delta n(\vec{r})} = \left.\frac{\delta F[n_1]}{\delta n(\vec{r})}\right|_{-} \tag{42}$$

(with no difference by a constant), and

$$-I(N=1) = \mu_{-}(N=1), \tag{43}$$

where the minus sign in the subscripts denotes that a left-side derivative is taken (in the zero-temperature ensemble scheme, the two one-sided derivatives are different in general, implying the existence of derivative discontinuities [76, 77]). We then have for ground-state-v-representable $n_1(\vec{r})$'s (and $n(\vec{r})$'s with $N \le 1$)

$$\mu_{-}[n] = \frac{\delta T_W[n]}{\delta n(\infty)}. \tag{44}$$

(For one-particle densities that correspond to excited states of the external potential delivered by Eq. (41), on the left-hand side of Eq. (44), only $-I[n]$ can be written.) The derivative of Eq. (44) with respect to $n(\vec{r})$,

$$\begin{aligned}\frac{\delta^2 T_W[n]}{\delta n(\vec{r}\,')\delta n(\infty)} = &-\frac{1}{4}\left(\frac{(\nabla n(\infty))^2}{(n(\infty))^3} - \frac{\nabla^2 n(\infty)}{(n(\infty))^2}\right)\delta(\infty - \vec{r}\,') \\ &+ \frac{1}{4}\frac{\nabla n(\infty)}{(n(\infty))^2}\nabla\delta(\infty - \vec{r}\,') \\ &- \frac{1}{4}\frac{1}{n(\infty)}\nabla^2\delta(\infty - \vec{r}\,')\end{aligned} \tag{45}$$

(where the corresponding asymptotic limits are to be taken), however, is ill-defined for electronic densities. The exponential asymptotic decay $\mathrm{e}^{-2\sqrt{2I}r}$ [79, 80] of such densities leads to infinite values of the factors of the delta functions above. (Note though that even without this, the delta functions would not make Eq. (45) a useful local descriptor.) This is not only a formal problem that can be avoided by writing Eq. (45) with the arguments ∞ and $\vec{r}\,'$ interchanged. The derivative of $\mu_{-}[n]$ does not exist for electronic densities! This can be seen by considering the infinitesimal increment $\delta\mu = \int \frac{\delta\mu[n]}{\delta n(\vec{r})}\delta n(\vec{r})\mathrm{d}\vec{r}$ of μ in a case where the ionization potential corresponding to an electronic density $n(\vec{r})$ decreases, that is, the decay of $\tilde{n}(\vec{r}) = n(\vec{r}) + \delta n(\vec{r})$ is slower than $n(\vec{r})$'s. In such case, as can be checked readily, Eq. (45) leads to an infinite $\delta\mu$, whereas it should be $I - \tilde{I}$, and this outcome remains the same even if we consider the full Taylor expansion of μ, that is, a full change $\Delta\mu$. (The increasing I case may also be considered, with all terms containing $\tilde{I}$ vanishing in the Taylor expansion.)

The Weizsäcker-functional derivative is not only a one-particle example, but $\frac{\delta T_W[n]}{\delta n(\vec{r})}$, a component of $\frac{\delta F[n]}{\delta n(\vec{r})}$ in the general case, *itself* gives $-I$ (which equals μ_{-} [76]) in the case of finite electron systems, which can be seen if one inserts the density decay $\mathrm{e}^{-2\sqrt{2I}r}$ [79, 80] in $\frac{\delta T_W[n]}{\delta n(\vec{r})}$,

$$\frac{\delta T_W[n]}{\delta n(\vec{r})} = \frac{1}{8}\left(\frac{\nabla n(\vec{r})}{n(\vec{r})}\right)^2 - \frac{1}{4}\frac{\nabla^2 n(\vec{r})}{n(\vec{r})} \underset{r\to\infty}{\to} -I. \tag{46}$$

Equation (45) then implies that the component of $\mu_{-}[n]$ that is the most essential for electronic densities yields an ill-defined contribution to $\left.\frac{\delta\mu[n}{\delta n(\vec{r})}\right|_{-}$ for such densities.

It is important to point out that the above finding is not only some peculiar feature of the ensemble extension [76] of the energy for fractional N's. In the case of other (possibly continuously differentiable) extensions, the derivatives of $T_W[n]$ and $F[n]$ may differ only by a (density-dependent) constant [53] at a one-particle density $n_1(\vec{r})$ (since the two functionals are equal for any $n_1(\vec{r})$). This implies that their second derivatives may differ only by some $c(\vec{r}) + c(\vec{r}\,')$, as can be seen by applying (1) the above constant-difference rule of derivatives to the derivative of $\frac{\delta F[n_1]}{\delta n(\vec{r})} = \frac{\delta T_W[n_1]}{\delta n(\vec{r})} + C[n_1]$ itself and (2) the symmetry property of second derivatives in $\vec{r}$ and $\vec{r}\,'$. Then, to obtain $\frac{\delta\mu[n_1]}{\delta n(\vec{r})}$ corresponding to a given fractional N generalization of $F[n]$, $c(\vec{r}\,') + c(\infty)$ needs to be added to Eq. (45), where the function c depends on the generalization. Thus, the problematic Eq. (45) will remain as a component of $\delta\mu/\delta n(\vec{r})$.

