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Local electrophilicity

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Abstract

In this work some possibilities for deriving a local electrophilicity are studied. First, we consider the original definition proposed by Chattaraj, Maiti, and Sarkar (J Phys Chem A 107:4973, 2003), in which the local electrophilicity is given by the product of the global electrophilicity, and the Fukui function for charge acceptance is derived by two different approaches, making use of the chain rule for functional derivatives. We also modify the proposals based on the electron density so as to have a definition with the same units of the original definition, which also introduces a dependence in the Fukui function for charge donation. Additionally, we also explore other possibilities using the tools of information theory and the temperature dependent reactivity indices of the density functional theory of chemical reactivity. The poor results obtained from the last two approaches lead us to conjecture that this is due to the fact that the global electrophilicity is not a derivative, like most of the other reactivity indices. The conclusion is that Chattaraj's suggestion seems to be the simplest, but at the same time a very reliable approach to this important property.

Keywords Chemical reactivity · Global and local electrophilicities · Hardness · Chemical potential · Fukui functions

Introduction

Density functional theory has contributed very much to the development of a theory of chemical reactivity [1–8]. Primordially, the works of Robert Parr have allowed quantification of many intuitive chemical concepts, like electronegativity [9] and hardness [10, 11]. It has also introduced new quantities, like the Fukui function [12, 13] $f(\mathbf{r})$, and the softness S [14]. Some rules of chemistry, like the principle of maximum hardness [15] and the HSAB principle [16–18], have also been theoretically justified [19–38]. Almost 20

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years ago, Parr et al. derived a formula to evaluate the electrophilicity [39–43],

$$\omega = \frac{\mu^2}{2\eta} \tag{1}$$

where μ, the chemical potential, is given by the derivative of the electronic energy, E, with respect to the number of electrons, N, at constant external potential, $v(\mathbf{r})$, that is,

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \tag{2}$$

and η is the hardness,

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v(\mathbf{r})} \tag{3}$$

If one makes a smooth quadratic interpolation [10] between the systems with $N_0 - 1$, N_0 and $N_0 + 1$ electrons, where N_0, an integer, is the number of electrons of the reference system, to determine the first and second derivatives of the energy and the electronic density with respect to N, one finds that,

$$\mu = -\frac{IP + EA}{2} \tag{4}$$

$$\eta = IP - EA \tag{5}$$

and therefore,

$$\omega = \frac{(IP + EA)^2}{8(IP - EA)} \qquad (6)$$

where $IP = E_{N_0-1} - E_{N_0}$ and $EA = E_{N_0} - E_{N_0+1}$ are the first ionization potential and the electron affinity, respectively.

Note that in contrast to the global properties, μ and η, the electrophilicity is not a derivative with respect to the number of electrons. These three quantities are global indices describing a characteristic of the molecule as a whole. However, almost all the global indices of density functional theory have their local counterpart, which is important because different atoms or groups in a molecule may react in a different way (regioselectivity). Hence, the number of electrons N has its counterpart in the electron density $\rho(\mathbf{r})$, the hardness η has its counterpart in the local hardness $\eta(\mathbf{r})$, and the softness S has its counterpart in the local softness $s(\mathbf{r})$. Therefore, it is logical to ask for the local counterpart of the electrophilicity defined in Eq. (1). The simplest way to do it, and the most used one, was proposed by Chattaraj et al. [44], who established the condition that the local electrophilicity integrated over the whole space should lead to the global electrophilicity, that is:

$$\omega = \int \omega(\mathbf{r}) \, d\mathbf{r} \qquad (7)$$

Thus, taking into account that the Fukui function,

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} \qquad (8)$$

integrates over the whole space to one,

$$\int f(\mathbf{r}) \, d\mathbf{r} = 1 \qquad (9)$$

Chattaraj et al. proposed that:

$$\omega = \omega \int f(\mathbf{r}) \, d\mathbf{r} = \int \omega \, f(\mathbf{r}) \, d\mathbf{r} = \int \omega(\mathbf{r}) \, d\mathbf{r} \qquad (10)$$

where the local electrophilicity is defined as:

$$\omega(\mathbf{r}) = \omega \, f(\mathbf{r}) \qquad (11)$$

The fact that the electron density as a function of the number of electrons at zero-temperature is given by a series of straight lines connecting the integer values of N [45–47] implies that the derivative from the left will be different to the derivative from the right, around an integer value of N. In terms of electron density differences, the Fukui function, Eq. (8), is given by:

$$f^-(\mathbf{r}) = \rho_{N_0}(\mathbf{r}) - \rho_{N_0-1}(\mathbf{r}) \qquad (12)$$

and

$$f^+(\mathbf{r}) = \rho_{N_0+1}(\mathbf{r}) - \rho_{N_0}(\mathbf{r}) \qquad (13)$$

where $\rho_{N_0-1}(\mathbf{r})$, $\rho_{N_0}(\mathbf{r})$ and $\rho_{N_0+1}(\mathbf{r})$ are the electron densities of the system with $N_0 - 1$, N_0 and $N_0 + 1$ electrons, respectively. The Fukui functions $f^-(\mathbf{r})$ and $f^+(\mathbf{r})$ are the left and right directional derivatives, $f^-(\mathbf{r})$ characterizes the sites from which the molecule will donate charge, while $f^+(\mathbf{r})$ characterizes the sites where the molecule will accept charge. Thus, since the electrophilicity concept is linked to charge accepted by the system when it is immersed in an idealized electron bath with zero chemical potential, the local electrophilicity expressed in Eq. (11), should be written as:

$$\omega(\mathbf{r}) = \omega \, f^+(\mathbf{r}) \qquad (14)$$

It is important to mention that using the inverse relationship at zero-temperature between hardness and softness [14, 48, 49], $\eta S = 1$, a condensed to atom [50–54] local electrophilicity based on the Fukui function had already been proposed [55, 56]. Also, using the minimization procedure discussed by Ayers and Parr [57] together with the variational principle for the Fukui function [58], the relationship given in Eq. (11) in terms of directional derivatives was derived [59].

On the other hand, based on the maximum charge transferred from an idealized bath with zero chemical potential, $\Delta N_{\max} = -\mu/\eta$, which is the charge that leads to the global electrophilicity expressed in Eq. (1), and making use of the fact that the Fukui function is the one that minimizes the energy change associated with a charge transfer [57], Cedillo and Contreras [60] expressed the electronic density change associated with the electrophilicity concept as:

$$\Delta \rho_{Elec-1}(\mathbf{r}) = \Delta N_{\max} \, f^+(\mathbf{r}) = -\frac{\mu}{\eta} \, f^+(\mathbf{r}) \qquad (15)$$

and multiplying this expression by $(-\mu/2)$,

$$\omega(\mathbf{r}) = -\frac{\mu}{2} \Delta \rho_{Elec-1}(\mathbf{r}) = \frac{\mu^2}{\eta} \, f^+(\mathbf{r}) = \omega \, f^+(\mathbf{r}) \qquad (16)$$

they recovered Eq. (14).

