Electrodonating and Electroaccepting Powers

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By introducing an electron bath that represents the chemical environment in which a chemical species is immersed, and by making use of the second-order Taylor series expansions of the energy as a function of the number of electrons in the intervals between $N-1$ and N, and N and $N+1$, we show that the electrodonating (ω^-) and the electroaccepting (ω^+) powers may be defined as $\omega^\mp = (\mu^\mp)^2/2\eta^\mp$, where $\mu^\mp$ are the chemical potentials and $\eta^\mp$ are the chemical hardnesses, in their corresponding intervals. Approximate expressions for ω^- and ω^+ in terms of the ionization potential I and the electron affinity A are established by assuming that $\eta^- = \eta^+ = \eta = \mu^+ - \mu^-$. The functions $\omega^\mp(\mathbf{r}) = \omega^\mp f^\mp(\mathbf{r})$, where $f^\mp(\mathbf{r})$ are the directional Fukui functions, derived from a functional Taylor series for the energy functional truncated at second order, represent the local electrodonating and electroaccepting powers.

1. Introduction

Charge-transfer models based on the second-order Taylor series expansion of the energy as a function of the number of electrons, around a reference state, have proven to be very useful to qualitatively describe and understand fundamental aspects of chemical interactions driven by donor–acceptor processes.[1–10] In these models, the energy change ΔE due to the electron transfer ΔN, when the external potential $v(\mathbf{r})$ is kept fixed, is approximated by

$$\Delta E = \mu \Delta N + \frac{1}{2}\eta(\Delta N)^2 \qquad (1)$$

where $\mu = (\partial E/\partial N)_v$ is the chemical potential and $\eta = (\partial^2 E/\partial N^2)_v$ is the chemical hardness.

Following this approach, Parr, Von Szentpály, and Liu,[4] prompted by the work of Maynard et al.,[11] have defined the electrophilicity index that measures the energy change of an electrophile when it becomes saturated with electrons, by considering the case when an electrophilic species is immersed in an idealized zero-temperature free electron sea of zero chemical potential. In such situation, the species becomes saturated with electrons when its chemical potential becomes equal to that of the electron sea. At this point, the maximum electron transfer is given by $\Delta N_{\max} = -\mu/\eta > 0$, and the energy change becomes $\Delta E = -\mu^2/2\eta < 0$, which suggests the definition of the electrophilicity as

$$\omega \equiv \mu^2/2\eta \qquad (2)$$

Thus, although the electron affinity measures the capability of a chemical system to accept one electron from a donor, the electrophilicity is related to the maximum amount of the electron flow that may be either less or more than 1, and it is given in terms of fundamental quantities that govern small changes away

from an initial reference state. The finite differences approximations to the derivatives of eq 1,

$$\mu = -(I+A)/2 \qquad \text{and} \qquad \eta = I - A \qquad (3)$$

imply that the electrophilicity may be approximated by

$$\omega \approx \frac{(I+A)^2}{8(I-A)} \qquad (4)$$

where it is clear that this global reactivity index depends not only on the electron affinity, A, but also on the ionization potential I.

However, it is important to note that due to the behavior of the energy as a function of the number of electrons at zero temperature,[12] the first derivative μ evaluated at some integral value of N will, in general, have one value when evaluated from the left, and a different value when evaluated from the right. That is, $\mu^+ = (\partial E/\partial N)_v^+ = -A$, and $\mu^- = (\partial E/\partial N)_v^- = -I$. Also, at zero temperature, the second derivative is 0 when the derivatives are taken from the right or the left, and it is infinite when a central difference formula is used. However, Ayers and Parr[13] have shown that some information remains, because $\eta(M) = (\mu^+ - \mu^-)\delta(M-N)$ for $N-1 < M < N+1$.

