

Why the traditional concept of local hardness does not work

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Abstract: The definition of local hardness by the derivative of the chemical potential with respect to the electron density has raised several questions, and its potential applicability as the local counterpart of chemical hardness has proved to be limited to (globally) hard molecules. Here, we point out that this traditional way of defining a local hardness concept is inherently incapable of yielding a proper local measure of hardness. To enlighten this fact more, we apply the same technique for defining a local version of the chemical potential itself.

I. Introduction

Chemical reactivity indices [1,2], defined within the framework of density functional theory (DFT), have found successful application in the study of chemical phenomena. The three most well known reactivity descriptors, the electronegativity [3] (or, in the language of DFT, chemical potential [4]), the chemical hardness, and softness [5] are basic constituents of essential principles governing chemical reactions – the electronegativity equalization principle [4,6], the hard/soft acid/base principle [5], and the maximum hardness principle [7]. An important aim of conceptual DFT [2] 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 [8], following from the definition of softness as the derivative of the electron number N with respect to the chemical potential μ . However, defining a local counterpart of hardness [9,10], the inverse of softness, has met essential difficulties [11-17], which undermine the applicability of the local hardness concept [17-19]. To cure these difficulties, very recently, a new approach to local hardness has been proposed [17], defining a local chemical potential (with the help of the concept of constrained derivatives [20]) first, 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 [21], which has proved to be a proper measure of local softness in the case of (globally) soft electron systems (as regards hard systems, this is not the case, as has been found recently [18,19]). Numerical tests [17] have also justified this choice as a proper local measure of hardness, giving proper results for the critical test molecule benzocyclobutadiene, for which the traditional definitions [9,10] have failed. It is not yet clear, however, (i) why the traditional way of defining a local hardness concept, via the derivative of the chemical potential with respect to the electron density $n(\vec{r})$, could not yield a (generally) correct local indicator of chemical hardness, and (ii) whether there is any possibility to gain a generally valid local hardness quantity from the traditional approach. Therefore, we will re-examine the idea of defining a local hardness concept, and also, a local chemical potential concept, via differentiation with respect to $n(\vec{r})$. We will show that in general the local quantities obtained in this way cannot yield proper regional indicators of hardness, and of chemical potential; consequently, they cannot be considered as proper local counterparts of η , and μ ,

respectively. However, they may still serve as useful quantities for quantum chemistry, as will be pointed out.

II. Traditional concept of local hardness

The inverse of chemical hardness, defined by [22]

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

is

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

which is called softness, and for which a corresponding local quantity, termed the local softness, can be readily introduced [8]:

$$s(\bar{r}) = \left(\frac{\partial n(\bar{r})}{\partial \mu} \right)_{v(\bar{r})}. \quad (3)$$

This has a direct connection to the Fukui function [21]

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

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

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

$s(\bar{r})$ integrates to S (just as the Fukui function integrates to 1), and it is natural to interpret it as a pointwise, i.e. local, softness. However, defining a corresponding local quantity for the hardness, Eq.(1), has met essential difficulties, due to the fact that there is no such obvious way to do this as in the case of softness. A local hardness concept was first introduced by Berkowitz et al. [9], who defined the local hardness as

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

This local index is then not a local quantity in the sense the local softness is, since it does not integrate to the hardness; consequently, its integral over a given region in the molecule won't give a regional global hardness. In fact, $\eta(\bar{r})$ times the Fukui function is what gives η by integration over the whole space,

$$\int \eta(\bar{r}) f(\bar{r}) d\bar{r} = \eta , \quad (7)$$

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

The biggest problem with the local hardness defined by Eq.(6) has been that it is not clear how to understand the fixed external potential $[v(\bar{r})]$ 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 $v(\bar{r})$ as one of the variables in $\mu[N, v]$ should be fixed when differentiating with respect to the electron density $n(\bar{r})$. However, this yields a trivial definition:

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

i.e., the local hardness equals the global hardness at every point in space. If one utilizes the DFT Euler-Lagrange equation