In a similar context, Morell et al. [61] defined the local electrophilicity just in terms of the electronic density term, but considering up to the second order contribution of the expansion of $\rho(\mathbf{r})$ as a function of N, that is

$$\Delta \rho_{Elec-2}(\mathbf{r}) = \Delta N_{\max} \, f(\mathbf{r}) + \frac{1}{2}(\Delta N_{\max})^2 \, \Delta f(\mathbf{r}) \qquad (17)$$

leading to

$$\Delta \rho_{Elec-2}(\mathbf{r}) = \omega \left[-\frac{2}{\mu} \, f(\mathbf{r}) + \frac{1}{\eta} \Delta f(\mathbf{r}) \right] \qquad (18)$$

where $\Delta f(\mathbf{r})$ is the dual descriptor [62, 63].

$$\Delta f(\mathbf{r}) = \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial N^2}\right)_{v(\mathbf{r})} = \left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} \qquad (19)$$

In the work of Morell et al., Eq. (18) was finally written in terms of the directional derivatives for the energy and for electron density. In the case of the derivatives of the energy, since E as a function N at zero temperature is also given by a series of straight lines connecting the integer values of N [45–47], one has that $\mu^- = -IP$ and $\mu^+ = -EA$. For the second derivatives of the energy and the electron density with respect to N one usually makes use of the smooth quadratic interpolation between the $N_0 - 1$, N_0, and $N_0 + 1$ that leads to Eq. (5) for the hardness and to

$$\Delta f(\mathbf{r}) = f^+(\mathbf{r}) - f^-(\mathbf{r}) \tag{20}$$

for the dual descriptor. This way, the final expression derived by Morell et al. was

$$\Delta\rho_{\omega-1}(\mathbf{r}) = \frac{(EA)^2}{2\,(IP-EA)}\left[\frac{2}{EA}\,f^+(\mathbf{r}) + \frac{1}{IP-EA}(f^+(\mathbf{r}) - f^-(\mathbf{r}))\right] \tag{21}$$

Recently, it was proposed that the local response of global descriptors may be obtained through the functional derivative of the global property with respect to the external potential at constant number of electrons [64]. Through this approach one is led to Eq. (18), which in the case of using the smooth quadratic interpolation for the energy, Eqs. (4) and (5) lead to the chemical potential and the hardness, respectively, while for the electron density the Fukui function is obtained from

$$f(\mathbf{r}) = \frac{f^-(\mathbf{r}) + f^+(\mathbf{r})}{2} \tag{22}$$

and the dual descriptor is given by Eq. (20), so that in this case Eq. (18) becomes equal to

$$\Delta\rho_{\omega-2}(\mathbf{r}) = \frac{(IP + EA)^2}{8\,(IP-EA)}\left[\frac{2}{IP+EA}\,(f^-(\mathbf{r}) + f^+(\mathbf{r})) + \frac{1}{IP-EA}(f^+(\mathbf{r}) - f^-(\mathbf{r}))\right] \tag{23}$$

Thus, one can see that the definition provided by Chattaraj et al. has the appeal of its simplicity, although it has been criticized [60, 64, 65] because within a molecule it has no more local information than the one provided by the Fukui function. On the other hand, the proposals related with Eqs. (21) and (23) are more complicated, but it is interesting to note that they depend not only on $f^+(\mathbf{r})$ but also on $f^-(\mathbf{r})$. However, it is important to note that these two proposals define the local electrophilicity through the electronic density, while the original proposal does it through the global electrophilicity, which is a quantity with units of energy.

The object of the present work is first to propose new approximations to the local electrophilicity and then to analyze the results obtained from the different expressions. Consequently, we derive first an expression for the local electrophilicity using tools of information theory. Then, we analyze two alternative approaches to derive Chattaraj's relationship, Eqs. (11) and (14), and a new proposal that considers Eq. (18) as the starting point. Next, motivated by one of the derivations analyzed, we also derive an equation based on the temperature dependent formulation, developed by Franco et al. [49, 66–68], of the density functional theory of chemical reactivity. Finally, we perform a comparison between the different formulations.

New proposals for a local electrophilicity

Local counterpart of a global property through functional derivatives

Recently, some of us developed a methodology to find the local and nonlocal counterparts of a global response function, namely a derivative of the zero temperature state function with respect to one of the global independent variables [69, 70, Franco-Pérez et al. to be publshed], basically making use of the chain rule for functional derivatives. Here we will only consider the local counterpart to derive the equation proposed by Chattaraj et al., Eqs. (11) and (14), for the local electrophilicity through two approaches.

In both, the starting point is to establish the condition that the local property $P(\mathbf{r})$ integrated over the whole space should lead to the corresponding global property P, that is:

$$P = \int P(\mathbf{r})d\mathbf{r} \tag{24}$$

In the first approach one may consider that the maximum amount of charge transferred may be rewritten in the form

$$\Delta N_{\max} = -\frac{\mu}{\eta} = -\mu\,S = -\left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})}\left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})}$$
$$= -\left(\frac{\partial E}{\partial \mu}\right)_{v(\mathbf{r})} \tag{25}$$

where we have used the inverse relationship at zero-temperature between the hardness and the softness, Eqs. (2) and (3), and the chain rule for derivatives. Now we make use of the chain rule for functional derivatives to write that

$$\left(\frac{\partial E}{\partial \mu}\right)_{v(\mathbf{r})} = \int \left(\frac{\partial E}{\partial \rho(\mathbf{r})}\right)_{v(\mathbf{r})} \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right)_{v(\mathbf{r})} d\mathbf{r} \tag{26}$$

The first derivative in the integrand is, from the variational principle of density functional theory [1, 9], equal to

$$\mu = \left(\frac{\partial E}{\partial \rho(\mathbf{r})}\right)_{v(\mathbf{r})} \tag{27}$$

while the second derivative in the integrand may be identified with the definition of local softness [14, 48], so that

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right)_{v(\mathbf{r})} = \left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})} \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}$$
$$= S \ f(\mathbf{r}) = \frac{1}{\eta} \ f(\mathbf{r}) \tag{28}$$

Multiplying Eq. (26) by $\mu/2$ and using Eqs. (27) and (28), one finds that

$$\frac{\mu}{2} \left(\frac{\partial E}{\partial \mu}\right)_{v(\mathbf{r})} = \int \frac{\mu^2}{2 \ \eta} \ f(\mathbf{r}) \ d\mathbf{r} \tag{29}$$

Now, using Eqs. (25) and (1), one can see that Eq. (29) is identical to Eq. (7), which implies that the local electrophilicity obtained through this procedure is identical with the one proposed by Chattaraj et al., Eq. (11) or Eq. (14) when the directional derivative is considered. However, the present derivation has been mathematically motivated by the chain rule for functional derivatives.

A second approach is based on the definition of a local chemical potential through the following chain rule [67, 69].

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} = \int \left(\frac{\partial E}{\partial \rho(\mathbf{r})}\right)_{v(\mathbf{r})} \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} d\mathbf{r}$$
$$= \int \mu \ f(\mathbf{r}) \ d\mathbf{r} = \int \mu_L(\mathbf{r}) \ d\mathbf{r} \tag{30}$$

which implies that

$$\mu_L(\mathbf{r}) = \mu \ f(\mathbf{r}) \tag{31}$$

together with the definition of a local hardness through the chain rule [Franco-Pérez et al. to be publshed].

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{v(\mathbf{r})} = \int \left(\frac{\partial \mu}{\partial \rho(\mathbf{r})}\right)_{v(\mathbf{r})} \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} d\mathbf{r}$$
$$= \int \eta \ f(\mathbf{r}) \ d\mathbf{r} = \int \eta_L(\mathbf{r}) \ d\mathbf{r} \tag{32}$$

which implies that

$$\eta_L(\mathbf{r}) = \eta \ f(\mathbf{r}) \tag{33}$$

It is important to note that in order to derive this expression we have considered that

$$\eta = \left(\frac{\partial \mu}{\partial \rho(\mathbf{r})}\right)_{v(\mathbf{r})} \tag{34}$$

because due to the Hohenberg-Kohn theorem [1, 71], the only possible variations of the electronic density at constant external potential are those arising from variations in the number of electrons. In fact, the relationships given by Eqs. (27) and (34) are manifestations of the chemical potential and the hardness equalizations [72–74].

Now, given that the global electrophilicity, according to Eq. (1), is given by the square of the global chemical potential divided by two times the global hardness, one could consider a local electrophilicity given by the square of a local chemical potential divided by two times a local hardness, that is:

$$\omega_L(\mathbf{r}) = \frac{(\mu_L(\mathbf{r}))^2}{2 \ \eta_L(\mathbf{r})} \tag{35}$$

If one replaces $\mu_L(\mathbf{r})$ and $\eta_L(\mathbf{r})$ by the expressions given in Eqs. (31) and (33), respectively, one obtains the expression proposed by Chattaraj et al., Eq. (11) or Eq. (14) when the directional derivative is considered. However, this derivation has been motivated through the definition of local counterparts for the chemical potential and the hardness.

