

Hierarchy of local chemical reactivity indices originated from a local energy

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Abstract: The traditional way of defining a local measure of chemical hardness has several drawbacks, which undermine the applicability of that local hardness concept. We propose a new approach to this problem, by originating a local chemical potential, a corresponding local hardness, and local hyperhardnesses, from a local energy concept. A chemical potential kernel is also defined, by which a recently proposed alternative local chemical potential and local hardness concept can also be incorporated into this scheme of local reactivity indices.

I. Introduction

Conceptual density functional theory (DFT) [1,2] offers a wide range of chemical reactivity indices for the description of chemical processes. An important aim of conceptual DFT 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. This would also make the establishment of local generalizations of the principles based on global reactivity descriptors, such as the electronegativity equalization principle [3], the hard/soft acid/base principle [4,5] or the maximum hardness principle [6,7], possible. Defining local counterparts of global quantities, of course, goes together with ambiguity issues, which has led to serious question marks regarding the applicability of local hardness [8-18], the local version of chemical hardness [4,19]. Even in the case of local softness [20], the definition of which seemed to be without problems on the basis of the softness concept, the inverse of hardness, it has been found that it is a proper local measure of softness only in (globally) soft electronic systems [14,17].

Very recently, a new approach to local hardness has been proposed [18], via defining a local chemical potential with the help of the concept of constrained derivatives [21], the derivative of which with respect to the electron number then delivers a local hardness, just as the derivative of the chemical potential with respect to N gives the hardness. This new local hardness has the advantageous properties of (i) integrating to the hardness, and (ii) being in a local inverse relation with the Fukui function [22], which has long been established as a proper measure of local softness in the case of soft electron systems. Numerical tests have also supported this choice as a local measure of hardness, giving proper results for the critical test molecule benzocyclobutadiene, for which the traditional definitions [8,9] have failed.

As it is not clear, however, to what extent the local chemical potential obtained as an auxiliary quantity towards a local hardness in [18] can be considered as a proper local counterpart of the chemical potential, in [23], an alternative way of defining a local chemical potential concept, and a corresponding local hardness concept, has been raised. Both approaches [18,23] to a local chemical potential concept have theoretical support behind it, and both are reasonable to expect that it can be a good basis for a local hardness concept; so the question raises which one to choose, or should we drop one of them at all? In this paper, both concepts will be shown to be parts of a unified hierarchy of local reactivity descriptors, emerging from a local energy concept.

II. Background

From the definition of softness,

$$S = \left(\frac{\partial N}{\partial \mu} \right)_{v(\bar{r})} , \quad (1)$$

an apparent way arises for defining a corresponding local quantity [20],

$$s(\bar{r}) = \left(\frac{\partial n(\bar{r})}{\partial \mu} \right)_{v(\bar{r})} , \quad (2)$$

named local softness, since we have a spatial distribution of the electron number N , the integral of which gives back this number. This way of originating a local measure of softness is strengthened by the fact that this $s(\bar{r})$ is proportional to the Fukui function [22],

$$f(\bar{r}) = \left(\frac{\partial n(\bar{r})}{\partial N} \right)_{v(\bar{r})} , \quad (3)$$

which had proved to be a good indicator of chemically reactive (i.e., soft) sites of molecules. The proportionality of $s(\bar{r})$ to $f(\bar{r})$ emerges simply from the definition of softness, as

$$s(\bar{r}) = \left(\frac{\partial n(\bar{r})}{\partial N} \right)_{v(\bar{r})} \left(\frac{\partial N}{\partial \mu} \right)_{v(\bar{r})} = f(\bar{r}) S , \quad (4)$$

where the chain rule of differentiation is applied. It can be seen easily that $s(\bar{r})$ integrates to S , just as $f(\bar{r})$ integrates to 1. The chemical potential μ is defined as

$$\mu = \left(\frac{\partial E[N, v]}{\partial N} \right)_{v(\bar{r})} , \quad (5)$$

with $E[N, v]$ denoting the ground-state energy of the N -electron system in external potential $v(\bar{r})$. μ has been identified [24] as the negative of electronegativity, and it appears, as the Lagrange-multiplier corresponding to the fixation of electron number, in the DFT Euler-Lagrange equation

$$\frac{\delta E_v[n]}{\delta n(\bar{r})} = \mu , \quad (6a)$$

i.e.

