# Variation of the Electrophilicity Index along the Reaction Path

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Some exact conditions for the extremals of the electrophilicity index, $\omega = \mu^2/2\eta$ (Parr, R. G.; von Szentpály, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922), along an arbitrary reaction coordinate, have been carefully examined. Implications within the widely used finite difference approximation for the density-functional based reactivity descriptors, their relationship with the maximum hardness principle, and the reliability of the general relationships have been tested in the framework of computational evidence for some simple systems of chemical interest.

## I. Introduction

The study of changes in the global and local reactivity profiles of a reacting system is important to understand the reactivity of the total chemical process. A great deal of work concerning the evolution of density-functional theory based[1] global quantities such as the chemical potential, $\mu$, and the hardness, $\eta$, as well as changes of local descriptors such as the Fukui function, $f(\mathbf{r})$, and the local softness $s(\mathbf{r})$, have been reported.[2] For instance, a careful examination of the conditions corresponding to the critical points obtained for the chemical potential and the global hardness along an arbitrary reaction coordinate has been recently performed by Chandra and Uchimaru.[3] Their work, based on a finite difference approximation to these global reactivity indexes, pointed out that the operational hardness passes through a minimum at the transition state (TS) position for a symmetric reaction coordinate, although it is not possible to generalize these results for arbitrary (i.e., nonsymmetrical) chemical reactions.[3,4] Closely related in the context of global quantities of chemical reactivity (i.e., thermodynamic), the elusive concept of electrophilicity takes a fundamental place.[5] Parr et al.[6] have recently defined an index for the global electrophilicity power of a system in terms of its chemical potential, and chemical hardness as

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

Such an index is intended to be a measure of the energy lowering of the chemical species due to maximum electron flow from a donor environment,[6] and it is a quantitative formulation of the model proposed previously by Maynard et al.[7] That is, $\omega$ is a measure of the capacity of species to accept an arbitrary number of electrons.

It was shown by von Szentpály that $\omega$ is an essential component of several models for the charge dependence of total ground-state energy of chemical systems.[8] Chattaraj and Maiti have reported dynamic profiles of this index in the framework of time-dependent density functional theory.[9] Pérez et al. have also reported detailed studies concerning the solvent effects on the electrophilicity.[10] Chattaraj et al. have undertaken recently the variation of the $\omega$ index along the intrinsic reaction coordinate for the intramolecular rearrangement reactions *trans*-$N_2H_4 \rightarrow$ *cis*-$N_2H_4$ and $F_2S_2 \rightarrow$ FSSF in both the gas and solution phases.[11] Given the actual available evidence concerning the electrophilicity index defined by eq 1,[9−12] it appears of general interest to study in more detail its variations along an arbitrary reaction pathway. In this work we have examined the simple exact conditions that electrophilicity index must satisfy to obtain a maximum or a minimum of electrophilicity along a reaction path. It will be clear that a simple connection with a general maximum hardness principle (MHP)[13] could be rationalized.

## II. Theory

To analyze the stationary points of $\omega$ along the reaction path, $s$, it is necessary to start from the following expression, which is the simple derivative of $\omega$ with respect to $s$, $\omega'$:

$$\omega' \equiv \frac{\partial \omega}{\partial s} = \frac{\mu}{\eta}\mu' - \frac{1}{2}\left(\frac{\mu}{\eta}\right)^2 \eta' \tag{2}$$

Because, in this subsection, all the derivatives will be taken with respect to the reaction path, $s$, it is simple to denote this derivative by primed symbols.

Leaving the trivial case of constant $\omega$ for constant $\mu$ and $\eta$, the simultaneous extremals in $\mu$ and $\eta$, imply, therefore, that of $\omega$.[11,14] It is clear that an extremum on the electrophilicity along the reaction path $s$, i.e., $\omega' = 0$, will occur when the following

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condition in eq 2 is satisfied:

$$\mu' = \frac{\mu}{2\eta}\eta' \tag{3}$$

Because $\mu < 0$ and $\eta > 0$ due to convexity in energy,[1] the extremum of the electrophilicity index occurs when the slope of the variation of the chemical potential and the hardness along the reaction coordinate are of the opposite sign. As reported by Chandra and Uchimaru,[3] this will be the general case for a noncomplete symmetrical reaction pathway. Equation 3 can also be satisfied at any other point of the reaction pathway. Of course, one cannot exclude a priori more than one extremum.[11]

It is also clear from eq 3, that under the conditions for the existence of a MHP,[13] i.e., constants $\mu$ and $v(\mathbf{r})$, there is also a minimum electrophilicity principle. Notice, however, that except for redox reactions, the condition of constant chemical potential is difficult to find in a chemical reaction. $v(\mathbf{r})$ is the external potential which, in absence of an electrical or magnetic potential, is the Coulomb potential due to the nucleus.