A very recent finding by Hellgren and Gross (HG) [81] gives further support of our conclusion regarding the ill-definedness of $\delta\mu/\delta n(\vec{r})$. These authors have showed that the right-side second derivative of the exchange–correlation (xc) component of $F[n]$ of the ensemble generalization for fractional N's [76] diverges (exponentially) as $r \to \infty$, by which they have also placed earlier findings regarding the asymptotic divergence of the xc kernel [82] onto sound theoretical grounds. This divergent behavior has been pointed out to emerge from the integer discontinuity of the xc kernel [81]. Since the left- and the right-side derivative at a given $n(\vec{r})$ may differ only by a constant (see Appendix of [83] for a proof), the difference between the left- and the right-side second derivative may only be some $c(\vec{r}) + c(\vec{r}^{\,\prime})$, on similar grounds as above (note that the left-side derivative and the right-side derivative of a functional at a given $n(\vec{r})$ may be considered as the derivatives of two different, continuously differentiable functionals that intersect on a subset of $n(\vec{r})$'s of a given N). HG has found that $g(\vec{r})$ of $g(\vec{r}) + g(\vec{r}^{\,\prime}) := \left.\frac{\delta^2 E_{\mathrm{xc}}[n]}{\delta n(\vec{r})\delta n(\vec{r}^{\,\prime})}\right|_{+} - \left.\frac{\delta^2 E_{\mathrm{xc}}[n]}{\delta n(\vec{r})\delta n(\vec{r}^{\,\prime})}\right|_{-}$, which is the so-called discontinuity of the xc kernel at integer electron number, diverges exponentially as $r \to \infty$. $F[n]$ is decomposed as $F[n] = T_s[n] + E_{\mathrm{xcH}}[n]$, with $T_s[n]$ being the noninteracting kinetic-energy density functional and $E_{\mathrm{xcH}}[n]$ the sum of $E_{\mathrm{xc}}[n]$ and the classical Coulomb repulsion, or Hartree, functional. Since the latter is continuously differentiable, $E_{\mathrm{xcH}}[n]$'s discontinuity properties are the same as $E_{\mathrm{xc}}[n]$'s. The divergent behavior of $\left.\frac{\delta^2 E_{\mathrm{xcH}}[n]}{\delta n(\vec{r})\delta n(\vec{r}^{\,\prime})}\right|_{+}$ is closely related with long-range correlation effects [81, 82], therefore it is unlikely to be canceled by $\left.\frac{\delta^2 T_s[n]}{\delta n(\vec{r})\delta n(\vec{r}^{\,\prime})}\right|_{+}$; consequently, $\left.\frac{\delta^2 F[n]}{\delta n(\vec{r})\delta n(\vec{r}^{\,\prime})}\right|_{+}$ diverges asymptotically, too. This then immediately gives that $\left.\frac{\delta\mu[n]}{\delta n(\vec{r})}\right|_{+} = \left.\frac{\delta^2 F[n]}{\delta n(\vec{r})\delta n(\infty)}\right|_{+}$ is ill-defined, being infinite at every $\vec{r}$!

Thus, the unrestricted derivative of μ with respect to the density is ill-defined—at least, as long as we insist that the zero of energy should be fixed according to $v(\infty) = 0$ for Coulombic potentials. If we chose some other, even though nonphysical, fixation such as $\int g(\vec{r})v(\vec{r})\mathrm{d}\vec{r} = 0$, for example, (where $g(\vec{r})$ is some fixed function that integrates to one and tends fast to zero with $\vec{r} \to \infty$), we would obtain $\mu[n] = \int g(\vec{r})\frac{\delta F[n]}{\delta n(\vec{r})}\mathrm{d}\vec{r}$ for any potentials, which, then, would yield a proper derivative—but not of the *real* chemical potential. We refer to [84] for further insight into this issue and for a discussion of the related issue of the ground-state energy as a functional solely of the density.

Since the appearance of a preliminary version of the present work as an arXiv preprint (arXiv:1107.4249v4), a related study has been published by Cuevas-Saavedra et al. [85]. These authors deal with the problem of how to calculate the unconstrained local hardness Eq. (17) and conclude from similar contradictions as those pointed out in [84] that this local hardness concept is infinitely ill-conditioned and argue further that it diverges exponentially fast asymptotically. Our conclusions thus go further; Eq. (17) is completely ill-defined for electronic systems.

5 Local hardness as a constrained derivative with respect to the density

It has thus been found that one cannot obtain a local hardness measure by $\eta(\vec{r}) = \left.\frac{\delta\mu[N[n],v[n]]}{\delta n(\vec{r})}\right|_{v} f(\vec{r})$, since one of the two mathematically allowed forms, Eq. (29), is ill-defined, while the other one, $\eta(\vec{r}) = \eta f(\vec{r})$, is simply a measure of local softness in the case of soft systems. However, one may raise the question: Could we consider Eq. (14) *directly* as some local hardness measure, irrespective of it being able to deliver a proper regional hardness concept or not? That is, one would not be interested in getting hardness values corresponding to regions of molecules, but only in obtaining a pointwise measure, which, besides, should deliver the global hardness [via Eq. (7)]—but not regional ones. Although this is a questionable concept [see the argument above Eq. (21)], it may still seem to be plausible to consider Eq. (14) some kind of local counterpart of hardness due to its intuitive interpretation as a measure of how the chemical potential changes if the number of electrons is increased locally (by an infinitesimal amount) in a given external potential setting. Therefore, we will explicitly examine this option, too.