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

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

$$E_v[n] = F[n] + \int n(\bar{r}) v(\bar{r}) d\bar{r} \quad (10)$$

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

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

Differentiating this expression with respect to N yields

$$\eta = \left(\frac{\partial \mu[N, v]}{\partial N} \right)_v = \int \frac{\delta^2 F}{\delta n(\bar{r}) \delta n(\bar{r}')} \left(\frac{\partial n(\bar{r}')}{\partial N} \right)_v d\bar{r}' = \int \frac{\delta^2 F}{\delta n(\bar{r}) \delta n(\bar{r}')} f(\bar{r}') d\bar{r}' . \quad (12)$$

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

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

Eq.(13) was proposed by Ghosh [10], and was discovered to be a constant giving the global hardness everywhere (for the ground-state density) by Harbola et al. [11]. Eq.(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 local

hardness equalization principle can be based on it [10,23,24], which says that $\eta(\bar{r})$ of Eq.(13) should be constant for the whole molecule for the real ground-state density – but only for that density. This principle is closely related with the long-known chemical potential (or electronegativity) equalization principle [4,24,25]; see also the discussion in Appendix below.

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

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

instead of a simple fixation of the variable $v(\bar{r})$ 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 $v(\bar{r})$, through the first Hohenberg-Kohn theorem [1], which constitutes a unique $n(\bar{r}) \rightarrow v(\bar{r})$ mapping, i.e. a $v(\bar{r})[n]$ functional. The result will be an ambiguous restricted derivative (see Sec.II of [26]), similarly to the case of derivatives restricted to a domain of densities with a given normalization N , which derivatives are determined only up to an arbitrary additive constant [1,27]. Harbola et al. [11], to characterize the ambiguity of the local hardness concept, first recognized by Ghosh [10], have given the explicit form

$$\eta(\bar{r}) = \int \frac{\delta^2 F}{\delta n(\bar{r})\delta n(\bar{r}')} \lambda(\bar{r}') d\bar{r}' \quad (15)$$

for the possible local hardness candidates, where $\lambda(\bar{r})$ is an arbitrary function that integrates to 1. The second derivative of $F[n]$, appearing in Eq.(15), is called the hardness kernel. The choice $\lambda(\bar{r}) = f(\bar{r})$ gives back Eq.(13), while another natural choice is $\lambda(\bar{r}) = n(\bar{r})/N$, which yields the original local hardness formula of Berkowitz et al. [9], who proposed it as a consequence of Eq.(6). Besides these two definitions for $\eta(\bar{r})$, another one, termed the unconstrained local hardness, has been proposed by Ayers and Parr [15,28]:

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

where the fixed- $v(\bar{r})$ constraint on the differentiation with respect to $n(\bar{r})$ is simply dropped. A substantial difficulty with this definition when used in practice [15] is the explicit appearance of the derivative of $v(\bar{r}')$ with respect to $n(\bar{r})$, as can be seen by

$$\eta(\bar{r}) = \frac{\partial\mu}{\partial N} + \int \frac{\delta\mu[N,v]}{\delta v(\bar{r}')} \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' = \eta + \int f(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}', \quad (17)$$

where the well-known fact

$$\frac{\delta E[N, v]}{\delta v(\bar{r})} = n(\bar{r}) \quad (18)$$

and Eqs.(1) and (4) have been utilized. We note that Eq.(16) 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.

III. An inherent problem with 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 known, and plausible, way of obtaining regional hardnesses from an $\eta(\bar{r})$ defined by Eq.(14) is

$$\eta(\Omega) = \int_{\Omega} \eta(\bar{r}) \left(\frac{\partial n(\bar{r})}{\partial N} \right)_v d\bar{r} = \int_{\Omega} \eta(\bar{r}) f(\bar{r}) d\bar{r} ; \quad (19)$$

i.e., the integral in Eq.(7) is carried out over the considered region Ω of space instead of the whole space. Eq.(19) has been applied in practical calculations to characterize the hardness of a given atom(ic region) or functional group in a molecule. Eq.(19) yields an extensive hardness concept: The total hardness of a species can be obtained as a sum of its regional hardnesses corresponding to a given (arbitrary) division of the species into regions. That is, roughly saying, a molecule that contains regions having high values of hardnesses 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.