In spite of the mathematical difficulties associated with the discontinuities, from the chemical perspective, it makes sense to differentiate the response of the system to charge donation, from the response to charge acceptance, a situation that indicates that the left and right derivatives of the energy with respect to the number of electrons could be different. However, although such differentiation has always been recognized for the case of the Fukui functions,[14] where $f^-(\mathbf{r})$ characterizes the sites for electrophilic attack, and $f^+(\mathbf{r})$ characterizes the sites for nucleophilic attack, it has not been considered, until recently,[15] for the cases of the chemical potential and the chemical hardness. In studies of reactivity trends based on these quantities, as defined in density functional theory, a single value for μ and a single value for η are used to describe charge donating and charge accepting processes. This situation is due to the fact that

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Electrodonating and Electroaccepting Powers

J. Phys. Chem. A, Vol. 111, No. 10, 2007 **1967**

the linear interpolation mentioned above obliterates second-order effects, so to include them, one makes use of a smooth interpolation around the reference point, like the quadratic one given by eq 1, that does not distinguish one response from the other one.

The objective of the present work is to elaborate on the concept of electrophilicity, as another specific application of the use of different response functions for the addition and subtraction of charge, to show the importance of such distinction.

Thus, we will first establish, from a general point of view, through a simple charge-transfer model, the global response of a chemical species when it is immersed in an idealized bath that may either withdraw or donate charge. Then, an alternative quadratic interpolation for the energy as a function of the number of electrons will be proposed to evaluate the response of a system to charge withdrawal or charge acceptance in terms of the ionization potential and the electron affinity. Finally, through the use of a functional Taylor series for the energy functional, the local response functions for charge withdrawal or charge acceptance will be derived.

2. Response of a System to Charge Donation and Charge Acceptance

The first ionization potential and the electron affinity are properties of a system that allow one to measure its propensity to donate or accept one electron. However, let us consider that we are interested in analyzing, through an energy change index, the propensity of a given chemical species to donate or accept fractional amounts of charge when it is immersed in a certain chemical environment. In this context, one may invoke the second-order Taylor series expansion of the energy as a function of the number of electrons around a reference state, eq 1. However, to distinguish between the charge donating and the charge accepting situations, through the intrinsic properties of the chemical species that govern small changes away from an initial reference state, we assume that for the interval between $N - 1$ and N, eq 1 adopts the form

$$\Delta E^- = \mu^- \Delta N + \frac{1}{2}\eta^-(\Delta N)^2 \qquad (5)$$

whereas for the interval between N and $N + 1$, it takes the form

$$\Delta E^+ = \mu^+ \Delta N + \frac{1}{2}\eta^+(\Delta N)^2 \qquad (6)$$

That is, in eqs 5 and 6 one explicitly recognizes that the first and second derivatives at the reference state can be different when evaluated from the left or from the right. However, it is important to note that within the zero-temperature grand canonical ensemble formulation of density functional theory, the energy as a function of the number of electrons consists of a series of straight lines connecting the ground state energies of integer numbers of particles.[12] This situation implies that the second derivatives in eqs 5 and 6 are equal to 0. Nevertheless, because the second-order terms contain important information from the chemical perspective, we assume that there exists a quadratic interpolation between integer values of the number of electrons that differentiates between the left and the right derivatives.

Now, to simulate the chemical environment, one may use the concept of an electron bath with chemical potential μ_{bath} in which the chemical species is immersed. In this case, the chemical species is an open system that can exchange electrons with the bath, and the change in its grand potential is given

by[16,17] $d\Omega^\mp = dE^\mp - \mu_{bath} dN$. For differential changes, $dE^\mp = \mu^\mp dN$, and due to the equilibrium and stability conditions, one has that $d\Omega^\mp = (\mu^\mp - \mu_{bath}) dN \leq 0$; therefore, the value of μ_{bath} determines the direction of the flow of charge. That is, when $\mu_{bath} > \mu^+$, the system accepts charge from the bath, increasing its chemical potential until it reaches the value μ_{bath}, and when $\mu_{bath} < \mu^-$, the system donates charge to the bath, decreasing its chemical potential until it reaches the value μ_{bath}.