Local electrophilicity from the changes in the electron density

It has already been mentioned that there have been proposals for the local electrophilicity based directly on the changes in the electronic density that arise from the acceptance of the fractional charge $\Delta N_{max} = -\mu/\eta > 0$. The two approaches reported in the literature [61, 64] lead to the same result, Eq. (18), when in the case of Morell et al. the series expansion of the density with respect to the number of electrons is truncated at second order. The differences between Eqs. (21) and (23) are due to the different approximations used to calculate the derivatives of the energy and of the electronic density with respect to N that appear in Eq. (18).

Now, recall that the approach developed by Cedillo and Contreras [60] was based first on approximating the change in the electron density through Eq. (15), and then multiplying it by $(-\mu/2)$ to obtain Eq. (16), that defines the local electrophilicity in terms of the appropriate units of energy per volume, so that when one integrates it over the whole space one obtains the global electrophilicity in energy units. Thus, one can proceed in a similar way in the approach developed by

Morell et al., in which the electronic density difference is determined through a Taylor series in ΔN, but instead of truncating it at first order that corresponds to what Cedillo and Contreras did, one may consider also the second order term, and multiply the expression, Eq. (18), by $(-\mu/2)$ finding that:

$$\omega_{Elec-2}(\mathbf{r}) = -\frac{\mu}{2}\Delta\rho_{Elec-2}(\mathbf{r}) = \omega\left[f(\mathbf{r}) - \frac{\mu}{2\eta}\Delta f(\mathbf{r})\right] \quad (36)$$

$$\omega_{Elec-2}(\mathbf{r}) = \frac{(IP+EA)^2}{4\left(IP-EA\right)}\left[f^{\,-}(\mathbf{r}) + f^{\,+}(\mathbf{r}) + \frac{(IP+EA)}{2\left(IP-EA\right)}(f^{\,+}(\mathbf{r}) - f^{\,-}(\mathbf{r}))\right]. \quad (37)$$

One may note that as in the case of Eqs. (21) and (23), this relationship depends on $f^{\,+}(\mathbf{r})$, but also on $f^{\,-}(\mathbf{r})$. However, the contribution to the local electrophilicity from $f^{\,+}(\mathbf{r})$ is greater in this expression than in the other two. Another important aspect is that it may be directly compared with Eq. (14) because both quantities have the same units.

The presence of $f^{\,-}(\mathbf{r})$ may be an important aspect because if one considers the original global electrophilicity proposed by Parr and collaborators, Eqs. (1) and (6), one can see that it depends on the electron affinity, which is a property certainly related with the acceptance of charge, but it also depends on the ionization potential, which is a property related with the donation of charge. Thus, in a certain way one may consider that the acceptance process may be influenced by properties related with the donation process, that is, the presence of $f^{\,-}(\mathbf{r})$ may be incorporating aspects related with the donation process at the local level.

Local counterpart of a global property through information theory

It is worth mentioning that recently some of us published a general procedure to get the local version of any global index using information theory [75], and it was applied, in particular, to obtain a local hardness. The procedure is inspired in the pioneer works of Nalewajski and Parr to derive the Hirshfeld atomic population analysis [76, 77].

In information theory if you have two distributions $p(r)$ and $q(r)$, the Kullback-Leibler divergence is defined as [78, 79].

$$D(p,q) = \int p(\mathbf{r})\ln\frac{p(\mathbf{r})}{q(\mathbf{r})}d\mathbf{r} \quad (38)$$

and using very simplistic interoperation, it measures the amount of information lost when one uses the distribution $p(\mathbf{r})$ instead of the expected distribution $q(\mathbf{r})$. In the context of density functional theory it was first successfully used by

Nalewaski and Parr to derive the atom in molecule methodology proposed by Hirshfeld [80]. More recently, besides the local hardness [75], Farnaz et al. [81–84] exhaustively investigated the properties and extensions of this definition.

In our case, to find an equation for a local electrophilicity, $\omega(\mathbf{r})$, we can use the initial distribution, $q(\mathbf{r})$, for the moment, as an arbitrary known local electrophilicity, $\omega^0(\mathbf{r})$. We have then to look for the distribution $p(\mathbf{r})$ that minimizes $D(p,q)$ under the restriction that

$$\int p(\mathbf{r})d\mathbf{r} = \omega \quad (39)$$

Then, one has to find the distribution $p(\mathbf{r})$ that is most similar to the distribution $\omega^0(\mathbf{r})$ in the sense of the Kullbach-Leibler divergence. Therefore, one has to minimize the following functional

$$\Omega = \int p(\mathbf{r})\ln\frac{p(\mathbf{r})}{\omega^0(\mathbf{r})}d\mathbf{r} - \lambda\left(\int p(\mathbf{r})d\mathbf{r} - \omega\right) \quad (40)$$

where λ is the Lagrange multiplier associated with the restriction of Eq. (39). By doing the minimization one finds that

$$p(\mathbf{r}) = \frac{\omega\omega^0(\mathbf{r})}{\int\omega^0(\mathbf{r})d\mathbf{r}} \quad (41)$$

Now, one has to choose, in an arbitrary way, the function $p(\mathbf{r})$. One simple choice, inspired by Eq. (39) is to say that $p(\mathbf{r}) = \omega(\mathbf{r})$. However, in this case the formula for the local electrophilicity (Eq. (41) with $\omega(\mathbf{r})$ instead of $p(\mathbf{r})$), has no local information about the real molecule. Therefore, it seems better to choose $p(\mathbf{r}) = \omega(\mathbf{r})f(\mathbf{r})$. This way, one has for the local electrophilicity that

$$\omega(\mathbf{r}) = \frac{\omega\,\omega^0(\mathbf{r})}{f(\mathbf{r})\int\omega^0(\mathbf{r})d\mathbf{r}} \quad (42)$$

This equation is very similar in structure to the one some of us proposed for the local hardness [75].

Now, one has to choose a model distribution where one knows the function $\omega^0(\mathbf{r})$. If $\omega^0(\mathbf{r})$ is based on an approximated model for ω, then the resulting local $\omega(\mathbf{r})$ will be chosen so that $\omega(\mathbf{r})\ f(\mathbf{r})$ in the true system is as close as possible to $\omega(\mathbf{r})\ f(\mathbf{r})$ in the model. The simplest choice is the noninteracting homogeneous electron gas,

$$\omega_{HEG}^0 == \frac{\left(\frac{1}{2}(3\pi^2)^{\frac{2}{3}}\rho^{\frac{2}{3}}\right)^2}{\frac{2}{3}(3\pi^2)^{\frac{2}{3}}\rho^{-\frac{1}{3}}} = C\rho^{\frac{5}{3}} \tag{43}$$

with the resulting

$$\omega^0(\mathbf{r}) = C\rho(\mathbf{r})^{\frac{5}{3}} \tag{44}$$

The final expression for the local electrophilicity is then

$$\omega(\mathbf{r}) = \frac{\omega\ C_F}{T_{TF}\ C}\rho(\mathbf{r})^{\frac{5}{3}} \tag{45}$$

where T_{TF} is the Thomas-Fermi kinetic energy and C_F is the Thomas-Fermi kinetic energy constant. As a result, this local electrophilicity is proportional to a power of the density and will have maxima at the position of the nuclei. Therefore, it does not seem to be a good candidate to measure the electrophilicity power of chemically significant regions of a molecule. A similar conclusion is obtained when a similar procedure is used to obtain a local hardness based on the noninteracting homogeneous electron gas [75].