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu , \quad (6b)$$

for the determination of the ground-state electron density in a given $v(\mathbf{r})$. $F[n]$ is a density functional giving the sum of the kinetic energy and the energy of interaction with each other

of the electrons for a given density $n(\bar{r})$, and with it, the ground-state energy density functional $E_v[n]$ is given as

$$E_v[n] = F[n] + \int n(\bar{r})v(\bar{r}) d\bar{r} , \quad (7)$$

which has been used to obtain Eq.(6b) from Eq.(6a).

In the case of hardness, defined as [19]

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_{v(\bar{r})} , \quad (8)$$

no such obvious way arises to define a local counterpart as in the case of softness, since the chemical potential does not emerge as the space integral of some chemical potential density. Therefore, Berkowitz et al. [8] has proposed to define a local hardness by

$$\eta(\bar{r}) = \left(\frac{\delta \mu}{\delta n(\bar{r})} \right)_{v(\bar{r})} . \quad (9)$$

This local index is not a local quantity in the sense the local softness is, since it does not integrate to the hardness. In fact, $\eta(\bar{r})$ times the Fukui function is what gives η by integration over the whole space,

$$\int \eta(\bar{r}) f(\bar{r}) d\bar{r} = \eta , \quad (10)$$

which emerges via an application of the chain rule, as can be seen from the definitions Eqs.(3) and (9). From Eq.(9), Berkowitz et al. deduced [8]

$$\eta(\bar{r}) = \int \frac{\delta^2 F}{\delta n(\bar{r}) \delta n(\bar{r}')} \frac{n(\bar{r}')}{N} d\bar{r}' , \quad (11)$$

which has been found to be a useful local indicator of hardness in many applications. Ghosh [9] has proposed an alternative expression,

$$\eta(\bar{r}) = \int \frac{\delta^2 F}{\delta n(\bar{r}) \delta n(\bar{r}')} f(\bar{r}') d\bar{r}' , \quad (12)$$

as local hardness, which, too, satisfies Eq.(10). However, as has been recognized by Harbola et al. [11], Eq.(12) gives just the global hardness in every point of space, which can be seen if one differentiates Eq.(6b) with respect to the density while keeping the $v(\mathbf{r})$ appearing explicitly in Eq.(6b) fixed, then inserts the result into Eq.(12), and uses Eq.(10). Or in short, $\mu[N, v]$ can be given on the basis of Eq.(6b) as

$$\mu[N, v] = \frac{\delta F}{\delta n(\mathbf{r})} [n[N, v]] + v(\mathbf{r}) , \quad (13)$$

from which then

$$\eta = \left(\frac{\partial \mu[N, v]}{\partial N} \right)_v = \int \frac{\delta^2 F}{\delta n(\bar{r}) \delta n(\bar{r}')} \left(\frac{\partial n(\bar{r}')}{\partial N} \right)_v d\bar{r}' = \eta(\bar{r}) . \quad (14)$$

Notice that an equivalent of Eq.(14) follows directly from the definition of $\eta(\bar{r})$ by Eq.(9), if the fixation of $v(\bar{r})$ is considered as a fixation of one of the variables of $\mu[N, v]$ as suggested by the definition of the hardness η itself, Eq.(8), since

$$\eta(\bar{r}) = \left(\frac{\delta \mu[N, v]}{\delta n(\bar{r})} \right)_v = \left(\frac{\partial \mu[N, v]}{\partial N} \right)_v \frac{\delta N}{\delta n(\bar{r})} = \eta , \quad (15)$$

by an application of the chain rule. The reason for that a nonuniform $\eta(\bar{r})$ is obtained in the form of Eq.(11) is that the fixed- $v(\bar{r})$ constraint in Eq.(9) may be considered as a constraint on the differentiation with respect to the density, i.e.

$$\eta(\bar{r}) = \left. \frac{\delta \mu[N[n], v[n]]}{\delta n(\bar{r})} \right|_{v(\bar{r})} , \quad (16)$$

to avoid the trivial local hardness concept of Eq.(15). However, as Eq.(16) is a restricted derivative, it is not uniquely determined (see Sec.II of [25] for a general discussion) – similar to the case of derivatives restricted to a domain of densities with a given normalization (i.e. particle number), which derivatives are determined only up to an arbitrary additive constant [1,26]. Consequently, Eq.(11) is not the only possible expression for $\eta(\bar{r})$ that can be obtained from Eq.(16). However, the property Eq.(10) will hold for any choice of $\eta(\bar{r})$ according to Eq.(16). Eq.(16) embraces even the case of no constraint on the differentiation at all,

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

which definition for $\eta(\bar{r})$ has been raised by Ayers and Parr [27,15].