Thus, because we are interested in the situation corresponding to small energy changes produced by the environment in which the species is immersed, μ_{bath} should take a value that lies close to μ^-, when one measures the propensity to donate charge, and it should take a value that lies close to μ^+, when one measures the propensity to accept charge. Therefore, by noting that both μ^- and μ^+ are negative quantities, one may assume that in the first case $\mu_{bath} = \alpha^-\mu^-$, where $\alpha^- > 1$ is a constant whose value should be slightly greater than 1 to ensure that $\mu_{bath} < \mu^-$, and in the second case $\mu_{bath} = \alpha^+\mu^+$, where $\alpha^+ < 1$ is a constant whose value should be slightly lower than 1 to ensure that $\mu_{bath} > \mu^+$.

Then, because $\Delta\Omega^\mp = \Delta E^\mp - \mu_{bath}\Delta N$, with $\Delta E^\mp$ given by eq 5 or 6, the equilibrium point may be obtained by minimizing the change in the grand potential with respect to the amount of transferred charge. This procedure leads, for the charge donating process, to $\Delta N^- = (\alpha^- - 1)\mu^-/\eta^-$, and to the energy change

$$\Delta E^- = \frac{((\alpha^-)^2 - 1)(\mu^-)^2}{2\eta^-} > 0 \qquad (7)$$

because $\alpha^- > 1$, indicating that the charge donating process is energetically unfavorable. On the other hand, for the charge accepting process, the above procedure leads to $\Delta N^+ = (\alpha^+ - 1)\mu^+/\eta^+$, and to the energy change

$$\Delta E^+ = \frac{((\alpha^+)^2 - 1)(\mu^+)^2}{2\eta^+} < 0 \qquad (8)$$

because $\alpha^+ < 1$, indicating that the charge accepting process is energetically favorable.

Now, because α is a constant that characterizes the bath, one can define, from eq 7, the electrodonating power as

$$\omega^- = \frac{(\mu^-)^2}{2\eta^-} \qquad (9)$$

and, from eq 8, the electroaccepting power as

$$\omega^+ = \frac{(\mu^+)^2}{2\eta^+} \qquad (10)$$

At this point, it is important to note that the same procedure outlined to derive eqs 9 and 10, could have been used with eq 1 instead of eqs 5 and 6. Because in such a case, $\mu^- = \mu^+ = \mu$ and $\eta^- = \eta^+ = \eta$, the original electrophilicity index is recovered, $\omega^- = \omega^+ = \omega = \mu^2/2\eta$. However, through the present approach, one can see that the definition of electrophilicity is not necessarily linked to the point at which the species becomes saturated with electrons ($\mu = \mu_{bath} = 0$). That is, eq 2 or eqs 9 and 10 establish that the electrodonating and the electroaccepting powers may be quantified in terms of the chemical potential and the chemical hardness, independently of the fractional amount of charge donated or accepted. However, it is important to note that whereas in the case of the

electroaccepting power $\Delta E < 0$, so that the larger values imply a larger capability to accept charge, in the case of the electrodonating power $\Delta E > 0$, so that the smaller values imply a larger capability to donate charge.

3. Alternative Interpolation of the Energy as a Function of the Number of Electrons

The combination of eqs 1 and 3 corresponds to the case when one carries out a smooth quadratic interpolation between the points $E(N - 1)$, $E(N)$, and $E(N + 1)$, which implies that the energy and its derivatives are continuous functions of the number of electrons around N. That is, in the case of eq 1 one has just one parabola, where the two derivatives, μ and η, may be determined from the two conditions $E(N - 1) - E(N) = I$, and $E(N) - E(N + 1) = A$, leading to eq 3.

However, in the case of eqs 5 and 6 one has different parabolas in the two intervals that have different slopes, μ^- and μ^+, and different curvatures η^- and η^+ at N. Therefore, in addition to the energy differences related with I and A, one needs two additional relationships, to determine the values of the two slopes and the two curvatures.