A problem with this local hardness/regional hardness scheme is that if η is extensive, with regional hardnesses given by Eq.(19), the quantity $\eta(\bar{r})f(\bar{r})$ should be considered to be the local hardness instead of $\eta(\bar{r})$ (of Eq.(14)). A local quantity $\rho(\bar{r})$ corresponding to a given extensive global quantity Θ emerges as $\rho(\bar{r}) = \lim_{\Delta V \rightarrow \bar{r}} \frac{\Delta \Theta}{\Delta V}$, implying $\Theta(\Omega) = \int_{\Omega} \rho(\bar{r}) d\bar{r}$.

At the same time, however, it seems plausible to take $\eta(\bar{r})$ 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 $n(\bar{r})$ at a given point of space in a given external potential – which 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 \bar{r} will yield a discontinuous density, so why should one bother himself with chemical potential changes corresponding to unphysical density changes? But there is a more physical/real argument against an $\eta(\bar{r})$ of Eq.(14). 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 due to a dN makes sense directly. $\frac{\delta\mu}{\delta n(\bar{r})}$ is, rather, an intermediate quantity that delivers the infinitesimal change in μ due to an infinitesimal change of some quantity determining the given electron system on which $n(\bar{r})$ depends – e.g.,

$$\left(\frac{\partial\mu}{\partial N}\right)_v = \int \frac{\delta\mu}{\delta n(\bar{r})} \bigg|_v \left(\frac{\partial n(\bar{r})}{\partial N}\right)_v d\bar{r} , \quad (20)$$

or

$$\left(\frac{\delta\mu}{\delta v(\bar{r})}\right)_N = \int \frac{\delta\mu}{\delta n(\bar{r}')} \bigg|_N \left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})}\right)_N d\bar{r}' . \quad (21)$$

(Of course, if an unconstrained/full derivative of μ with respect to $n(\bar{r})$, $\frac{\delta\mu}{\delta n(\bar{r})}$, exists, it can be used in both equations.) Thus, it may be more appropriate to term Eq.(14) as local hardness factor (instead of local hardness), which indicates its conceptual relevance for the hardness concept.

However, it can be shown that $\eta(\bar{r})f(\bar{r})$, with $\eta(\bar{r})$ given by Eq.(14), and the regional hardnesses given by Eq.(19), cannot be considered as local, or regional, measures of hardness, respectively. Consider Eqs.(20) and (21) with the integrals taken only over a given region of space. This gives Eq.(19) and

$$f_\Omega(\bar{r}) = \int_\Omega \frac{\delta\mu}{\delta n(\bar{r}')} \bigg|_N \left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})}\right)_N d\bar{r}' , \quad (22)$$

Eq.(21) being just the Fukui function,

$$f(\bar{r}) = \left(\frac{\delta\mu}{\delta v(\bar{r})}\right)_N , \quad (23)$$

due to Eq.(18). What these regional integrals tell us? They can be viewed as entities that give the contributions, to the infinitesimal changes of μ , that come from the change of the density over the given region due to an increment of N and $v(\bar{r})$, respectively. To ease understanding,