To go further we will now use the same procedure to get a condensed version of the local electrophilicity. Now, the distribution to be minimized will be $p_k = \omega_k f_k$, where f_k is the condensed Fukui function [50–54]. The restriction is now $\omega = \sum_k \omega_k f_k$ and the function to minimize is

$$\Omega = \sum p_k \ln\frac{p_k}{p_k^0} - \lambda\left(\sum_k p_k - \omega\right) \tag{46}$$

The simplest choice for the reference distribution seems to be the atomic electrophilicity, $p_k^0 = \omega_k^0$. In this way, one obtains for the local condensed electrophilicity that

$$\omega_k = \frac{\omega}{f_k^+}\frac{\omega_k^0}{\sum_l \omega_l^0} \tag{47}$$

so that the regional information about the reactivity is captured by the condensed Fukui function f_k^+, where the subindex k indicates the kth atom in the molecule.

Local electrophilicity within the finite-temperature grand-canonical formalism

We have already seen that an alternative to define a local electrophilicity is to use available expressions for local chemical potential and for local hardness. In addition to the ones described previously, one may consider expressions that have been recently developed by Franco et al. [67] within a finite temperature framework of the density functional theory of chemical reactivity [49, 66–68].

In order to develop the temperature dependent expressions for the chemical reactivity descriptors one makes use of the grand canonical formalism, in which the molecule under consideration is considered to be very diluted in the solvent (the electrons reservoir). In this context, one may consider the molecule as an open system that may exchange electrons with the solvent, and the independent variables are the chemical potential of the bath, μ_{Bath}, the temperature, T, and the external potential.

Thus, by making use of an ensemble formed by the ground states of the systems with $N_0 - 1$, N_0, and $N_0 + 1$, where N_0, an integer, is the number of electrons of the molecule of interest, it has been established that the local electronic chemical potential, $\mu_{eT}(\mathbf{r})$, when integrated over the whole space leads to the global electronic chemical potential, μ_e, given by [67].

$$\begin{aligned}\mu_{eT}(\mathbf{r}) = &-\frac{1}{2}(IP f^-(\mathbf{r}) + EA f^+(\mathbf{r}))\\ &+ (IP f^-(\mathbf{r}) - EA f^+(\mathbf{r}))\frac{(\langle N\rangle - N_0)}{2\ \alpha}\\ &- (f^+(\mathbf{r}) - f^-(\mathbf{r}))(IP - EA)\gamma^{-1}\end{aligned} \tag{48}$$

where the subscripts e and T stand for electronic and temperature, respectively, $\langle N\rangle$ is the average number of electrons, so that $(\langle N\rangle - N_0)$ represents the fractional charge,

$$\langle N\rangle - N_0 = \frac{\exp[\beta(EA + \mu_{Bath})] - \exp[-\beta(IP + \mu_{Bath})]}{1 + \exp[\beta(EA + \mu_{Bath})] + \exp[-\beta(IP + \mu_{Bath})]} \tag{49}$$

$$\alpha = \left((\langle N\rangle - N_0)^2 + 4\left(1 - (\langle N\rangle - N_0)^2\right)\exp[-\beta(IP - EA)]\right)^{1/2} \tag{50}$$

and

$$\gamma = 4 + e^{\beta(IP + \mu_{Bath})} + e^{-\beta(EA + \mu_{Bath})} \tag{51}$$

$\beta = 1/k_B T$, k_B is Boltzmann's constant, and the Fukui functions are given by Eqs. (12) and (13).

Associated with this local chemical potential, a local hardness has been defined [67] through the expression

$$\eta_{eT}(\mathbf{r}) = IP f^-(\mathbf{r}) - EA f^+(\mathbf{r})$$
$$+ \frac{(\langle N \rangle - N_0)}{2}(IP - EA)(f^+(\mathbf{r}) - f^-(\mathbf{r})) \qquad (52)$$

When this local hardness is integrated over the whole space, it leads to a global hardness $\eta_{eT} = IP - EA$, which, as mentioned before, Parr and Pearson have shown [10] corresponds to the value of the second derivative of the energy with respect to the number of electrons obtained when one makes use of a smooth quadratic interpolation of the energy between the systems with $N_0 - 1$, N_0, and $N_0 + 1$ electrons.

By analogy with the definition of a local electrophilicity in terms of a local chemical potential and a local hardness, Eq. (35), one can define the temperature-dependent electrophilicity as:

$$\omega_{eT}(\mathbf{r}) = \frac{(\mu_{eT}(\mathbf{r}))^2}{2\eta_{eT}(\mathbf{r})} \qquad (53)$$

which depends on the variables μ_{Bath} and T that are independent of the system, $(\langle N \rangle - N_0)$, which appears explicitly in the expressions for the chemical potential, and the hardness depends on μ_{Bath} and T, according to Eq. (49). Thus, to make the local electrophilicity independent of μ_{Bath} and T, it is convenient to take the limit when $T \to 0$ and to consider, as in the original definition of electrophilicity, an idealized electron reservoir with zero chemical potential ($\mu_{Bath} = 0$) such that the fractional charge $(\langle N \rangle - N_0)$ is positive (the system gains electrons). However, the relation between μ_{Bath} and $(\langle N \rangle - N_0)$ in the limit $T \to 0$ is not a smooth function but a sequence of step functions (see Fig. 1) with $(\langle N \rangle - N_0)$ restricted to the interval $(-1,1)$. In the limit $T \to 0$ $(\beta \to \infty)$, $(\langle N \rangle - N_0)$ is positive and equal to 1 whenever $\mu_{Bath} > -A$. In other words, setting $\mu_{Bath} = 0$ or $\mu_{Bath} = \lim_{x \to -A^+} x$ yield in both cases that $(\langle N \rangle - N_0) = 1$. Nevertheless, the final expression for the local electrophilicity will depend on the value chosen for μ_{Bath}.
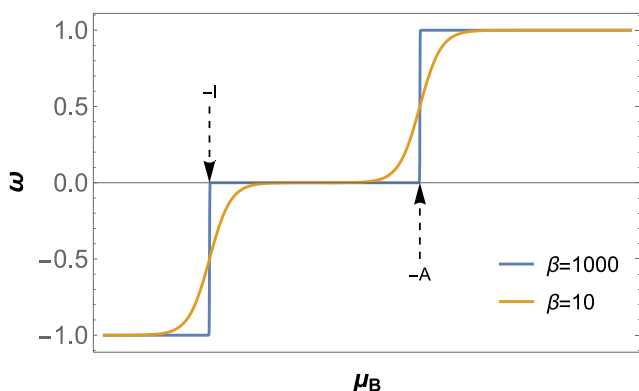

Fig. 1 Fractional charge of a molecule as a function of the chemical potential of the bath for high finite temperature $(\beta = 10 E_0^{-1}, \ T \approx 30000 \ K)$ and for close to room temperature $(\beta = 1000 E_0^{-1}, \ T \approx 300 \ K)$

Here, we choose $\mu_{Bath} = 0$ and take the limit of Eq. (53) when $T \to 0$ $(\beta \to \infty)$ and $(\langle N \rangle - N_0) \to 1$, which results in the following expression for the local electrophilicity,

$$\omega_{T \to 0}^{\mu_B=0}(\mathbf{r}) = \frac{(EA)^2 f^+(\mathbf{r})^2}{(EA + IP) f^-(\mathbf{r}) + (IP - 3EA) f^+(\mathbf{r})} \qquad (54)$$

Equation (54) seems appealing as a definition of local electrophilicity because as in the case of Eqs. (21) and (23), it carries information of both Fukui functions. In this case it may be interpreted as a consequence of the grand canonical ensemble: although overall a system gains electrons, there is always a fluctuation in N and information on how the system losses electrons should be present, which is the case of the $f^-(\mathbf{r})$ in the denominator. Nevertheless, this brings several inconveniences into the definition of the local electrophilicity: i) $\omega_{T \to 0}^{\mu_B=0}(\mathbf{r})$ does not integrate to the global electrophilicity or to a unique function of I and A [85]. ii) $\omega_{T \to 0}^{\mu_B=0}(\mathbf{r})$ could diverge because the denominator is not exempt to cancel out. We foresee two ways in which this could happen. In the case of neutral planar molecules it is common that $f^-(\mathbf{r})$ is negative around the nodal plane of π orbitals, which makes $\omega_{T \to 0}^{\mu_B=0}(\mathbf{r})$ indeterminate in the places where $(A + I)f^-(\mathbf{r}) = (3A - I)f^+(\mathbf{r})$. In the case of cations, which is the case of most electrophiles, an extra reason for indetermination is the fact that $(I - 3A)$ can easily be negative because the electron affinity of a cation is of the same order of magnitude as the ionization potential [11]. iii) As a consequence of the reasons given in ii), $\omega_{T \to 0}^{\mu_B=0}(\mathbf{r})$ could be negative; although this is also possible for $\omega(\mathbf{r}) = \omega f^+(\mathbf{r})$ because $f^+(\mathbf{r})$ can be negative, though very rarely.