Now, by taking into account that the differentiation of the response of the system to charge donation, from the response to charge acceptance is important from the chemical viewpoint, and that the direction of flow of charge is fundamentally driven by the chemical potential, a new interpolation with these characteristics may be derived by assuming that $\eta^- = \eta^+ = \eta$, and that $\eta = \mu^+ - \mu^-$. Consequently, through the use of these two relationships together with the energy differences for I and A, one finds that

$$\eta = \frac{1}{2}(I - A) \qquad \mu^- = -\frac{1}{4}(3I + A) \qquad \mu^+ = -\frac{1}{4}(I + 3A) \tag{11}$$

Certainly, according to what we established in the previous sections, the distinction between η^- and η^+ would also be desirable, but nevertheless, through these assumptions one can see that the hardness remains proportional to $(I - A)$, and that, although μ^- (the chemical potential governing the charge donation process) gives more emphasis to the ionization potential than the electron affinity, μ^+ (the chemical potential governing the charge accepting process) shows the opposite behavior by giving more emphasis to the electron affinity than the ionization potential, in contrast with eq 3, which gives equal emphasis to I and A in both processes. Thus, through this approach one is able to differentiate, at least partially, charge addition from charge subtraction, and at the same time, it is as simple as the smooth one parabola interpolation in the sense that it allows one to express all the parameters in terms of the ionization potential and the electron affinity.

In Figure 1 one can see that the present interpolation scheme, with three parameters, instead of two, is closer to the straight lines connecting the integer N values. Hence, this procedure not only allows one to differentiate the charge accepting from the charge donating processes but also provides a reasonable approximation to calculate small changes away from an initial reference state.

Now, with respect to the indexes expressed in eqs 9 and 10, using eq 11 one finds that the propensity to donate charge, or electrodonating power, in the present interpolation is given by

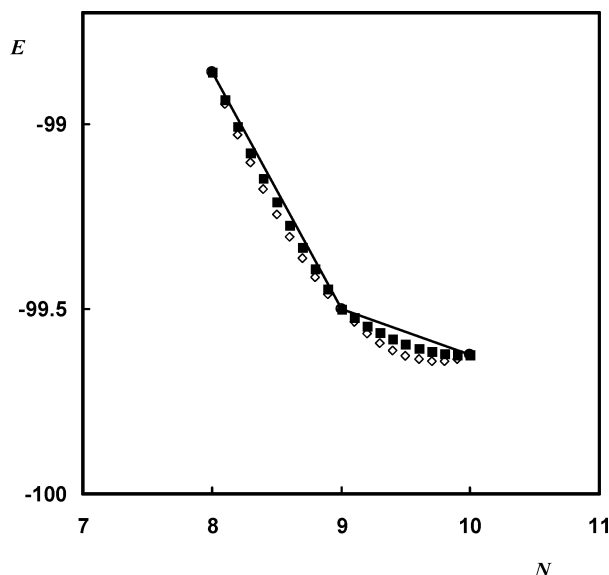$$\omega^- \equiv \frac{(\mu^-)^2}{2\eta} \approx \frac{(3I + A)^2}{16(I - A)} \tag{12}$$

Figure 1. Plot of the total energy as a function of the number of electrons for the fluorine atom. Straight lines represent the exact values (ref 11), open diamonds correspond to the one parabola model, eqs 1 and 3, and solid squares correspond to the two parabola model, eqs 5, 6, and 11.

and that, the propensity to accept charge, or electroaccepting power, is given by

$$\omega^+ \equiv \frac{(\mu^+)^2}{2\eta} \approx \frac{(I + 3A)^2}{16(I - A)} \tag{13}$$

In comparison with eq 4, eq 13 gives more emphasis to the electron affinity, indicating that ω^+ will have a better correlation with A than ω. This situation is confirmed in Figure 2, where it may be seen that the ω^+ values show less dispersion than the ω values for the 61 atoms and 55 molecules reported in the work of Parr, Von Szentpály, and Liu.[4] The behavior of the two expressions, eq 4 and eq 13, may be analyzed by performing a binomial expansion, assuming that $I \gg A$, and retaining the zeroth- and first-order terms. This way one finds that for eq 4, $\omega \approx (3/8)A + (1/8)I + ...$, whereas for eq 13, $\omega^+ \approx (7/16)A + (1/16)I + ...$ Thus, one can see that the weight of I is lower in eq 13 than in eq 4, and that the weight of A is larger in eq 13 than in eq 4, leading to a better correlation, specially in the region where A is small.