So, we are interested in finding a fixation of the ambiguity of Eq. (14) that would properly characterize the chemical potential change due to a density change at $\vec{r}$ when the density domain is restricted to densities corresponding to a given $v(\vec{r}^{\,\prime})$. This requires a proper modification of the unconstrained "gradient" $\frac{\delta\mu}{\delta n(\vec{r})}$, which leads us to the concept of constrained derivatives [86–88]. (Note the difference of the names "restricted derivative" and "constrained derivative" [53]. This is not a canonized terminology yet, but the names should be different for these two conceptually, and also manifestly, different entities.) To see how this concept works, consider the case of the simple

N-conservation constraint, $\int n(\vec{r})\mathrm{d}\vec{r}=N$; that is, the domain of $n(\vec{r})$'s is restricted to those integrating to a given N. The functional derivative $\frac{\delta A[n]}{\delta n(\vec{r})}$ is obtained from the first-order differential Eq. (25a) by inserting $\Delta n(\vec{r}^{\,\prime})=\delta(\vec{r}^{\,\prime}-\vec{r})$. That is, we obtain the functional derivative (i.e., gradient) by weighting all (independent) directions in the functional domain equally. In a case the functional domain is restricted by some constraint $C[n]=C$, the allowed directions are restricted by Eq. (26); consequently, $\delta(\vec{r}^{\,\prime}-\vec{r})$ cannot be inserted in Eq. (25a). We need to find a modification of $\delta(\vec{r}^{\,\prime}-\vec{r})$, or in general, of $\Delta n(\vec{r}^{\,\prime})$, that is in accordance with the constraint. For the N-conservation constraint, this is achieved by $\Delta_N n(\vec{r}^{\,\prime})=\int\Big(\delta(\vec{r}^{\,\prime}-\vec{r}^{\,\prime\prime})-u(\vec{r}^{\,\prime})\Big)\Delta n(\vec{r}^{\,\prime\prime})d\vec{r}^{\,\prime\prime}$ [86–88], where $u(\vec{r})$ is a function that integrates to one. Inserting this $\Delta_N n(\vec{r}^{\,\prime})$ in Eq. (25a) and taking $\Delta n(\vec{r}^{\,\prime\prime})=\delta(\vec{r}^{\,\prime\prime}-\vec{r})$ yields the proper modification of a derivative $\frac{\delta A[n]}{\delta n(\vec{r})}$: $\frac{\delta A[n]}{\delta_N n(\vec{r})}=\frac{\delta A[n]}{\delta n(\vec{r})}-\int u(\vec{r}^{\,\prime})\frac{\delta A[n]}{\delta n(\vec{r}^{\,\prime})}\mathrm{d}\vec{r}^{\,\prime}$. The key for obtaining the constrained derivative for a given constraint $C[n]=C$, thus, is to find the $\Delta_C n(\vec{r}^{\,\prime})$'s that obey the constraint, that is, $C[n+\Delta_C n]-C[n]=0$.

Now, consider the domain determined by the fixed-$v(\vec{r})$ constraint. This domain of $n(\vec{r})$'s will be a very thin domain—literally; it will be a single chain of densities $n(\vec{r})[N,v]$, with only N changing (nondegeneracy is assumed, of course, which is a basic requirement when dealing with $n(\vec{r})[v]$). Consequently, there is not much choice in writing a proper $\Delta_v n(\vec{r}^{\,\prime})$. The only possible form is

$$\Delta_v n(\vec{r}^{\,\prime})=\frac{\partial n(\vec{r}^{\,\prime})[N,v]}{\partial N}\Delta N+\text{higher-order terms}. \tag{47}$$

Inserting this in Eq. (25a),

$$D(A)[n,\Delta_v n]=\frac{\partial A[n[N,v]]}{\partial N}\Delta N+\text{higher-order terms} \tag{48}$$

arises via an application of the chain rule of differentiation. By utilizing $\Delta N=\int\Delta n(\vec{r}^{\,\prime})\mathrm{d}\vec{r}^{\,\prime}$ and taking $\Delta n(\vec{r}^{\,\prime})=\delta(\vec{r}^{\,\prime}-\vec{r})$ (while neglecting the terms higher-order in $\Delta n(\vec{r})$, which appear due to the nonlinearity of the constraint [88]), from Eq. (48), we then obtain

$$\frac{\delta A[n]}{\delta_v n(\vec{r})}=\frac{\partial A[n[N,v]]}{\partial N} \tag{49}$$

as the constrained derivative corresponding to the $v(\vec{r})$-conservation constraint. Interestingly, though not surprisingly (considering the very restrictive nature of the fixed-$v(\vec{r})$ constraint), there is no ambiguity at all in this expression—contrary to the N-conserving derivative, for example, where $u(\vec{r})$ represents an ambiguity.