Results

In order to make a comparison of the different expressions for the local electrophilicity presented in previous sections, we will consider first, for simplicity, the cases when the Fukui functions may be condensed to atoms [50–54]. These include the expressions given by Eqs. (14), (37), and (47). Equation (47) is already expressed in terms of the condensed Fukui function, while in all the rest one has to replace $f^+(\mathbf{r})$ by f_k^+, and $f^-(\mathbf{r})$ by f_k^-, where appropriate. We do not recommend condensing Eq. (54) due to the presence of the Fukui functions in the denominator, and the fact that it does not integrate to the global quantity.

Now, according to the relationship found by information theory, Eq. (47), an atom in a molecule will be a good electrophilic site when the free atom electrophilicity is high and the condensed Fukui function at this site is low. We are aware that sites with a small condensed Fukui function could be

problematic because generally the hydrogen atoms in a molecule are the ones with lowest value of the condensed Fukui function, and they are certainly not the most reactive. Here, we summed the condensed value of the Fukui function of hydrogen atoms to the heavy atom they are bonded to, and eliminated the hydrogen atoms in the summation $\sum_{l} \omega_l^0$ in Eq. (47).

Thus, we applied Eqs. (14), (37), and (47) to a set of ethylene derivatives that act as dienophiles showing an electrophile character in Diels Alder cycloaddition reactions with dienes that show a nucleophile character [55]. In the cases presented, the most electrophilic site corresponds to the carbon atom bonded to only hydrogen atoms, which is identified in this study as C2, the other carbon atom in the double bond identified as C1, is the one to which the different substituents considered in this study are bonded.

The electronic structure of the molecules considered was calculated with the program Gaussian09 [86], with the Kohn-sham method [1, 87] using the functional B3LYP for the exchange correlation energy approximation [88–92], and the basis set 6–311++G(d,p). The ionization potential and the electron affinity were determined through energy differences, $IP = E_{N_0-1} - E_{N_0}$ and $EA = E_{N_0} - E_{N_0+1}$, and from these the chemical potential, the hardness and the global electrophilicity were determined from Eqs. (4), (5), and (6), respectively. The condensed Fukui functions were calculated by the response-of-molecular-fragment approach [54] using finite differences

between the atomic charges of the systems of interest (N_0) and its "anion" ($N_0 + 1$) for $f_k^+ = q_k^{N_0} - q_k^{N_0+1}$ or its cation ($N_0 - 1$) for $f_k^- = q_k^{N_0-1} - q_k^{N_0}$, as previously mentioned the subindex k indicates the kth atom in the molecule. The charges were calculated fitting the electrostatic potential [93], CHelpG, or using the natural population analysi [94], NPA.

The results are shown in Table 1. One can see that the expression established by Chattaraj et al., Eq. (14), leads to the correct description in all the cases considered because the condensed electrophilicity at C2 is always greater than the one at C1. The same situation applies to Eq. (37); however, in this formulation, the differences between the values for C2 and C1 are smaller in some cases and larger in others. On the other hand, the description provided by Eq. (47), which comes from information theory, leads to the opposite values in most cases, since C1 shows a greater condensed electrophilicity than C2.

In the case of Eq. (54) we chose two examples to show how the spatial distribution of $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ looks. The first one is the diphenylmethyl cation. In Fig. 2 one can see that $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ wrongly predicts that the carbon bearing the formal positive charge (C^+) has a negative electrophilicity (blue in Fig. 2a). However, this molecule is a textbook example of a carbocation that prefers to react with nucleophiles through the C^+ despite the delocalization of charge by resonance with the aromatic fragments. Besides, $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ is positive (red in Fig. 2a) only close to one of the three carbon atoms of the

Table 1 Condensed local electrophilicity for a selected set of dienophiles involved in Diels-Alder reactions in eV

| Molecule	Site	Eq. (14)		Eq. (37)		Eq. (47)	
		CHelpG	NPA	CHelpG	NPA	CHelpG	NPA
1,1dicyanoethylene	C1	0.326	0.329	0.327	0.320	1.839	1.826
	C2	0.589	0.681	0.598	0.647	0.702	0.731
nitroethylene	C1	−0.113	0.074	−0.106	0.048	40.683	3.637
	C2	0.602	0.517	0.552	0.466	0.728	0.884
acrolein	C1	−0.023	0.109	−0.020	0.081	2.049	1.237
	C2	0.335	0.460	0.320	0.405	0.371	0.379
acrylonitrile	C1	0.191	0.288	0.227	0.286	1.415	1.331
	C2	0.394	0.549	0.424	0.520	0.683	0.458
methyl vinyl ketone	C1	−0.031	0.116	−0.019	0.088	8.688	1.606
	C2	0.394	0.400	0.343	0.345	0.491	0.586
methyl acrylate	C1	0.123	0.185	0.121	0.184	1.893	1.114
	C2	0.359	0.451	0.369	0.406	0.451	0.488
ethylene	C1	−0.924	0.106	−0.535	0.219	1.324	1.324
	C2	−0.924	0.106	−0.535	0.219	1.324	1.324
acetylene	C1	−0.674	0.144	−0.348	0.266	1.425	1.425
	C2	−0.674	0.144	−0.348	0.266	1.425	1.425
methyl vinyl ether	C1	−0.393	0.002	−0.264	0.030	−12.039	1.945
	C2	−0.373	0.049	−0.141	0.141	1.019	2.308
dimethylvinyl amine	C1	−0.457	−0.007	−0.344	−0.006	−0.737	−25.825
	C2	−0.065	0.031	0.060	0.107	0.765	5.653

a)