Just as ω and ω^+ are correlated with the electron affinity, one could expect, from the analysis presented in section 2, that ω and ω^- should also show some degree of correlation with the ionization potential. In Figure 3, one can see that indeed there is some correlation. Additionally, they both follow the same trends of I. The behavior of the two expressions, eq 4 and eq 12, can also be analyzed in terms of the binomial expansion for $I \gg A$, and retaining the zeroth- and first-order terms. In this case one finds that for eq 4, again, $\omega \approx (1/8)I + (3/8)A + ...$, whereas for eq 12, $\omega^- \approx (9/16)I + (15/16)A + ...$, which shows that the slope will be greater for eq 12, as can be observed in Figure 3, and that the dispersion for eq 12 will be greater because it gives more weight to the electron affinity values, a situation that can also be observed in Figure 3.

4. Local Electrodonating and Electroaccepting Powers

Although global reactivity criteria provide information of the behavior of a chemical species as a whole, local reactivity
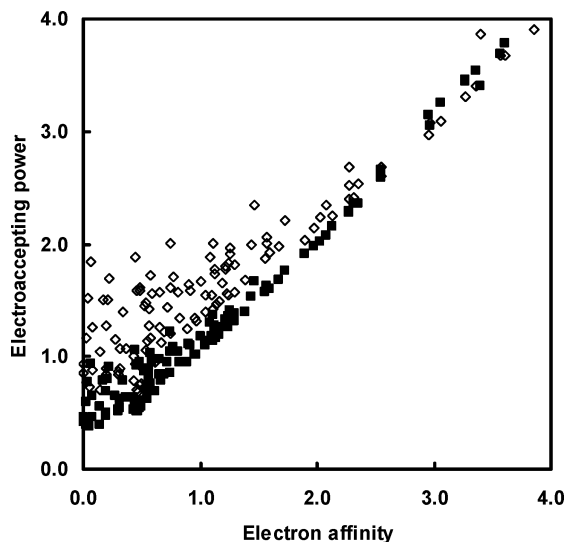
Electrodonating and Electroaccepting Powers

J. Phys. Chem. A, Vol. 111, No. 10, 2007 **1969**

Figure 2. Correlation between the electroaccepting power and the electron affinity of 61 neutral atoms and 55 molecules (values in electronvolts taken from ref 4), open diamonds correspond to eq 4, and solid squares correspond to eq 13.
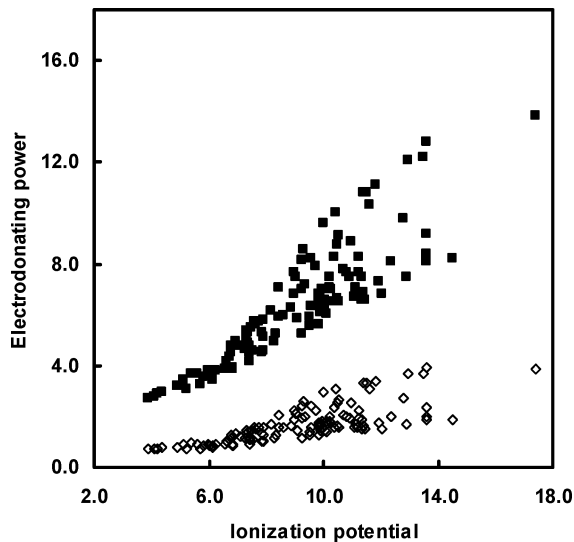

Figure 3. Correlation between the electrodonating power and the ionization potential of 61 neutral atoms and 55 molecules (values in electronvolts taken from ref 4), open diamonds correspond to eq 4, and solid squares correspond to eq 12.

criteria provide information about the behavior of specific sites within a molecule, which is very important to study reactivity and selectivity trends.