compare this with the finite-dimensional example of a function $g(x(t), y(t))$ (with a derivative $\dot{g} = \frac{\partial g}{\partial x} \frac{dx}{dt} + \frac{\partial g}{\partial y} \frac{dy}{dt}$ with respect to t), for which a “regional integral”, or partial sum, means $\dot{g}_x = \frac{\partial g}{\partial x} \frac{dx}{dt}$ – 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 $v(\bar{r})$, induces a density change $\delta n(\bar{r})$, then the regional integral Eq.(19), or Eq.(22), tells us how much the part of $\delta n(\bar{r})$ that falls on the given domain Ω contributes to the whole change $\delta\mu$ of μ due to $\delta n(\bar{r})$, via $(\delta\mu)_\Omega = \int_\Omega \frac{\delta\mu}{\delta n(\bar{r})} \delta n(\bar{r}) d\bar{r}$. This implies that Eq.(19) cannot be considered as a regional measure of hardness. The case of Eq.(22) shows that these regional integrals do not deliver the regional measures of global quantities even more clearly. $f_\Omega(\bar{r})$ is a function over the whole space; it gives how much contribution to $f(\bar{r})$ at a given \bar{r} can be attributed to a given region Ω of the molecule. I.e., $\sum_i f_{\Omega_i}(\bar{r}) = f(\bar{r})$.

We emphasize, in addition, that Eqs.(19) and (22) do not uniquely define regional quantities, because of the nonuniqueness of the restricted derivatives with respect to $n(\bar{r})$ present in the integrands. In the case of Eq.(22), this nonuniqueness manifests itself in a simple additive constant; that is, in the place of $\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_N$, any other $\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_N + c$ can be taken as a choice for the chemical potential derivative over the N -restricted domain of $n(\bar{r})$ ’s. If the full derivative of μ , with respect to $n(\bar{r})$, exists, we may write

$$\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_N = \frac{\delta\mu}{\delta n(\bar{r})} + c . \quad (24)$$

This ambiguity leads to an ambiguity by $+c \left(\frac{\delta N_\Omega}{\delta v(\bar{r})} \right)_N$ in $f_\Omega(\bar{r})$. Another particular choice

for $\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_N$, in the place of $\frac{\delta\mu}{\delta n(\bar{r})}$, is

$$\left(\frac{\delta\mu[N, v[n]]}{\delta n(\bar{r})} \right)_N \equiv \int \left(\frac{\delta\mu[N, v]}{\delta v(\bar{r}')} \right)_N \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' \equiv \int f(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' , \quad (25)$$

the analogue of Eq.(8), with which

$$f_\Omega(\bar{r}) = \int f(\bar{r}'') \int_\Omega \frac{\delta v(\bar{r}'')}{\delta n(\bar{r}')} \left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})} \right)_N d\bar{r}' d\bar{r}'' . \quad (26)$$

(It can be seen that if Ω is chosen to be the whole space, Eq.(26) gives back the Fukui function.) As regards $\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_v$, it is determined only up to a term $+\int c(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}'$ (with $c(\bar{r})$ arbitrary), emerging from the fixed $v(\bar{r})$ constraint, $v(\bar{r}') [n(\bar{r})] = v(\bar{r}')$, since a term such this will cancel in the definition of functional derivative under the fixed $v(\bar{r})$ constraint on the $n(\bar{r})$ -domain [26]. If the full derivative $\frac{\delta\mu}{\delta n(\bar{r})}$ exists, this ambiguity may be exhibited

as

$$\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_v = \frac{\delta\mu}{\delta n(\bar{r})} + \int c(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' , \quad (27a)$$

or with the particular choice Eq.(8), as

$$\left. \frac{\delta\mu}{\delta n(\bar{r})} \right|_v = \eta + \int c(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' . \quad (27b)$$

With Eq.(27b), e.g., the ambiguity of Eq.(19) may be given as

$$\eta(\Omega) = \eta \int_{\Omega} f(\bar{r}') d\bar{r}' + \int c(\bar{r}'') \int_{\Omega} \frac{\delta v(\bar{r}'')}{\delta n(\bar{r}')} f(\bar{r}') d\bar{r}' d\bar{r}'' . \quad (28)$$

On the basis of the argument given above regarding these regional integrals, there is no reason to expect that for any particular choice of $c(\bar{r})$, Eq.(28) will yield a proper regional hardness measure. We note finally that in the case of the whole integrals of Eqs.(20) and (21), the ambiguity of the restricted derivatives present cancels out, due to the corresponding constraint on their multipliers, $\left(\frac{\partial n(\bar{r})}{\partial N} \right)_v$ and $\left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})} \right)_N$; see Appendix of [26] for a general proof.