To avoid the drawbacks associated with Eqs.(9) and (16), in [18], it has been proposed that one should go back to the original route of gaining a local quantity for the softness, and a local chemical potential $\mu(\bar{r})$ should be defined first, the derivative of which with respect to N then would deliver a local hardness concept:

$$\eta(\bar{r}) = \left(\frac{\partial \mu(\bar{r})[N, v]}{\partial N} \right)_{v(\bar{r})} . \quad (18)$$

$\mu(\bar{r})$ was defined in [18] as

$$\mu(\bar{r}) = \frac{n(\bar{r})}{N} \mu , \quad (19)$$

by utilizing the fact that the chemical potential emerges as the additive constant term in the N -conserving derivative of the energy density functional $E_v[n]$ with respect to $n(\bar{r})$, i.e.

$$\mu = \frac{1}{N} \int n(\bar{r}) \frac{\delta E_v[n]}{\delta n(\bar{r})} d\bar{r} . \quad (20)$$

Eq.(19) then yields

$$\eta(\bar{r}) = -f(\bar{r}) \left(-\frac{\mu}{N} \right) + \frac{n(\bar{r})}{N} \left(\eta - \frac{\mu}{N} \right) , \quad (21)$$

which shows the appealing feature of being in a kind of inverse relation with the Fukui function, as both bracketed factors are non-negative. As an alternative way to define a local chemical potential, more recently, it has been raised [23] that the route shown by Eq.(16) to define a local quantity could be applied one level earlier in the hierarchy of reactivity descriptors, i.e. already in the definition of μ by Eq.(5). This gives

$$\mu(\bar{r}) = \left. \frac{\delta E[N[n], v[n]]}{\delta n(\bar{r})} \right|_{v(\bar{r})} , \quad (22)$$

which embraces the possibly most appealing choice

$$\mu(\bar{r}) = \frac{\delta E[N[n], v[n]]}{\delta n(\bar{r})} . \quad (23)$$

For Eqs.(22) and (23), an analogue of Eq.(10) holds:

$$\mu = \int \mu(\bar{r}) f(\bar{r}) d\bar{r} . \quad (24)$$

We note that the concept of a local chemical potential was already proposed by Chan and Handy in the more general framework of shape chemical potentials [28]; however, as the only possibility, the trivial case $\mu(\bar{r}) = \mu$, the analogue of Eqs.(14) and (15), has been considered. Eq.(23) yields

$$\mu(\bar{r}) = \mu + \int n(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' , \quad (25)$$

which then gives the local hardness expression

$$\eta(\bar{r}) = \eta + \int f(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' + \iint n(\bar{r}') \frac{\delta^2 v(\bar{r}')}{\delta n(\bar{r}) \delta n(\bar{r}'')} f(\bar{r}'') d\bar{r}' d\bar{r}'' , \quad (26)$$

via differentiation with respect to N . This gives a correction to [15]

$$\eta(\bar{r}) = \eta + \int f(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' , \quad (27)$$

the unconstrained local hardness, Eq.(17).

III. Local energy and its derivatives with respect to the electron number

Just as the idea of defining a local hardness by Eq.(9) can be applied a level earlier in the hierarchy of reactivity indices, the question arises: why not to apply the idea of defining a local hardness through a local chemical potential already in defining a local chemical potential, defining it through a local (total) energy? Consider the N -electron Schrödinger equation

$$\left(\hat{T} + \hat{V}_{ee} + \hat{V}_{ne}\right)\psi(\vec{r}_1s_1, \dots, \vec{r}_Ns_N) = E\psi(\vec{r}_1s_1, \dots, \vec{r}_Ns_N) , \quad (28)$$

where

$$\begin{aligned} \hat{T} &= \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 , \\ \hat{V}_{ee} &= \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} , \\ \hat{V}_{ne} &= \sum_{i=1}^N v(\vec{r}_i) . \end{aligned}$$