b)
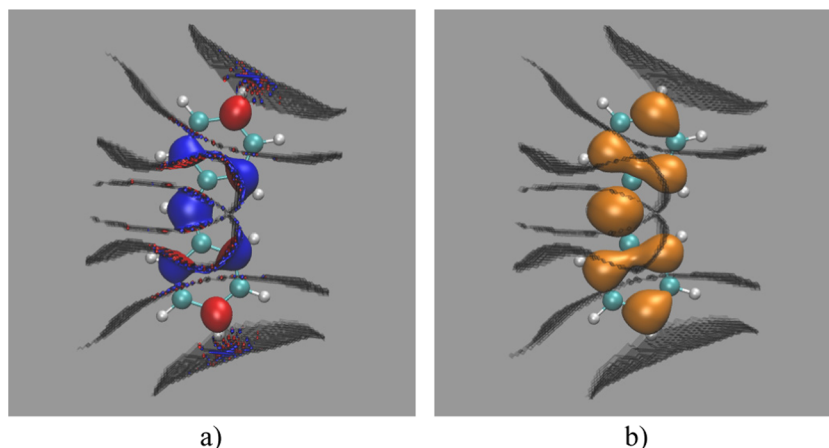
Fig. 2 **a)** Isosurfaces of the local electrophilicity $\omega^{\mu_B=0}_{T->0}(\mathbf{r}) = \pm 1 \times 10^{-2} eV/a_0^3$, Eq. (54), Red corresponds to positive values and blue to negative ones. The surfaces in gray are the separatrixes of negative and positive values. **b)** Chattaraj local electrophilicity $\omega f^+(\mathbf{r}) = 1 \times 10^{-2} eV/a_0^3$, Eq. (14). The separatrixes of a) are also shown. Fukui functions where computed using the frozen core approximation, and IP and EA where evaluated using the Koopmans' approximation
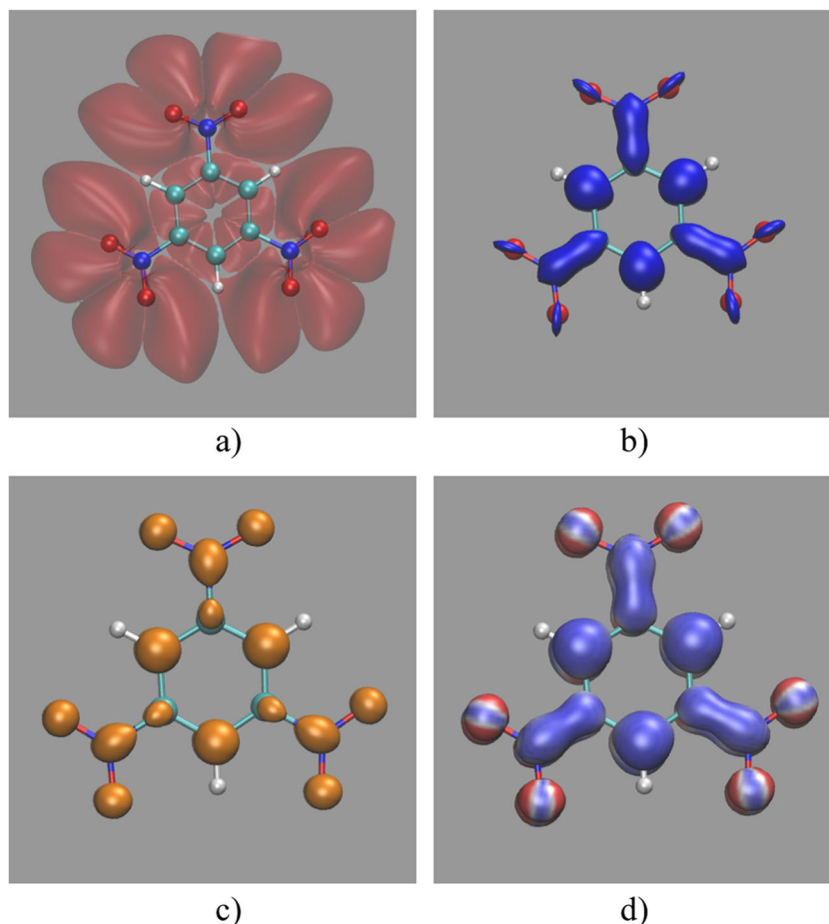

a)

b)

c)

d)

Fig. 3 **a)** Isosurfaces of the denominator of the ensemble local electrophilicity $\omega^{\mu_B=0}_{T->0}(\mathbf{r})$, $(A+I)f^-(\mathbf{r}) + (I-3A)f^+(\mathbf{r}) = 5 \times 10^{-6} eV/a_0^3$. Small values of the denominator of $\omega^{\mu_B=0}_{T->0}(\mathbf{r})$ are indicatives of regions where $\omega^{\mu_B=0}_{T->0}(\mathbf{r})$ tends to diverge. **b)** negative-valued isosurface of the denominator of $\omega^{\mu_B=0}_{T->0}(\mathbf{r})$, $(A+I)f^-(\mathbf{r}) +$ $(I-3A)f^+(\mathbf{r}) = -5 \times 10^{-3} eV/a_0^3$. **c)** Chattaraj's local electrophilicity $\omega f^+(\mathbf{r}) = 1.5 \times 10^{-2} eV/a_0^3$. **d)** Isosurface of the numerator of $\omega^{\mu_B=0}_{T->0}(\mathbf{r})$, $A^2 f^+(\mathbf{r})^2 = 5 \times 10^{-5} eV^2/a_0^6$ colored according to the values of the denominator of $\omega^{\mu_B=0}_{T->0}(\mathbf{r})$. The color code is such that dark blue corresponds to $-5 \times 10^{-3} eV/a_0^3$ and dark red to $5 \times 10^{-3} eV/a_0^3$

aromatic rings that could bear a positive charge in the Lewis resonant structures. Also, note that the negative isosurfaces (blue) are abruptly cut by separatrixes. This is indicative of regions where $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ diverges, for instance, at the carbon next to the C^+. Contrarily, Chattaraj's local electrophilicity $\omega f^+(\mathbf{r})$ (Fig. 2b) nicely recovers the correct regioselectivity of the diphenylmethyl cation because it takes its maximum value close to the C^+, and it is also large in the three carbons of the aromatic rings that could bear a positive charge.

The second example is the neutral electrophile 1,3,5-trinitrobenzene (see Fig. 3). Despite being a neutral molecule, the electron affinity of this electrophile is still a large fraction of the ionization potential ($3A = 1.3I$). Hence, the inconveniences *ii)* and *iii)* still apply to this case. Namely, the denominator takes very small values in chemically significant regions of the molecule (Fig. 3a), which makes $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ diverge or extremely difficult to evaluate in a finite grid. Also, note that the denominator takes negative values (Fig. 3b) where it holds, approximately, that $f^+(\mathbf{r}) > 7.6f^-(\mathbf{r})$. That is, when $\omega_{T->0}^{\mu_B=0}(\mathbf{r}) < 0$ it becomes proportional to the negative of $f^+(\mathbf{r})$, and the molecule is predicted to be less electronegative where $\omega f^+(\mathbf{r})$ predicts the opposite (Fig. 3c). This time the divergence of $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ made it impossible to compute accurate isosurfaces of it. However, to illustrate the structure of $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$, in Fig. 3d we plotted an isosurface of the numerator of $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ $(A^2 f^+(\mathbf{r})^2 = 5 \times 10^{-5} eV^2/a_0^6$) colored according to the values that take the denominator of $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ in a range from $-5 \times 10^{-3} eV/a_0^3$ (dark blue) to $5 \times 10^{-3} eV/a_0^3$ (dark red). The pale blue color (which is exactly zero) indicates that in those regions $\omega_{T->0}^{\mu_B=0}(\mathbf{r})$ tends to diverge from below. However, those regions include just the ortho carbons that are expected to be the most electrophilic atoms.

Conclusions

In order to discuss the concept of local electrophilicity, we considered several approaches. Thus, we analyzed the original proposal of Chattaraj et al. and presented two alternative procedures to derive the expression. We also connected the recent approaches [61, 64] related with the description of the local electrophilicity in terms of the electron density into one formulation that leads to a local electrophilicity with the same units as the one proposed by Chattaraj et al., but that introduces $f^-(\mathbf{r})$ in addition to the natural Fukui function for charge acceptance $f^+(\mathbf{r})$. On the other hand, to explore other possibilities for this important concept, we derived an expression for the condensed electrophilicity based on information theory, and we also considered the temperature dependent approach, through the use of a local chemical potential and a local hardness.

The poor results obtained for the last two approaches lead us to conjecture that the reason may be associated with the fact that the global electrophilicity is not a derivative of one of the Taylor series of the energy or any thermodynamical potential because certainly these two approaches have been successfully applied to describe other reactivity indicators.

In summary, it seems that the best way to obtain a local version of the electrophilicity is using Chattaraj's suggestion, which is the simplest one, and it has been mathematically motivated by two different approaches in the present work.