Thus, to derive the local expressions associated with the electrodonating and electroaccepting powers, let us analyze the energy change for the case in which the chemical species is immersed in the electron bath, starting from the functional Taylor series for the energy functional,

$$E_{v_0}[\rho_0 + \Delta\rho] = E_{v_0}[\rho_0] + \int \frac{\delta E_{v_0}[\rho_0]}{\delta\rho(\mathbf{r})} \Delta\rho(\mathbf{r}) \, d\mathbf{r} +$$
$$\frac{1}{2} \int \int \frac{\delta^2 E_{v_0}[\rho_0]}{\delta\rho(\mathbf{r'}) \, \delta\rho(\mathbf{r})} \Delta\rho(\mathbf{r}) \, \Delta\rho(\mathbf{r'}) \, d\mathbf{r} \, d\mathbf{r'} + \dots \quad (14)$$

Now, we assume, as in the case of eqs 5 and 6, that one can truncate the series at second order and differentiate between the left and right derivatives. Thus, for the addition of a small fraction of charge, ΔN, to the N_0-electron system with external

potential $v_0(\mathbf{r})$ and exact ground-state density $\rho_{N_0}(\mathbf{r})$, one has that

$$E_{v_0}^+[\rho_{N_0} + \Delta\rho] = E_{v_0}[\rho_{N_0}] + \int \mu^+[\rho_{N_0}] \, \Delta\rho(\mathbf{r}) \, d\mathbf{r} +$$
$$\frac{1}{2} \int \int \eta^+[\rho_{N_0}; \mathbf{r}, \mathbf{r'}] \, \Delta\rho(\mathbf{r}) \, \Delta\rho(\mathbf{r'}) \, d\mathbf{r} \, d\mathbf{r'} \quad (15)$$

where $E_{v_0}[\rho_{N_0}]$ is the exact ground-state energy,

$$\mu^+[\rho_{N_0}] = (\delta E[\rho_{N_0}]/\delta\rho(\mathbf{r}))^+ \quad (16)$$

is the chemical potential and it is constant throughout the whole space,

$$\eta^+[\rho_{N_0}; \mathbf{r}, \mathbf{r'}] = (\delta^2 E[\rho_{N_0}]/\delta\rho(\mathbf{r}) \, \delta\rho(\mathbf{r'}))^+ \quad (17)$$

is the hardness kernel, and

$$\Delta N = \int \Delta\rho(\mathbf{r}) \, d\mathbf{r} > 0 \quad (18)$$

Now, Ayers and Parr[13] have established that because for a given value of ΔN, the first two terms in eq 15 are independent of the position, then, the best way to add a fraction ΔN of an electron to a molecule is to add it to the place defined by the function $\Delta\rho(\mathbf{r})$ that minimizes the last term in eq 15. This way they have shown that the minimizing function is the Fukui function, $f^+[\rho_{N_0}; \mathbf{r}] = (\partial\rho_{N_0}(\mathbf{r})/\partial N)_v^+$, so that

$$\Delta\rho(\mathbf{r}) = \Delta N f^+[\rho_{N_0}; \mathbf{r}] \quad (19)$$

and they have recovered the known result

$$\eta^+[\rho_{N_0}] = \int f^+[\rho_{N_0}; \mathbf{r'}] \, \eta^+[\rho_{N_0}; \mathbf{r}, \mathbf{r'}] \, d\mathbf{r'} \quad (20)$$

Thus, substituting eqs 19 and 20 in eq 15, the energy change can be expressed in the form

$$\Delta E^+ = E_{v_0}^+[\rho_0 + \Delta\rho] - E_0[\rho_{N_0}] =$$
$$\int \left(\mu^+[\rho_{N_0}]\Delta N + \frac{1}{2}\eta^+[\rho_{N_0}](\Delta N)^2\right) f^+[\rho_{N_0}; \mathbf{r}] \, d\mathbf{r} \quad (21)$$

and because $\int f^+[\rho_{N_0}; \mathbf{r}] \, d\mathbf{r} = 1$, one can see that eq 21 reduces to eq 6. However, eq 21 implies that one can define a local energy change per unit volume associated with the addition of a fraction ΔN of an electron given by

$$\Delta\epsilon^+(\mathbf{r}) = \left(\mu^+[\rho_{N_0}]\Delta N + \frac{1}{2}\eta^+[\rho_{N_0}](\Delta N)^2\right) f^+[\rho_{N_0}; \mathbf{r}] \quad (22)$$

By an analogous reasoning, the local energy change per unit volume for the removal of a fraction ΔN of an electron will be given by

$$\Delta\epsilon^-(\mathbf{r}) = \left(\mu^-[\rho_{N_0}]\Delta N + \frac{1}{2}\eta^-[\rho_{N_0}](\Delta N)^2\right) f^-[\rho_{N_0}; \mathbf{r}] \quad (23)$$