Thus, we obtain that the only mathematically allowed derivative of μ with respect to the density under the fixed-$v(\vec{r})$ constraint (that may bear relevance *in itself*) is

$$\frac{\delta\mu}{\delta_v n(\vec{r})}=\frac{\partial\mu[N,v]}{\partial N} \tag{50}$$

(that is, the $v(\vec{r})$-constrained, or "$v(\vec{r})$-conserving," derivative of the chemical potential with respect to the density is simply its partial derivative with respect to N). Note that $\mu[N[n[N,v]],v[n[N,v]]]=\mu[N,v]$. It turns out, thus, that the severe ambiguity of Eq. (14), embodied in Eq. (35), can be narrowed down to the single choice of $\lambda(\vec{r})=0$—which is the constant local hardness of Eq. (8). That is, while the definition of a functional derivative leads to an ambiguity, Eq. (35), under a fixed-$v(\vec{r})$ constraint, this ambiguity disappears if one wishes to use this derivative *in itself* as a physical quantity. However, the constant local hardness will not give a *local counterpart* of hardness.

We can sum up our findings so far as: Here, we have shown that Eq. (8) is the only mathematically allowed choice if one wishes to obtain a local hardness measure *directly by* Eq. (14), while previously we have shown that if we want to have a local hardness measure by $\left.\frac{\delta\mu}{\delta n(\vec{r})}\right|_v f(\vec{r})$, in order to have regional hardnesses as well, *then* the only allowed choices are $\eta f(\vec{r})$ and Eq. (29)—but the former cannot be a (general) local hardness measure because of its proportionality to the Fukui function.

6 The parallel problem of defining a local chemical potential

Defining a local hardness via Eq. (14) naturally raises the idea of defining a local counterpart of the chemical potential $\mu=\left(\frac{\partial E[N,v]}{\partial N}\right)_{v(\vec{r})}$ itself in a similar fashion. By a local counterpart of μ, we mean a local index that indicates the local distribution of μ *within* a given ground-state system, that is, not some $\vec{r}$-dependent chemical potential concept, like that of [13], that yields μ as its special, ground-state, case. We may introduce the following local quantity:

$$\tilde{\mu}(\vec{r})=\left.\frac{\delta E[N[n],v[n]]}{\delta n(\vec{r})}\right|_{v(\vec{r})}, \tag{51}$$

which parallels Eq. (14). Of course, we then have the same kind of ambiguity problem as in the case of Eq. (14).

Fixing $v(\vec{r})$ as one of the variables of $E[N,v]$ will not yield a $\tilde{\mu}(\vec{r})$ that is a local measure of the chemical potential, similarly to Eq. (8), since this $\tilde{\mu}(\vec{r})$ will be constant in space—the chemical potential itself:

$$\tilde{\mu}(\vec{r}) = \left(\frac{\partial E[N,v]}{\partial N}\right)_{v(\vec{r})} \frac{\delta N}{\delta n(\vec{r})} = \mu. \tag{52}$$

Equation (52) may be obtained in another way as well, since the ground-state energy as a functional of the ground-state density can be obtained via two routes:

$$E[n] \equiv E[N[n], v[n]] \equiv E_{v[n]}[n]. \tag{53}$$

The first route is through $E[N,v]$, while the second is through the energy density functional Eq. (10) of DFT—in both cases, the functional dependence of $v(\vec{r})$ on $n(\vec{r})$ is inserted into the corresponding places. Then, specifically, $\left.\frac{\delta E[n]}{\delta n(\vec{r})}\right|_v$ may be $\left(\frac{\delta E_v[n]}{\delta n(\vec{r})}\right)_v$, which equals μ on the basis of Eq. (9), giving the $\tilde{\mu}(\vec{r})$ of Eq. (52). We note here that the idea of a local chemical potential concept has been raised previously by Chan and Handy [89], as a limiting case of their more general concept of shape chemical potentials; however, they automatically took the energy derivative with respect to the density as the constant $\left(\frac{\delta E_v[n]}{\delta n(\vec{r})}\right)_v$, ignoring other possibilities. The constant local chemical potential concept of Eq. (52) is of course not without use; it may be considered as an equalized $\vec{r}$-dependent chemical potential, defined by $\mu(\vec{r}) \doteq \frac{\delta F[n]}{\delta n(\vec{r})} + v(\vec{r})$ [13], which gives a formal background for the electronegativity equalization principle [13]. The latter $\mu(\vec{r})$, however, is not a local chemical potential in the sense that it would be the local counterpart of a global property (μ), but it is rather a kind of intensive quantity, which becomes constant when reaching equilibrium (here, ground state). Similar can be said of the $\vec{r}$-dependent, generalized hardness concept defined by Eq. (13) for general densities.