It is convenient to recall that eq 1 has been proposed from a second-order expansion of energy in terms of the number of electrons $N$ and that approximate expressions for $\omega$ can be obtained once we choose the model to be used for the total energy in function of the number of electrons, $E(N)$.[6] Former approximations[1] to the chemical potential and hardness, in terms of the ionization potential, $I$, and the electron affinity, $A$, yield simply

$$\mu \approx -\frac{I+A}{2} \qquad \eta \approx \frac{I-A}{2} \tag{4}$$

which under a finite difference approximation,[1] provides the following operational formulas:

$$\mu = -\frac{1}{2}(I+A) = \frac{1}{2}(E_{N+1} - E_{N-1})$$

$$\eta = \frac{1}{2}(I-A) = \frac{1}{2}(E_{N+1} + E_{N-1} - 2E_N) \tag{5}$$

where $E_N$, $E_{N-1}$, and $E_{N+1}$ represent the energy of the systems with $N$, $N-1$, and $N+1$ electrons, respectively. Inserting eq 5 into eq 3 we immediately obtain

$$\left[\eta - \frac{1}{2}\mu\right]E'_{N+1} - \left[\eta + \frac{1}{2}\mu\right]E'_{N-1} + \mu E'_N = 0 \tag{6}$$

The last equation can be also easily rearranged in terms of the ionization potential $I$ as

$$[2\eta - \mu]\eta' - (2\eta + \mu)I' = \mu E'_N \tag{7}$$

or in terms of the electron affinity $A$ as

$$[2\eta + \mu]\mu' + \mu A' = 0 \tag{8}$$

Within these approximations to the reactivity descriptors, it is clear that at the TS position, eq 7 will reduce simply to

$$[2\eta - \mu]_{TS}\eta'_{TS} - [2\eta + \mu]_{TS}I'_{TS} = 0 \tag{9}$$

Therefore, assuming the validity of MHP at TS with the necessary condition of $\mu$ being constant[13,15] or an extremum at the TS position,[14,16] the electrophilicity, $\omega$, will be always an extremum at TS (eq 3). This implies that the systems with $N+1$ and with $N-1$ electrons, under a finite difference approach, must also have an energy extremum at this fixed geometry. This is an improbable result that indicates the need for a critical reexamination of validity of finite difference approximations widely employed, and of the quality of the calculations of the energy of the cation and the anion. In general, at the TS position, the following exact condition must be satisfied

$$\left[\frac{2\eta - \mu}{2\eta + \mu}\right] = \frac{E'_{N-1}|_{TS}}{E'_{N+1}|_{TS}} \tag{10}$$

Evidently, the general conditions for $\omega$ to be a maximum or a minimum could be inferred directly from the sign of its second derivative with respect to $s$, viz.,

$$\omega'' \equiv \frac{\partial^2\omega}{\partial s^2} = \frac{1}{\eta}[\mu']^2 + \frac{\mu^2}{\eta^3}[\eta']^2 - 2\frac{\mu}{\eta^2}\mu'\eta' + \frac{\mu}{\eta}\mu'' - \frac{1}{2}\frac{\mu^2}{\eta^2}\eta'' \tag{11}$$

Hence, validity of MHP implies[13] that $\mu$ is a constant and $\eta$ is a maximum for the reactant, the product or an intermediate and a minimum[15] at the TS, which dictates that $\omega$ is a minimum for the reactant/product/intermediate and a maximum at the TS. If both $\mu$ and $\eta$ are maxima (minima) at any point $s$ along the reaction coordinate, $\omega$ will be a minimum (maximum) at that point because $\mu < 0$ and $\eta > 0$. Relative magnitudes of the last two terms of eq 11 will determine the exact nature of extremals in $\omega$ in case $\mu$ is a maximum and $\eta$ is a minimum or vice versa.