References

1. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, New York
2. Chermette H (1998) Density functional theory: a powerful tool for theoretical studies in coordination chemistry. Coord Chem Rev 180:699–721
3. Geerlings P, De Proft F, Langenaeker W (2003) Conceptual density functional theory. Chem Rev 103:1793–1873. https://doi.org/10.1021/cr990029p
4. Ayers PW, Anderson JSM, Bartolotti LJ (2005) Perturbative perspectives on the chemical reaction prediction problem. Int J Quantum Chem 101:520–534. https://doi.org/10.1002/qua.20307
5. Gázquez J (2008) Perspectives on density functional theory of chemical reactivity. J Mex Chem Soc 52:3–10
6. Ayers PW, Yang WT, Bartolotti LJ (2009) Fukui function. In: Chattaraj PK (ed) Chemical reactivity theory: a density functional view. CRC, Boca Raton, pp 255–267
7. Liu S-B (2009) Conceptual density functional theory and some recent developments. Acta Phys -Chim Sin 25:590–600
8. Fuentealba P, Cardenas C (2015) Density functional theory of chemical reactivity. In: Springborg M, Joswig OJ (eds) Chemical modelling, vol 11. The Royal Society of Chemistry, pp 151-174. https://doi.org/10.1039/9781782620112-00151
9. Parr RG, Donnelly RA, Levy M, Palke WE (1978) Electronegativity: the density functional viewpoint. J Chem Phys 68:3801–3807. https://doi.org/10.1063/1.436185
10. Parr RG, Pearson RG (1983) Absolute hardness - companion parameter to absolute electronegativity. J Am Chem Soc 105:7512–7516
11. Cárdenas C, Heidar-Zadeh F, Ayers PW (2016) Benchmark values of chemical potential and chemical hardness for atoms and atomic ions (including unstable anions) from the energies of isoelectronic series. Phys Chem Chem Phys 18:25721–25734. https://doi.org/10.1039/C6CP04533B
12. Parr RG, Yang WT (1984) Density functional approach to the frontier-electron theory of chemical reactivity. J Am Chem Soc 106:4049–4050
13. Yang WT, Parr RG, Pucci R (1984) Electron density, Kohn-sham frontier orbitals, and Fukui functions. J Chem Phys 81:2862–2863. https://doi.org/10.1063/1.447964
14. Yang WT, Parr RG (1985) Hardness, softness, and the Fukui function in the electron theory of metals and catalysis. Proc Natl Acad Sci USA 82:6723–6726. https://doi.org/10.1073/pnas.82.20.6723

15. Pearson RG (1987) Recent advances in the concept of hard and soft acids and bases. J Chem Ed 64:561–567

16. Pearson RG (1963) Hard and soft acids and bases. J Am Chem Soc 85:3533–3539

17. Pearson RG (1966) Acids and bases. Science 151:172–177

18. Pearson RG (1967) Hard and soft acids and bases. Chem Britain 3: 103–107

19. Chattaraj PK, Lee H, Parr RG (1991) HSAB principle. J.Am Chem Soc 113:1855–1856

20. Parr RG, Chattaraj PK (1991) Principle of maximum hardness. J Am Chem Soc 113:1854–1855

21. Pearson RG, Palke WE (1992) Support for a principle of maximum hardness. J Phys Chem 96:3283–3285. https://doi.org/10.1021/j100187a020

22. Gázquez JL (1993) Hardness and softness in density functional theory. Struct Bond 80:27–43

23. Gázquez JL, Méndez F (1994) The hard and soft acids and bases principle - an atoms in molecules viewpoint. J Phys Chem 98: 4591–4593. https://doi.org/10.1021/j100068a018

24. Chattaraj PK, Liu GH, Parr RG (1995) The maximum hardness principle in the Gyftopoulos-Hatsopoulos three-level model for an atomic or molecular species and its positive and negative ions. Chem Phys Lett 237:171–176

25. Gázquez JL (1997) Bond energies and hardness differences. J Phys Chem A 101:9464–9469

26. Gázquez JL (1997) The hard and soft acids and bases principle. J Phys Chem A 101:4657–4659

27. Chattaraj PK (2001) Chemical reactivity and selectivity: local HSAB principle versus frontier orbital theory. J Phys Chem A 105:511–513

28. Torrent-Sucarrat M, Luis JM, Duran M, Sola M (2001) On the validity of the maximum hardness and minimum polarizability principles for nontotally symmetric vibrations. J Am Chem Soc 123:7951–7952

29. Ayers PW (2005) An elementary derivation of the hard/soft-acid/base principle. J Chem Phys 122:141102

30. Chattaraj PK, Ayers PW (2005) The maximum hardness principle implies the hard/soft acid/base rule. J Chem Phys 123:086101

31. Ayers PW, Parr RG, Pearson RG (2006) Elucidating the hard/soft acid/base principle: a perspective based on half-reactions. J Chem Phys 124:194107

32. Ayers PW (2007) The physical basis of the hard/soft acid/base principle. Faraday Discuss. 135:161–190

33. Chattaraj PK, Ayers PW, Melin J (2007) Further links between the maximum hardness principle and the hard/soft acid/base principle: insights from hard/soft exchange reactions. Phys Chem Chem Phys 9:3853–3856

34. Chattaraj PK (2007) A minimum electrophilicity perspective of the HSAB principle. Indian J Phys 81:871–879

35. Reed JL (2012) Hard and soft acids and bases: structure and process. J Phys Chem A 116:7147–7153. https://doi.org/10.1021/jp301812j

36. Ayers PW, Cardenas C (2013) Communication: a case where the hard/soft acid/base principle holds regardless of acid/base strength. J Chem Phys 138:181106

37. Cardenas C, Ayers PW (2013) How reliable is the hard-soft acid-base principle? An assessment from numerical simulations of electron transfer energies. Phys Chem Chem Phys 15:13959–13968. https://doi.org/10.1039/c3cp51134k

38. Miranda-Quintana RA, Kim TD, Cárdenas C, Ayers PW (2017) The HSAB principle from a finite-temperature grand-canonical perspective. Theor Chem Accounts 136:135

39. Parr RG, Von Szentpaly L, Liu SB (1999) Electrophilicity index. J Am Chem Soc 121:1922–1924

40. Chattaraj PK, Sarkar U, Roy DR (2006) Electrophilicity index. Chem Rev 106:2065–2091. https://doi.org/10.1021/cr040109f

41. Chattaraj PK, Roy DR (2007) Update 1 of: Electrophilicity index. Chem Rev 107:PR46–PR74

42. Chattaraj PK, Chakraborty A, Giri S (2009) Net electrophilicity. J Phys Chem A 113:10068–10074

43. Chattaraj PK, Giri S, Duley S (2011) Update 2 of: electrophilicity index. Chem Rev 111:PR43–PR75. https://doi.org/10.1021/cr100149p

44. Chattaraj PK, Maiti B, Sarkar U (2003) Philicity: a unified treatment of chemical reactivity and selectivity. J Phys Chem A 107: 4973–4975

45. Perdew JP, Parr RG, Levy M, Balduz JL (1982) Density-functional theory for fractional particle number - derivative discontinuities of the energy. Phys Rev Lett 49:1691–1694. https://doi.org/10.1103/PhysRevLett.49.1691

46. Yang WT, Zhang YK, Ayers PW (2000) Degenerate ground states and a fractional number of electrons in density and reduced density matrix functional theory. Phys Rev Lett 84:5172–5175. https://doi.org/10.1103/PhysRevLett.84.5172

47. Ayers PW (2008) The dependence on and continuity of the energy and other molecular properties with respect to the number of electrons. J Math Chem 43:285–303. https://doi.org/10.1007/s10910-006-9195-5

48. Berkowitz M, Parr RG (1988) Molecular hardness and softness, local hardness and softness, hardness and softness kernels, and relations among these quantities. J Chem Phys 88:2554–2557

49. Franco-Pérez M, Gázquez JL, Ayers PW, Vela A (2015) Revisiting the definition of the electronic chemical potential, chemical hardness, and softness at finite temperatures. J Chem Phys 143:154103