The above analysis is worth extending by the introduction of a local quantity corresponding to the chemical potential, which may be termed local chemical potential factor. It has been proposed in [17] that instead of replacing the electron number with the electron density in the hardness expression Eq.(1) to obtain a local hardness, the chemical potential should be replaced there by a local counterpart. In [17], by utilizing that the chemical potential emerges as the additive constant term in the N -conserving derivative of $E_v[n]$ [20],

$$\mu = \frac{1}{N} \int n(\bar{r}) \frac{\delta E_v[n]}{\delta n(\bar{r})} d\bar{r} , \quad (29)$$

a local version of μ has been identified as

$$\mu(\bar{r}) = \frac{n(\bar{r})}{N} \mu . \quad (30)$$

Then, a corresponding local hardness concept can be immediately obtained via

$$\eta(\bar{r}) = \left(\frac{\partial \mu(\bar{r})[N, v]}{\partial N} \right)_v . \quad (31)$$

The question may naturally arise as to whether we may obtain a better, physically possibly more appealing local chemical concept by applying the idea behind Eq.(14) to μ itself, i.e. by

$$\mu(\bar{r}) = \frac{\delta E[N[n], v[n]]}{\delta n(\bar{r})} \Big|_v . \quad (32)$$

Of course, we then have the same kind of ambiguity problem as in the case of Eq.(14). Fixing $v(r)$ as one of the variables of $E[N, v]$ will not yield a $\mu(\bar{r})$ that is a useful local measure of the chemical potential, similarly to Eq.(8), since this $\mu(\bar{r})$ will be constant in space – the chemical potential itself:

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

We note here that the idea of a local chemical potential concept has already been raised by Chan and Handy [29], 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 that of Eq.(33), ignoring other possibilities.

A general property of a $\mu(\bar{r})$ defined through Eq.(32) is

$$\mu = \int \frac{\delta E[n]}{\delta n(\bar{r})} \Big|_{v(\bar{r})} \left(\frac{\partial n(\bar{r})[N, v]}{\partial N} \right)_{v(\bar{r})} d\bar{r} = \int \mu(\bar{r}) f(\bar{r}) d\bar{r} ; \quad (34)$$

i.e., it gives the chemical potential after integration when multiplied by the Fukui function – analogously to Eq.(7). The ground-state energy as a functional of the ground-state density can be obtained via two routes:

$$E[n] \equiv E[N[n], v[n]] \equiv E_{v[n]}[n] ; \quad (35)$$

the first one is through $E[N, v]$, while the second one is through the energy density functional Eq.(10) of DFT – in both cases, the functional dependence of $v(\bar{r})$ on $n(\bar{r})$ is inserted into

the corresponding places. Specifically, $\frac{\delta E[n]}{\delta n(\bar{r})} \Big|_v$ may be $\left(\frac{\delta E_v[n]}{\delta n(\bar{r})} \right)_{v(\bar{r})}$, which equals μ (on the

basis of Eq.(9)), giving back Eq.(33). We emphasize here again that in spite of the great extent of ambiguity in Eq.(32), all choices will indeed give μ in Eq.(34), due to the fact that

the density in $\left(\frac{\partial n(\bar{r})}{\partial N}\right)_{v(\bar{r})}$ is varied with the external potential fixed, and in cases like this, the ambiguity of the inner derivative cancels out [26].