A general property of a $\tilde{\mu}(\vec{r})$ defined through Eq. (51) is

$$\int \tilde{\mu}(\vec{r}) f(\vec{r}) \mathrm{d}\vec{r} \equiv \int \left.\frac{\delta E[n]}{\delta n(\vec{r})}\right|_v \left(\frac{\partial n(\vec{r})[N,v]}{\partial N}\right)_v \mathrm{d}\vec{r} = \mu; \tag{54}$$

that is, it gives the chemical potential after integration when multiplied by the Fukui function—analogously to Eq. (7). We emphasize again that in spite of the great extent of ambiguity in Eq. (51), all choices will indeed give μ in Eq. (54), due to the fact that the density in $\left(\frac{\partial n(\vec{r})}{\partial N}\right)_v$ is varied with the external potential fixed, and in cases like this, the ambiguity of the inner derivative of the composite functional cancels out [53].

An appealing choice of the restricted derivative in Eq. (51) may be the unrestricted derivative,

$$\tilde{\mu}(\vec{r}) = \frac{\delta E[N[n], v[n]]}{\delta n(\vec{r})}. \tag{55}$$

This quantity gives to what extent the ground-state energy changes when the density is changed by an infinitesimal amount at a given point in space. There will be places $\vec{r}$ in a given molecule where an infinitesimal change of $n(\vec{r})$ (at the given $\vec{r}$) would imply a greater change of the energy, while at other places, it would imply a smaller change in E, going together with a higher and a lower local value of $|\tilde{\mu}(\vec{r})|$, respectively. The most sensitive site of a molecule toward receiving an additional amount of electron (density) will be the site with the lowest value of $\tilde{\mu}(\vec{r})$, implying the biggest decrease in the energy due to an increase in the density at $\vec{r}$ by an infinitesimal amount—but only if the external potential changes accordingly. [Note that since the fixed external potential setting is an inherent part of the concept of the chemical potential, Eq. (55) cannot be a local counterpart of the chemical potential, but when multiplied by the Fukui function, below, a fixation of $v(\vec{r})$ appears in the emerging $\mu(\vec{r})$.] Equation (55) can be evaluated as

$$\begin{aligned} \tilde{\mu}(\vec{r}) &= \frac{\partial E[N,v]}{\partial N} + \int \frac{\delta E[N,v]}{\delta v(\vec{r}\,')} \frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})} \mathrm{d}\vec{r}\,' \\ &= \mu + \int n(\vec{r}\,') \frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})} \mathrm{d}\vec{r}\,', \end{aligned} \tag{56a}$$

or alternatively,

$$\begin{aligned} \tilde{\mu}(\vec{r}) &= \frac{\delta E_v[n]}{\delta n(\vec{r})} + \int \frac{\delta E_v[n]}{\delta v(\vec{r}\,')} \frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})} \mathrm{d}\vec{r}\,' \\ &= \mu + \int n(\vec{r}\,') \frac{\delta v(\vec{r}\,')}{\delta n(\vec{r})} \mathrm{d}\vec{r}\,', \end{aligned} \tag{56b}$$

where Eqs. (9) and (10) have been utilized. Note that the second term of Eqs. (56a, 56b) integrates to zero when multiplied by $f(\vec{r})$, as $v(\vec{r})$ is independent of N.

Equation (55) is not only an appealing choice in Eq. (51), but also, on the basis of the argument given in the case of the local hardness in Sect. 3, it is one of the two mathematically allowed choices to obtain a local chemical potential concept. The emerging local chemical potential is

$$\mu(\vec{r}) = \frac{\delta E}{\delta n(\vec{r})} f(\vec{r}), \tag{57}$$

which gives regional chemical potentials via

$$\mu_\Omega = \int_\Omega \mu(\vec{r}) \mathrm{d}\vec{r}. \tag{58}$$

(Just as in the case of Eq. (29), applying other choices of $\tilde{\mu}(\vec{r})$ of Eq. (51) in Eq. (57) would lead to an improper modification of the regional chemical potential values.) Unfortunately, however, the evaluation of $\frac{\delta E}{\delta n(\vec{r})}$ meets the same principal problem as the evaluation of $\frac{\delta \mu}{\delta n(\vec{r})}$. Inserting Eq. (37) in Eq. (56) gives

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \mu + N\frac{\delta \mu[n]}{\delta n(\vec{r})} - \int n(\vec{r}\,')\frac{\delta^2 F[n]}{\delta n(\vec{r})\delta n(\vec{r}\,')}\mathrm{d}\vec{r}\,', \tag{59}$$

which shows that $\mu[n]$'s derivative appears as a component in $E[n]$'s derivative.

It is interesting to observe that the last term of Eq. (59) is just the original local hardness expression of Berkowitz et al. [32], Eq. (16), times N. Equation (59) indicates that large (positive) values of Eq. (16) imply that the global value μ is more decreased by them at the given points in space. This throws more light upon the recent finding [90] that Eq. (16) is a local indicator of *sensitivity* toward perturbations, which goes against the essence of the concept of local hardness. (The latter is not surprising in the view of Sects. 3 and 5—actually nothing supports Eq. (16) as a formula for local hardness.)