**Canonical Ensemble Description of Variations of Electrophilicity.** We recall that from a first-order functional expansion of $\omega = \omega[N, v(\mathbf{r})]$, we can write

$$d\omega = \left[\frac{\partial\omega}{\partial N}\right]_{v(\mathbf{r})} dN + \int\left[\frac{\delta\omega}{\delta v(\mathbf{r})}\right]_N \delta v(\mathbf{r})\, d\mathbf{r} \tag{12}$$

where the derivatives can be straightforwardly obtained in terms of previously reported high-order electronic descriptors of chemical reactivity such as $\gamma$,[17] i.e., one-third of the derivative of $\eta$ with respect to the electron number $N$,

$$\left[\frac{\partial\omega}{\partial N}\right]_{v(\mathbf{r})} = 2\mu - \frac{3\mu^2}{2\eta^2}\gamma \tag{13}$$

and the first derivative of the Fukui function with respect to $N$, $f^{(2)}(\mathbf{r})$,[18]

$$\left[\frac{\delta\omega}{\delta v(\mathbf{r})}\right]_N = \frac{\mu}{\eta}f(\mathbf{r}) - \frac{1}{4}\frac{\mu^2}{\eta^2}f^{(2)}(\mathbf{r}) \tag{14}$$

where former definitions[17,18] for the reactivity indexes have been used.

It is to be expected that higher order derivatives will be retained only as small contributions to the global and local changes in the electrophilicity. These relationships, therefore, emphasize that the global variation in the electrophilicity index will be modulated through the chemical potential and that the corresponding local variations will be mapped in the more reactive site, as indicated through the Fukui function. Furthermore, the electrophilicity index defined in eq 1 can always be written[19] in terms of contributions of local (i.e., within a condensed-to-centers model) electrophilic Fukui quantities $f_k^+$,

$$\omega_k \equiv \omega f_k^+ \tag{15}$$

which means that the variation of the electrophilic power will

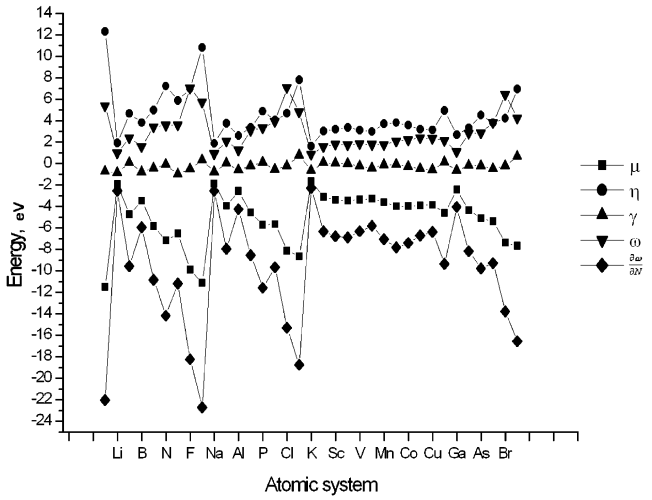


**Figure 1.** Global reactivity indices $\mu$, $\eta$, $\gamma$, $\omega$, and $\partial\omega/\partial N$, using the parameter set of ref 17, for neutral atoms from He to Kr. All numbers in electronvolts within a finite difference scheme model.

be directed to the sites where the Fukui function for nucleophilic attacks is important.[19]

## III. Computational Details

To test the numerical reliability of the above points, various different examples will be discussed. First, the calculation of all global indices, $\mu$, $\eta$, $\gamma$, $\omega$, and $\partial\omega/\partial N$ for atomic systems has been done using the parameter set of ref 17. Then for molecules, we have studied at the B3LYP/6-311++G(2dp,p) level of theory the variation of the chemical potential, hardness, and electrophilicity indexes along the intrinsic reaction coordinate of the benchmark rearrangement of HCN to CNH. Finally, we have also examined in detail some simple proton-transfer reactions from oxygen to oxygen and from oxygen to sulfur in the *H***O**—C(═**O**)—C(═S)—OH and *H***S**—C(═**O**)—C(═S)—OH thioxalic acid derivatives, respectively.[20] All calculations have been performed with the Gaussian 98 package of programs.[21]

## IV. Results and Discusion

Figure 1 shows the values of $\mu$, $\eta$, $\gamma$, $\omega$, and $\partial\omega/\partial N$ for neutral atoms from He to Kr. It is clear that the hardness presents a minimum for the alkaline metal atoms and a maximum for the noble gas atoms. The electrophilicity index $\omega$ follows clearly the hardness trend. It is important, however, to notice that the