An appealing choice of the restricted derivative in Eq.(32) may be the unrestricted derivative,

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

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 \bar{r} in a given molecule where the same amount of infinitesimal change of $n(\bar{r})$ (at the given \bar{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 $\mu(\bar{r})$, respectively. The unrestricted way of considering the change of E with respect to the density may be a reasonable way to obtain a relevant local reactivity index, since in reality, the density change always goes together with a change of the external potential setting, as another molecule approaches the considered system. The most sensitive site of a molecule towards receiving an additional amount of electron (density) will be the site with the lowest value of $\mu(\bar{r})$, implying the biggest decrease of the energy due to an increase of the density at \bar{r} by an infinitesimal amount. Eq.(36) can be evaluated via

$$\mu(\bar{r}) = \frac{\partial E[N, v]}{\partial N} + \int \frac{\delta E[N, v]}{\delta v(\bar{r}')} \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' = \mu + \int n(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' , \quad (37a)$$

or alternatively,

$$\mu(\bar{r}) = \frac{\delta E_v[n]}{\delta n(\bar{r})} + \int \frac{\delta E_v[n]}{\delta v(\bar{r}')} \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' = \mu + \int n(\bar{r}') \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' , \quad (37b)$$

where Eqs.(9) and (10) have been utilized. Note that the second term of Eq.(27) integrates to zero when multiplied by the Fukui function.

However, irrespective of the concrete choice of Eq.(32), the same conceptual and mathematical problems arise as in the case of $\eta(\bar{r})$ of Eq.(14). Most importantly, the regional integral

$$\mu(\Omega) = \int_{\Omega} \mu(\bar{r}) \left(\frac{\partial n(\bar{r})}{\partial N}\right)_v d\bar{r} \equiv \int_{\Omega} \mu(\bar{r}) f(\bar{r}) d\bar{r} \quad (38)$$

will not deliver a regional measure of μ . This fact can be nicely exhibited by considering the regional version of

$$\left(\frac{\delta E}{\delta v(\bar{r})} \right)_N = \int \frac{\delta E}{\delta n(\bar{r}')} \bigg|_N \left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})} \right)_N d\bar{r}' ; \quad (39)$$

namely,

$$n_{\Omega}(\bar{r}) = \int_{\Omega} \frac{\delta E}{\delta n(\bar{r}')}\bigg|_N \left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})} \right)_N d\bar{r}' . \quad (40)$$

Eq.(40) gives a density component that can be viewed as the contribution of the given region Ω to $n(\bar{r})$.

Eq.(40) offers a possible application of Eq.(36). A natural decomposition of the density is the one in terms of the occupied Kohn-Sham orbitals,

$$n(\bar{r}) = \sum_{i=1}^N |\phi_i(\bar{r})|^2 . \quad (41)$$

One may then look for regions Ω_i ($i=1, \dots, N$) of the given molecule that contribute $n_i(\bar{r}) = |\phi_i(\bar{r})|^2$ to $n(\bar{r})$. Of course, this may imply a highly ambiguous result; however, the number of possible divisions of the molecule into Ω_i can be significantly reduced by searching for Ω_i 's around the intuitively expectable regions where the single $n_i(\bar{r})$'s are dominant. In this way, one may find a spatial division of a molecule into subshells. This is probably an idea that is way too bold to be taken seriously, not to mention its practical evaluation, but is naturally suggested by Eq.(40). To go even further, one might assume that by applying the regions Ω_i found in this way in Eq.(22), the corresponding $f_{\Omega_i}(\bar{r})$'s might emerge to be $f_{\Omega_i}(\bar{r}) = \partial n_i(\bar{r}) / \partial N$.

For any possible application of Eqs.(16) and (36), a proper method to evaluate the derivative of $v(\bar{r})$ with respect to the density is necessary, as shown by Eqs.(17) and (37). To close this study, we describe a route to carry out this task. $v(\bar{r})$ is given as a functional of $n(\bar{r})$ by Eq.(9); namely,

$$v(\bar{r}') [n] = \mu[n] - \frac{\delta F[n]}{\delta n(\bar{r}')} . \quad (42)$$