The other possible way to obtain a local chemical potential measure is

$$\mu(\vec{r}) = \left(\frac{\delta E[N,v]}{\delta n(\vec{r})}\right)_v f(\vec{r}) = \mu f(\vec{r}), \tag{60}$$

similar to the case of local hardness. In that case, $\eta(\vec{r}) = \eta f(\vec{r})$ could not give a correct local hardness measure since the Fukui function $f(\vec{r})$ is actually not an indicator of hard sites, while here the question is as to whether $f(\vec{r})$ can be considered an indicator of local electronegativity, $-\mu(\vec{r})$, or not (note that μ is negative, and minus the chemical potential is the electronegativity). A positive answer would imply, for example, that two soft systems interact through their highest-local-electronegativity sites. However, to judge the appropriateness of such a possible role of $f(\vec{r})$, it should first be clarified what to expect from a local electronegativity concept—a matter well-worth of future studies. We note that Eq. (60) gives a possible local hardness index via $\eta(\vec{r}) = \left(\frac{\partial \mu(\vec{r})}{\partial N}\right)_v$.

Also just as in the case of the local hardness, one may examine the question as to what choices of Eq. (51) are allowed if one wishes to use Eq. (51) *itself* as a local chemical potential measure, without obtaining regional chemical potentials via $\mu_\Omega = \int_\Omega \tilde{\mu}(\vec{r}) f(\vec{r})\mathrm{d}\vec{r}$. Similarly, as in Sect. 5, it can be shown that actually the only possible choice to fix Eq. (51)'s ambiguity is given by the unique constrained derivative of the energy (with respect to the density) corresponding to the fixed-$v(\vec{r})$ constraint, which turns out to be

$$\frac{\delta E}{\delta_v n(\vec{r})} = \frac{\partial E[N,v]}{\partial N}, \tag{61}$$

that is, the constant $\tilde{\mu}(\vec{r})$ of Eq. (52). That is, Eq. (51) cannot be taken as the direct definition of a local chemical potential, as it will only give back the chemical potential itself. Of course, as noted earlier, a constant local chemical potential can still be a special, equalized, case of a generalized, $\vec{r}$-dependent, chemical potential concept [13]—but it will not give a local reactivity index, characterizing molecular sites within individual species. We emphasize that Eq. (61) is not a trivial result obtained by the explicit fixation of $v(\vec{r})$ of $E[N[n],v]$, that is, by $\left(\frac{\delta E[N[n],v]}{\delta n(\vec{r})}\right)_v$, but it is the derivative of $E[N[n],v[n]]$ with respect to $n(\vec{r})$ under the constraint of fixed $v(\vec{r})$.

Finally, in parallel with Sect. 3, we may consider the external potential derivative of the energy,

$$\left(\frac{\delta E}{\delta v(\vec{r})}\right)_N = \int \left(\frac{\delta E[N,v[n]]}{\delta n(\vec{r}\,')}\right)_N \left(\frac{\delta n(\vec{r}\,')}{\delta v(\vec{r})}\right)_N d\vec{r}\,', \tag{62}$$

which gives the density, Eq. (19). External potential-based reactivity indices have proved to be useful and have been much investigated [91–101]. The regional contributions to Eq. (62) are

$$n_\Omega(\vec{r}) = \int_\Omega \left(\frac{\delta E[N,v[n]]}{\delta n(\vec{r}\,')}\right)_N \left(\frac{\delta n(\vec{r}\,')}{\delta v(\vec{r})}\right)_N d\vec{r}\,'. \tag{63}$$

Equation (63) gives a density component that can be viewed as the contribution of the given region Ω to $n(\vec{r})$. Here, an interesting application of Eq. (63) may be worth mentioning (disregarding the fact that $(\delta E/\delta n(\vec{r}))_N$ is ill-defined). A natural decomposition of the density is the one in terms of the occupied Kohn–Sham orbitals,

$$n(\vec{r}) = \sum_{i=1}^{N} |\varphi_i(\vec{r})|^2. \tag{64}$$

One may then look for regions Ω_i ($i = 1,\ldots,N$) of the given molecule that contribute $n_{\Omega_i}(\vec{r}) = |\varphi_i(\vec{r})|^2$ to $n(\vec{r})$ on the basis of Eq. (63). Of course, this may imply a highly ambiguous result; however, the number of possible divisions of the molecule into Ω_i's can be significantly reduced by searching for Ω_i's around the intuitively expectable regions where the single $n_i(\vec{r})$'s are dominant. In this way, one would find a spatial division of a molecule into subshells. To go even further, one might assume that by applying the regions Ω_i found in this way in Eq. (23), the corresponding $f_{\Omega_i}(\vec{r})$'s would emerge to be $f_{\Omega_i}(\vec{r}) = \partial n_i(\vec{r})/\partial N$.