Integrating this equation multiplied by $\psi^*(\vec{r}_1s_1, \dots, \vec{r}_Ns_N)$ in all the coordinates but one and summing it in the spin variables [or alternatively, acting on this equation with the operator

$$\hat{n}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r}_i - \vec{r}) \quad (29)$$

of the density then taking the expectation value divided by N] gives

$$t(\vec{r}) + v_{ee}(\vec{r}) + v_{ne}(\vec{r}) = \frac{E}{N}n(\vec{r}) , \quad (30)$$

with

$$t(\vec{r}) = (1/N)\langle\psi|\hat{n}(\vec{r})\hat{T}|\psi\rangle , \quad (31a)$$

$$v_{ee}(\vec{r}) = (1/N)\langle\psi|\hat{n}(\vec{r})\hat{V}_{ee}|\psi\rangle , \quad (31b)$$

$$v_{ne}(\vec{r}) = (1/N)\langle\psi|\hat{n}(\vec{r})\hat{V}_{ne}|\psi\rangle . \quad (31c)$$

Eq.(30) is the starting point for Bader's Atoms in Molecule theory [29]. Integration of Eq.(30) over the whole space gives $T + V_{ee} + V_{ne} = E$, and Eqs.(31) may be considered as a kinetic energy density (though with negative values at certain regions of space), an electron-electron interaction energy density, and an energy density of the interaction with the external potential, respectively [30]. On the basis of Eq.(30), a proportionality of the energy corresponding to a given segment of the molecule with the number of electrons contained in that segment can be

concluded. However, Eq.(30) gives even more: The expression on its right-hand side can be considered as a total energy density, or local total energy,

$$e(\bar{r}) = \frac{E}{N} n(\bar{r}) . \quad (32)$$

Note that Eq.(32) is not just one of the many possible choices for a total energy density, but it is obtained (through the left side) just as the electron density is constructed from the wave function, from which the electron number can be got back by a final integration – just as Eq.(30) leads to the total energy. Eq.(32) distributes the energy according to the electron distribution, more precisely, according to $n(\bar{r})/N$ – which definitely makes sense.

The derivatives of Eq.(32) with respect to the electron number, with $v(\bar{r})$ held fixed, naturally leads to concepts of a local chemical potential, a local hardness, and local hyper-hardnesses. A local chemical potential can be defined as

$$\mu(\bar{r}) = \left(\frac{\partial e(\bar{r})[N, v]}{\partial N} \right)_{v(\bar{r})} . \quad (33)$$

This $\mu(\bar{r})$ characterizes the change of the energy corresponding to a given point in a molecule due to a change in the electron number of the molecule, with nuclei kept fixed. Eq.(33) gives

$$\mu(\bar{r}) = f(\bar{r}) \frac{E}{N} + \frac{n(\bar{r})}{N} \left(\mu - \frac{E}{N} \right) . \quad (34)$$

From Eq.(33), a local hardness can be obtained according to Eq.(18), which, with the use of Eq.(34), yields

$$\eta(\bar{r}) = \frac{\partial f(\bar{r})}{\partial N} \frac{E}{N} + \frac{2}{N} f(\bar{r}) \left(\mu - \frac{E}{N} \right) + \frac{n(\bar{r})}{N} \left(\eta - 2 \frac{\mu}{N} + 2 \frac{E}{N^2} \right) . \quad (35)$$

As can be seen, Eq.(34) corrects Eq.(19) by a term $\left(f(\bar{r}) - \frac{n(\bar{r})}{N} \right) \frac{E}{N}$, while Eq.(35) corrects

Eq.(21) by $\frac{\partial f(\bar{r})}{\partial N} \frac{E}{N} + \frac{1}{N} f(\bar{r}) \left(\mu - 2 \frac{E}{N} \right) + \frac{n(\bar{r})}{N} \left(-\frac{\mu}{N} + 2 \frac{E}{N^2} \right)$. This seems to be much over-

complication of the local hardness of Eq.(21); however, we should not forget that the Fukui function is a proper indicator of local softness only for soft systems, so the inverse relation with the Fukui function exhibited by Eq.(21) has to be corrected in some way to gain a proper local indicator of hardness for hard systems too.

The local reactivity indices that can be obtained as the derivatives of Eq.(32) with respect to the electron number all integrate to the corresponding global reactivity index, due to the fact that Eq.(32) integrates to the energy. Therefore, we may term these local indices

densities; that is, Eq.(33) is a chemical potential density, and Eq.(35) is a hardness density. This terminology will be useful to distinguish these indices from the local indices defined in the next section.