50. Yang WT, Mortier WJ (1986) The use of global and local molecular-parameters for the analysis of the gas-phase basicity of amines. J Am Chem Soc 108:5708–5711

51. Contreras RR, Fuentealba P, Galvan M, Perez P (1999) A direct evaluation of regional Fukui functions in molecules. Chem Phys Lett 304:405–413

52. Fuentealba P, Perez P, Contreras R (2000) On the condensed Fukui function. J Chem Phys 113:2544–2551

53. Ayers PW, Morrison RC, Roy RK (2002) Variational principles for describing chemical reactions: condensed reactivity indices. J Chem Phys 116:8731–8744

54. Bultinck P, Fias S, Van Alsenoy C, Ayers PW, Carbo-Dorca R (2007) Critical thoughts on computing atom condensed Fukui functions. J Chem Phys 127:034102

55. Domingo LR, Aurell MJ, Perez P, Contreras R (2002) Quantitative characterization of the local electrophilicity of organic molecules. Understanding the regioselectivity on Diels- Alder reactions. J Phys Chem A 106:6871–6875

56. Pérez P, Toro-Labbé A, Aizman A, Contreras R (2002) Comparison between experimental and theoretical scales of electrophilicity in benzhydryl cations. J Org Chem 67:4747–4752

57. Ayers PW, Parr RG (2000) Variational principles for describing chemical reactions: the Fukui function and chemical hardness revisited. J Am Chem Soc 122:2010–2018

58. Chattaraj PK, Cedillo A, Parr RG (1995) Variational method for determining the Fukui function and chemical hardness of an electronic system. J Chem Phys 103:7645–7646

59. Gázquez JL, Cedillo A, Vela A (2007) Electrodonating and electroaccepting powers. J Phys Chem A 111:1966–1970. https://doi.org/10.1021/jp065459f

60. Cedillo A, Contreras R (2012) A local extension of the electrophilicity index concept. J Mex Chem Soc 56:257–260

61. Morell C, Gázquez JL, Vela A, Guegan F, Chermette H (2014) Revisiting electroaccepting and electrodonating powers: proposals for local electrophilicity and local nucleophilicity descriptors. Phys Chem Chem Phys 16:26832–26842. https://doi.org/10.1039/c4cp03167a

62. Morell C, Grand A, Toro-Labbé A (2005) New dual descriptor for chemical reactivity. J Phys Chem A 109:205–212. https://doi.org/10.1021/jp046577a

63. Morell C, Grand A, Toro-Labbé A (2006) Theoretical support for using the Delta f(r) descriptor. Chem Phys Lett 425:342–346. https://doi.org/10.1016/j.cplett.2006.05.003

64. Heidar-Zadeh F, Fias S, Vöhringer-Martinez E, Verstraelen T, Ayers PW (2017) The local response of global descriptors. Theor Chem Accounts 136:19

65. Tognetti V, Morell C, Joubert L (2015) Quantifying electro/nucleophilicity by partitioning the dual descriptor. J Comput Chem 36:649–659. https://doi.org/10.1002/jcc.23840

66. Franco-Pérez M, Ayers PW, Gázquez JL, Vela A (2015) Local and linear chemical reactivity response functions at finite temperature in density functional theory. J Chem Phys 143:244117

67. Franco-Pérez M, Ayers PW, Gázquez JL, Vela A (2017) Local chemical potential, local hardness, and dual descriptors in temperature dependent chemical reactivity theory. Phys Chem Chem Phys 19:13687–13695

68. Franco-Pérez M, Heidar-Zadeh F, Ayers PW, Gázquez JL, Vela A (2017) Going beyond the three-state ensemble model: the electronic chemical potential and Fukui function for the general case. Phys Chem Chem Phys 19:11588–11602

69. Polanco-Ramírez CA, Franco-Pérez M, Carmona-Espíndola J, Gázquez JL, Ayers PW (2017) Revisiting the definition of local hardness and hardness kernel. Phys Chem Chem Phys 19:12355–12364. https://doi.org/10.1039/c7cp00691h

70. Franco-Perez M, Polanco-Ramirez CA, Gazquez JL, Ayers PW (2018) Reply to the 'Comment on "Revisiting the definition of local hardness and hardness kernel"' by C. Morell, F. Guegan, W. Lamine, and H. Chermette, Phys Chem Chem Phys, 2018, 20, doi:10.1039/C7CP04100D. Phys Chem Chem Phys 20:9011–9014. https://doi.org/10.1039/c7cp07974e

71. Hohenberg P, Kohn W (1964) Inhomogeneous electron gas. Phys Rev B 136:B864–B871

72. Ayers PW, Parr RG (2008) Local hardness equalization: exploiting the ambiguity. J Chem Phys 128:184108

73. Ayers PW, Parr RG (2008) Beyond electronegativity and local hardness: higher-order equalization criteria for determination of a ground-state electron density. J Chem Phys 129:054111

74. Gázquez JL, Vela A, Chattaraj PK (2013) Local hardness equalization and the principle of maximum hardness. J Chem Phys 138:214103

75. Heidar-Zadeh F, Fuentealba P, Cardenas CA, Ayers P (2014) An information-theoretic resolution of the ambiguity in the local hardness. Phys Chem Chem Phys 16:6019-6060-6026

76. Nalewajski RF, Parr RG (2000) Information theory, atoms in molecules, and molecular similarity. Proc Natl Acad Sci USA 97:8879–8882

77. Nalewajski RF, Parr RG (2001) Information theory thermodynamics of molecules and their Hirshfeld fragments. J Phys Chem A 105:7391–7400

78. Kullback S, Leibler RA (1951) On information and sufficiency. Ann Math Stat 22:79–86

79. Kullback S (1997) Information theory and statistics. Dover, Mineola

80. Hirshfeld FL (1977) Bonded-atom fragments for describing molecular charge-densities. Theor Chim Acta 44:129–138

81. Heidar-Zadeh F, Vinogradov I, Ayers PW (2017) Hirshfeld partitioning from non-extensive entropies. Theor Chem Accounts 136:54

82. Heidar-Zadeh F, Ayers PW (2017) Fuzzy atoms in molecules from Bregman divergences. Theor Chem Accounts 136:92

83. Heidar-Zadeh F, Ayers PW, Verstraelen T, Vinogradov I, Vöhringer-Martinez E, Bultinck P (2017) Information-theoretic approaches to atoms-in-molecules: Hirshfeld family of partitioning schemes. J Phys Chem A 122:4219–4245

84. Heidar Zadeh F (2017) Variational information-theoretic atoms-in-molecules. McMaster University, Hamilton

85. Gonzalez MM, Cardenas C, Rodríguez JI, LIU S, Heidar-Zadeh F, Miranda-Quintana RA, Ayers PW, Martínez GM, Carlos C, Juan IR (2017) Quantitative electrophilicity measures. Acta Phys Chim Sin 34:662–674

86. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark MJ, Heyd J, Brothers EN, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell AP, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09. Gaussian Inc., Wallingford

87. Kohn W, Sham LJ (1965) Self-consistent equations including exchange and correlation effects. Phys Rev 140:1133–1138

88. Becke AD (1993) Density functional thermochemistry. III. The role of exact exchange. J Chem Phys 98:5648–5652

89. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J Phys Chem 98:11623–11627

90. Kim K, Jordan KD (1994) Comparison of density functional and MP2 calculations on the water monomer and dimer. J Phys Chem 98:10089–10094

91. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38:3098–3100

92. Lee CT, Yang WT, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron-density. Phys Rev B 37:785–789

93. Breneman CM, Wiberg KB (1990) Determining atom-centered monopoles from molecular electrostatic potentials - the need for high sampling density in formamide conformational-analysis. J Comput Chem 11:361–373

94. Reed AE, Weinstock RB, Weinhold F (1985) Natural-population analysis. J Chem Phys 83:735–746. https://doi.org/10.1063/1.449486