7 Conclusions

The traditional approach to defining a local measure of chemical hardness, by the derivative of the chemical potential with respect to the density subject to the constraint of a fixed external potential, has been re-examined. Although several problematic aspects of this approach, most importantly its ambiguity, had been pointed out before, it had still been widely taken as a necessary framework to define a local hardness index. The ambiguity aspect is a negative feature since one then needs to find the proper choice among the many possibilities, but at the same time, it gives hope that other concrete choice(s) to fix the ambiguity than those having proved to have various deficiencies may be found to serve better as a local hardness measure. However, we have shown in this study that the traditional approach is actually not ambiguous. The only mathematically allowed local hardness definitions emerging via that approach are (1) the one that gives the hardness itself in every point of space and (2) the one where the external potential constraint is actually dropped. In the latter case, however, the emerging local quantity is not yet to be considered a local hardness, but it should be multiplied by the Fukui function to get that. The first option arises as the unique constrained derivative corresponding to the fixed external potential constraint. The constancy of this quantity, however, makes it a useless concept as a local reactivity indicator. Although the local hardness concept emerging from the unrestricted chemical potential derivative [option (2)] may be intuitively appealing, unfortunately it has been found that this concept is ill-defined, due to the fact that the chemical potential as a functional solely of the density is given by the asymptotic value of the derivative of the electronic internal energy density functional. Similar problems have been pointed out in defining a local chemical potential, as a local reactivity indicator, by the derivative of the ground-state energy with respect to the electron density. Our conclusion is that making the electron number local in the definitions of hardness and chemical potential, by substituting it with the electron density, is not a feasible approach to obtain local counterparts of these global reactivity descriptors; therefore, an essentially new way of defining corresponding local descriptors is necessary to be found.

Acknowledgments The author acknowledges grants from the Netherlands Fund for Scientific Research (NWO) and the U.S. Department of Energy TMS Program (Grant No. DE-SC0002139). A preliminary version of this paper was published as an arXiv preprint (arXiv:1107.4249v4) on 30 August 2011.

References

1. Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, New York
2. Chermette H (1999) J Comput Chem 20:129
3. Geerlings P, De Proft F, Langenaeker W (2003) Chem Rev 103:1793
4. Ayers PW, Anderson JSM, Bartolotti LJ (2005) Int J Quantum Chem 101:520
5. Cohen MH, Wasserman A (2007) J Phys Chem A 111:2229
6. Gázquez JL (2008) J Mex Chem Soc 52:3
7. Geerlings P, De Proft F (2008) Phys Chem Chem Phys 10:3028
8. Liu SB (2009) Acta Phys Chim Sin 25:590
9. Roy RK, Saha S (2010) Annu Rep Prog Chem Sect C Phys Chem 106:118
10. Pauling L (1932) J Am Chem Soc 54:3570
11. Mulliken RS (1934) J Chem Phys 2:782
12. Iczkowski RP, Margrave JL (1961) J Am Chem Soc 83:3547
13. Parr RG, Donnelly RA, Levy M, Palke WE (1978) J Chem Phys 68:3801
14. Pearson RG (1963) J Am Chem Soc 85:3533
15. Parr RG, Pearson RG (1983) J Am Chem Soc 105:7512
16. Sen KD (ed) (1993) Chemical hardness, Structure and bonding, vol 80. Springer, Heidelberg
17. Pearson RG (1997) Chemical hardness: applications from molecules to solids. Wiley-VCH, Oxford
18. Sanderson RT (1951) Science 114:670
19. Chattaraj PK, Lee H, Parr RG (1991) J Am Chem Soc 113:1855
20. Gázquez JL (1997) J Phys Chem A 101:4657
21. Gázquez JL (1997) J Phys Chem A 101:9464
22. Ayers PW (2005) J Chem Phys 122:141102
23. Ayers PW, Parr RG, Pearson RG (2006) J Chem Phys 124:194107
24. Ayers PW (2007) Faraday Discuss 135:161
25. Pearson RG (1987) J Chem Educ 64:561
26. Parr RG, Chattaraj PK (1991) J Am Chem Soc 113:1854
27. Pearson RG (1999) J Chem Educ 76:267
28. Ayers PW, Parr RG (2000) J Am Chem Soc 122:2010
29. Torrent-Sucarrat M, Luis JM, Duran M, Solà M (2001) J Am Chem Soc 123:7951
30. Chattaraj PK, Ayers PW, Melin J (2007) Phys Chem Chem Phys 9:3853
31. Yang WT, Parr RG (1985) Proc Natl Acad Sci USA 82:6723
32. Berkowitz M, Ghosh SK, Parr RG (1985) J Am Chem Soc 107:6811
33. Ghosh SK (1990) Chem Phys Lett 172:77
34. Harbola MK, Chattaraj PK, Parr RG (1991) Isr J Chem 31:395
35. Gázquez JL (1993) Struct Bond 80:27
36. Chattaraj PK, Roy DR, Geerlings P, Torrent-Sucarrat M (2007) Theor Chem Acc 118:923
37. Torrent-Sucarrat M, Salvador P, Solà M, Geerlings P (2008) J Comput Chem 29:1064
38. Ayers PW, Parr RG (2008) J Chem Phys 128:184108
39. Saha S, Roy RK (2008) Phys Chem Chem Phys 10:5591
40. Gál T, Geerlings P, De Proft F, Torrent-Sucarrat M (2011) Phys Chem Chem Phys 13:15003
41. Torrent-Sucarrat M, De Proft F, Geerlings P, Ayers PW (2008) Chem Eur J 14:8652
42. Torrent-Sucarrat M, De Proft F, Ayers PW, Geerlings P (2010) Phys Chem Chem Phys 12:1072
43. Li Y, Evans JNS (1995) J Am Chem Soc 117:7756