To obtain the derivative of Eq.(42) with respect to $n(\bar{r})$, we need to determine $\frac{\delta \mu}{\delta n(\bar{r})}$, which

is just the unconstrained local hardness of Eq.(16). We cannot determine $\frac{\delta \mu}{\delta n(\bar{r})}$ without

further information on $\mu[n]$, since

$$\begin{aligned}
\frac{\delta\mu[n]}{\delta n(\bar{r})} &= \frac{\partial\mu}{\partial N} + \int \frac{\delta\mu[N, v]}{\delta v(\bar{r}')} \frac{\delta v(\bar{r}')}{\delta n(\bar{r})} d\bar{r}' = \eta + \int f(\bar{r}') \frac{\delta}{\delta n(\bar{r})} \left(\mu[n] - \frac{\delta F[n]}{\delta n(\bar{r}')} \right) d\bar{r}' \\
&= \eta + \frac{\delta\mu[n]}{\delta n(\bar{r})} - \int f(\bar{r}') \frac{\delta^2 F[n]}{\delta n(\bar{r}) \delta n(\bar{r}')} d\bar{r}' , \tag{43}
\end{aligned}$$

which is an identity, involving Eq.(12). However, by restricting ourselves to external potentials with $v(\infty) = 0$ (which embraces all the class of real Coulombic potentials), $\mu[n]$ can be determined – by applying this condition as a boundary condition in Eq.(42). With this,

$$\mu[n] = \frac{\delta F[n]}{\delta n(\infty)} . \tag{44}$$

Using Eqs.(42) and (44), then, Eq.(37) becomes

$$\mu(\bar{r}) = \mu + N \frac{\delta^2 F[n]}{\delta n(\bar{r}) \delta n(\infty)} - \int n(\bar{r}') \frac{\delta^2 F[n]}{\delta n(\bar{r}) \delta n(\bar{r}')} d\bar{r}' . \tag{45}$$

Similarly,

$$\eta(\bar{r}) = \frac{\delta^2 F[n]}{\delta n(\bar{r}) \delta n(\infty)} \tag{46}$$

arises for Eq.(16). Notice that Eq.(46) corresponds to the choice $\lambda(\bar{r}') = \delta(\bar{r}' - \infty)$ in Eq.(15). Eqs.(45) and (46) probably cannot be applied with using approximations for $F[n]$ that construct $F[n]$ simply in a form $F[n] = \int g(n(\bar{r}), \nabla n(\bar{r}), \nabla^2 n(\bar{r}), \dots) d\bar{r}$, since in this case, delta functions $\delta(\bar{r} - \infty)$ appear as multipliers in the components of the second term of Eq.(45), and in Eq.(46), making them zero. As pointed out by Tozer et al. [30], a proper density functional $F[n]$ should yield an exchange-correlation potential that has a non-vanishing asymptotic value, which then leads to a non-vanishing second term in Eq.(45) and Eq.(46).

Between Eqs.(16) and (36), a link can be established in the form of

$$\eta(\bar{r}) = \left(\frac{\partial\mu(\bar{r})}{\partial N} \right)_v - \iint n(\bar{r}') \frac{\delta^2 v(\bar{r}')}{\delta n(\bar{r}) \delta n(\bar{r}'')} f(\bar{r}'') d\bar{r}' d\bar{r}'' . \tag{47}$$

Finally, it is worth pointing out the relationship

$$\eta = \iint \frac{\delta\mu}{\delta n(\bar{r})} \Big|_v \frac{\delta\mu}{\delta n(\bar{r}')} \Big|_v \left(\frac{\delta n(\bar{r}')}{\delta v(\bar{r})} \right)_N d\bar{r} d\bar{r}' = \iint \eta(\bar{r}) \eta(\bar{r}') \left(\frac{\delta E}{\delta v(\bar{r}) \delta v(\bar{r}')} \right)_N d\bar{r} d\bar{r}' , \tag{48}$$

with $\eta(\bar{r})$ given by Eq.(14), which can be obtained by insertion of Eq.(21) in Eq.(20) through Eq.(23).

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