To close this section, we may mention an argument which exhibits a weak point in defining the local softness via Eq.(2). For the chemical potential, it is also possible to define an inverse quantity,

$$\mu^{-1} = \left(\frac{\partial N}{\partial E} \right)_{v(\bar{r})} ,$$

provided the function $E(N)$ is one-to-one, which is true in the case of molecular systems, where the energy is monotonously decreasing with N . Then, a corresponding local quantity may readily be defined by

$$\mu^{-1}(\bar{r}) = \left(\frac{\partial n(\bar{r})}{\partial E} \right)_{v(\bar{r})} ,$$

analogously with Eq.(2). This $\mu^{-1}(\bar{r})$ will be proportional to $f(\bar{r})$,

$$\mu^{-1}(\bar{r}) = \left(\frac{\partial n(\bar{r})}{\partial N} \right)_{v(\bar{r})} \left(\frac{\partial N}{\partial E} \right)_{v(\bar{r})} = f(\bar{r}) \mu^{-1} ,$$

just as $s(\bar{r})$! Can these two local quantities be the measures of the same local information, or they should be defined in some other way ... ?

IV. Chemical potential kernel

It is worth introducing the chemical potential kernel

$$\mu(\bar{r}, \bar{r}') = \frac{\delta e(\bar{r})[N[n], v[n]]}{\delta n(\bar{r}')} , \quad (36)$$

which may serve as basis for originating local reactivity indices. Eq.(36) gives Eq.(23), which we term as local chemical potential, by a simple integration over the whole space,

$$\mu(\bar{r}') = \int \mu(\bar{r}, \bar{r}') d\bar{r} , \quad (37)$$

while Eq.(36) yields the chemical potential density, Eq.(33), if before integration in its second variable, it is multiplied by the Fukui function:

$$\mu(\bar{r}) = \int \mu(\bar{r}, \bar{r}') f(\bar{r}') d\bar{r}' . \quad (38)$$

The chemical potential itself can be obtained from $\mu(\bar{r}, \bar{r}')$ as

$$\mu = \iint \mu(\bar{r}, \bar{r}') f(\bar{r}') d\bar{r} d\bar{r}' . \quad (39)$$

One can define regional chemical potentials as well, by integrating $\mu(\bar{r})$ or $\mu(\bar{r})f(\bar{r})$ only over a given region of space – though the chemical meaning of this regional indicator in the case of the latter is unclear. Using Eq.(32), Eq.(36) can be given explicitly as

$$\mu(\bar{r}, \bar{r}') = \mu(\bar{r}') \frac{n(\bar{r})}{N} + \frac{E}{N} \delta(\bar{r} - \bar{r}') - \frac{E}{N} \frac{n(\bar{r})}{N}. \quad (40)$$

It can be observed that the last two terms of Eq.(40) may be written as $\frac{E}{N} \frac{\delta n(\bar{r})}{\delta_N n(\bar{r}')}$ [21].

Differentiating Eqs.(37) and (38) with respect to N , it can be seen that the following derived quantity is worth introducing:

$$\mu(\bar{r}, \bar{r}', \bar{r}'') = \frac{\delta e(\bar{r})[N[n], v[n]]}{\delta n(\bar{r}') \delta n(\bar{r}'')}. \quad (41)$$

With this, the hardness density and the local hardness Eq.(26) can be obtained as

$$\eta(\bar{r}) = \iint \mu(\bar{r}, \bar{r}', \bar{r}'') f(\bar{r}') f(\bar{r}'') d\bar{r}' d\bar{r}'' + \int \mu(\bar{r}, \bar{r}') \frac{\partial f(\bar{r}')}{\partial N} d\bar{r}' \quad (42)$$

and

$$\eta(\bar{r}') = \iint \mu(\bar{r}, \bar{r}', \bar{r}'') f(\bar{r}'') d\bar{r} d\bar{r}'' , \quad (43)$$

respectively.

Acknowledgments: The author acknowledges grants from the Fund for Scientific Research – Flanders (FWO), the Netherlands Fund for Scientific Research (NWO), and the U.S. Department of Energy TMS program (Grant No. DE-SC0002139).

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