44. Chattaraj PK (2001) J Phys Chem A 105:511
45. Melin J, Aparicio F, Subramanian V, Galván M, Chattaraj PK (2004) J Phys Chem A 108:2487
46. Anderson JSM, Melin J, Ayers PW (2007) J Chem Theory Comp 3:358
47. Parr RG, Yang WT (1984) J Am Chem Soc 106:4049
48. Datta D (1986) J Phys Chem 90:4216
49. Ayers PW (2007) Chem Phys Lett 438:148
50. Ayers PW, Parr RG (2008) J Chem Phys 129:054111
51. Ghosh DC, Islam N (2010) Int J Quantum Chem 111:1961
52. Ayers PW (2007) Theor Chem Acc 118:371
53. Gál T (2007) J Math Chem 42:661
54. Parr RG, Bartolotti LJ (1983) J Phys Chem 87:2810
55. Berkowitz M, Parr RG (1988) J Chem Phys 88:2554
56. Chattaraj PK, Cedillo A, Parr RG (1995) J Chem Phys 103:7645
57. Mignon P, Loverix S, Steyaert J, Geerlings P (2005) Nucl Acid Res 33:1779
58. Olasz A, Mignon P, De Proft F, Veszpremi T, Geerlings P (2005) Chem Phys Lett 407:504
59. Ozen AS, De Proft F, Aviyente V, Geerlings P (2006) J Phys Chem A 110:5860
60. Wiśniewski M, Gauden PA (2009) Appl Surf Sci 255:4782
61. Saha S, Roy RK (2007) J Phys Chem B 111:9664
62. Gupta VP, Rawat P, Singh RN, Tandon P (2012) Comput Theor Chem 983:7
63. Garza J, Robles J (1994) Int J Quantum Chem 49:159
64. Ghanty TK, Ghosh SK (1994) J Phys Chem 98:9197
65. Chattaraj PK, Cedillo A, Parr RG (1995) J Chem Phys 103:10621
66. Fuentealba P (1995) J Chem Phys 103:6571
67. Liu SB, De Proft F, Parr RG (1997) J Phys Chem A 101:6991
68. Torrent-Sucarrat M, Geerlings P (2006) J Chem Phys 125:244101
69. Borgoo A, Torrent-Sucarrat M, De Proft F, Geerlings P (2007) J Chem Phys 126:234104
70. Sarkar U, Khatua M, Chattaraj PK (2012) Phys Chem Chem Phys 14:1716
71. Langenaeker W, De Proft F, Geerlings P (1995) J Phys Chem 99:6424
72. Jameson CJ, Buckingham AD (1980) J Chem Phys 73:5684, and references therein
73. Tozer DJ, Handy NC, Green WH (1997) Chem Phys Lett 273:183
74. Tozer DJ (1997) Phys Rev A 56:2726
75. Tozer DJ, Handy NC (1998) J Chem Phys 109:10180
76. Perdew JP, Parr RG, Levy M, Balduz JL (1982) Phys Rev Lett 49:1691
77. Gál T, Geerlings P (2010) J Chem Phys 133:144105
78. Sagvolden E, Perdew JP (2008) Phys Rev A 77:012517
79. Katriel J, Davidson ER (1980) Proc Natl Acad Sci USA 77:4403
80. Levy M, Perdew JP, Sahni V (1984) Phys Rev A 30:2745
81. Hellgren M, Gross EKU (2012) Phys Rev A 85:022514
82. Gritsenko O, Baerends EJ (2004) J Chem Phys 121:655
83. Gál T, Ayers PW, De Proft F, Geerlings P (2009) J Chem Phys 131:154114
84. T. Gál, arXiv:1108.3865v2 (2011)
85. Cuevas-Saavedra R, Rabi N, Ayers PW (2011) Phys Chem Chem Phys 13:19594
86. Gál T (2001) Phys Rev A 63:022506, 74:029901(E)
87. Gál T (2002) J Phys A 35:5899
88. Gál T (2010) J Phys A 43:425208
89. Chan GK-L, Handy NC (1998) J Chem Phys 109:6287
90. Ayers PW, Liu S, Li T (2011) Phys Chem Chem Phys 13:4427
91. Fuentealba P, Parr RG (1991) J Chem Phys 94:5559
92. Senet P (1996) J Chem Phys 105:6471
93. Contreras R, Domingo LR, Andrés J, Pérez P, Tapia O (1999) J Phys Chem A 103:1367
94. Ayers PW, Levy M (2000) Theor Chem Acc 103:353
95. Chamorro E, Contreras R, Fuentealba P (2000) J Chem Phys 113:10861
96. Ayers PW, Parr RG (2001) J Am Chem Soc 123:2007
97. Morell C, Grand A, Toro-Labbé A (2005) J Phys Chem A 109:205
98. Morell C, Grand A, Toro-Labbé A (2006) Chem Phys Lett 425:342
99. Liu S, Li T, Ayers PW (2009) J Chem Phys 131:114106
100. Sablon N, De Proft F, Ayers PW, Geerlings P (2010) J Chem Theory Comput 6:3671
101. Sablon N, De Proft F, Geerlings P (2010) Chem Phys Lett 498:192