Therefore, using the results of section 2 for the quantity in parentheses in the right-hand side of eqs 22 and 23, one finds that the local electrodonating powers may be expressed as

$$\omega^-(\mathbf{r}) = \frac{(\mu^-)^2}{2\eta^-} f^-[\rho_{N_0}; \mathbf{r}] = \omega^- f^-[\rho_{N_0}; \mathbf{r}] \quad (24)$$

and that the local electroaccepting power is given by

$$\omega^+(\mathbf{r}) = \frac{(\mu^+)^2}{2\eta^+} f^+[\rho_{N_0}; \mathbf{r}] = \omega^+ f^+[\rho_{N_0}; \mathbf{r}] \quad (25)$$

and because the integral of the Fukui function is equal to 1, then $\int \omega^{\mp}(\mathbf{r})\,d\mathbf{r} = \omega^{\mp}$.

It is important to mention that a local extension of the electrophilicity index has been proposed by Cedillo and Contreras,[18] by making use of the minimization procedure of Ayers and Parr, for the distribution of the charge $\Delta N_{max} = -\mu/\eta$, however, they did not considered the functional expansion. Also, an expression similar to eq 25 for the regional electrophilicity, using the condensed Fukui, was proposed by Pérez et al.,[19] and its generalization, the philicity concept of Chattaraj, Maiti, and Sarkar[20] is equal to the result expressed in eqs 24 and 25, when $\omega^- = \omega^+ = \omega$. However, in both cases, the Fukui function is incorporated by multiplying the global index by the integral of the Fukui function, because the latter integrates to 1. In contrast, in the present approach, the Fukui function appears as a consequence of the variational principle of Chattaraj, Cedillo, and Parr,[21] in the minimization procedure of Ayers and Parr.[13] Thus, the present derivation strengthens the local philicity concept, which has proven to be very useful to explain the behavior of a wide variety of chemical species under different circumstances.[22-35] It is important to mention that for intramolecular reactivity sequences, philicity indices do not provide additional information to the one obtained from local softness or Fukui function indices,[30] and for intermolecular reactivity trends, philicity indices can be used only in limited cases.[34]

5. Concluding Remarks

The analysis presented in this work, for the specific case of the measure of the propensity of a system to donate or accept charge, seems to indicate that, from a chemical perspective, the distinction between the left and right derivatives may be very important, not only for the Fukui functions but also for the chemical potential and the chemical hardness. Certainly, one must carry out further studies in this direction.

With respect to the elaboration on the electrophilicity concept, there are three conclusions that can be established from the analysis presented in this work. The first one is related to the response of a chemical species to donate or accept charge. Our analysis shows that through the appropriate definition of a bath, representing the environment in which the species is immersed, one can express its propensity to donate or accept fractional amounts of charge in terms of the square of the chemical potential, divided by the hardness, leading to the concepts of electrodonating and electroaccepting powers. In contrast with the derivation of Parr, Von Szentpály, and Liu,[4] the present approach shows that this response can be established by considering a vicinity of points close to the reference system, so that it is not necessarily linked to the point of electron saturation, and that, if one does not distinguish the left and right first derivatives of the energy with respect to the number of electrons, the index that measures the propensity to donate charge becomes equal to the index that measures the propensity to accept charge.

The second conclusion is related with the new interpolation scheme, which shows that one may keep a simple quadratic charge-transfer model in terms of chemically meaningful quantities as the chemical potential (electronegativity) and the hardness but at the same time differentiate the response of the system when it donates or accepts charge, through the chemical potential values of μ^- and μ^+. This differentiation may be important in the description of donor–acceptor type interactions, and particularly, in those related with donation and back-donation.

The third conclusion is related to the analysis performed to derive the local reactivity indexes. The fact that the Fukui function appears as a consequence of a variational principle provides a strong support to the local philicity index. Additionally, one can see that eqs 20 and 21 may turn out to be useful to describe, at the local level, donor–acceptor processes.

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