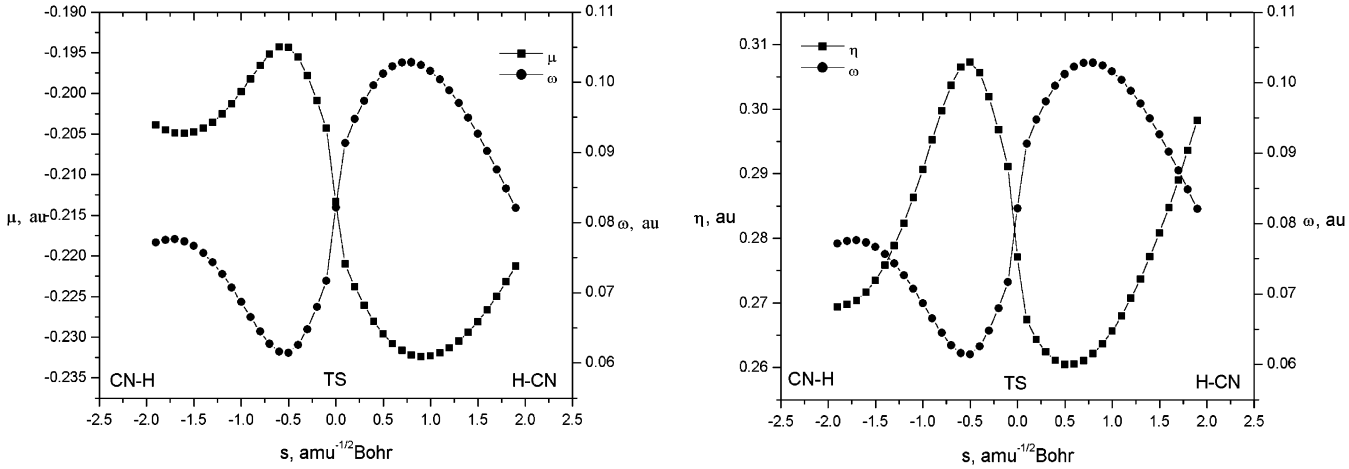


**Figure 2.** Change in the chemical potential, hardness, and electrophilicity at the B3LYP/6-311++G(2d,p) level of theory along the IRC pathway corresponding to the CNH → HCN isomerization reaction. Negative values of *s* corresponds to the evolution of the CNH species toward the TS ($s = 0$), and the positive ones to their transformation toward the HCN system.

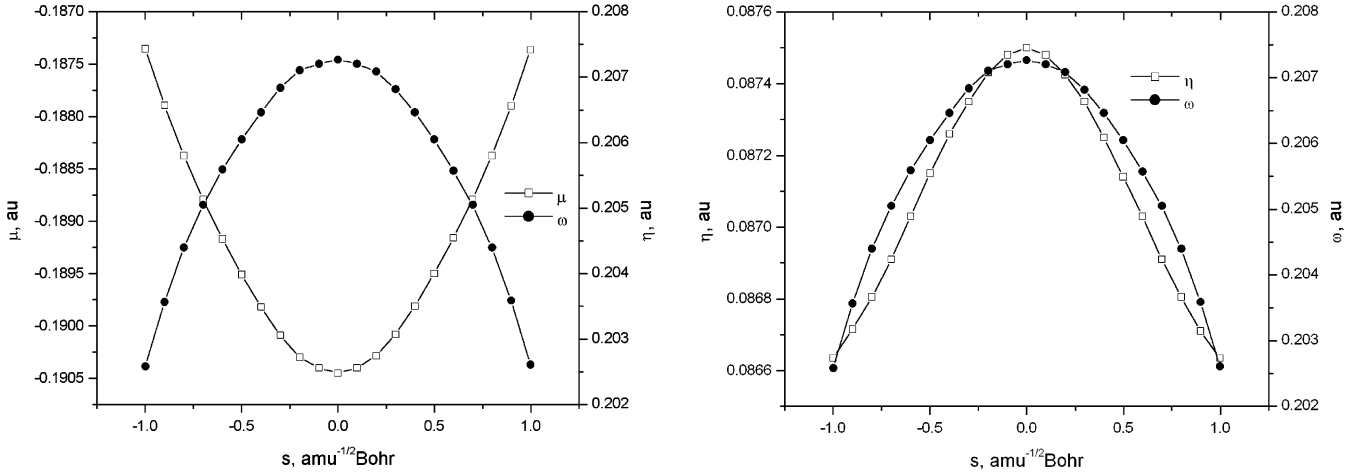


**Figure 3.** Change in the chemical potential, hardness, and electrophilicity at the B3LYP/6-311+G(d,p) level of theory along the IRC pathway corresponding to the symmetric oxygen to oxygen proton-transfer reaction in the *H***O**—C(═**O**)—C(═S)—OH system. Negative values of *s* correspond to the evolution of the *H***O**—C(═**O**)—C(═S)—OH system toward the symmetrical TS ($s = 0$), and the positive ones to their transformation toward the isomeric **O**═C(—**O***H*)—C(═S)—OH system.

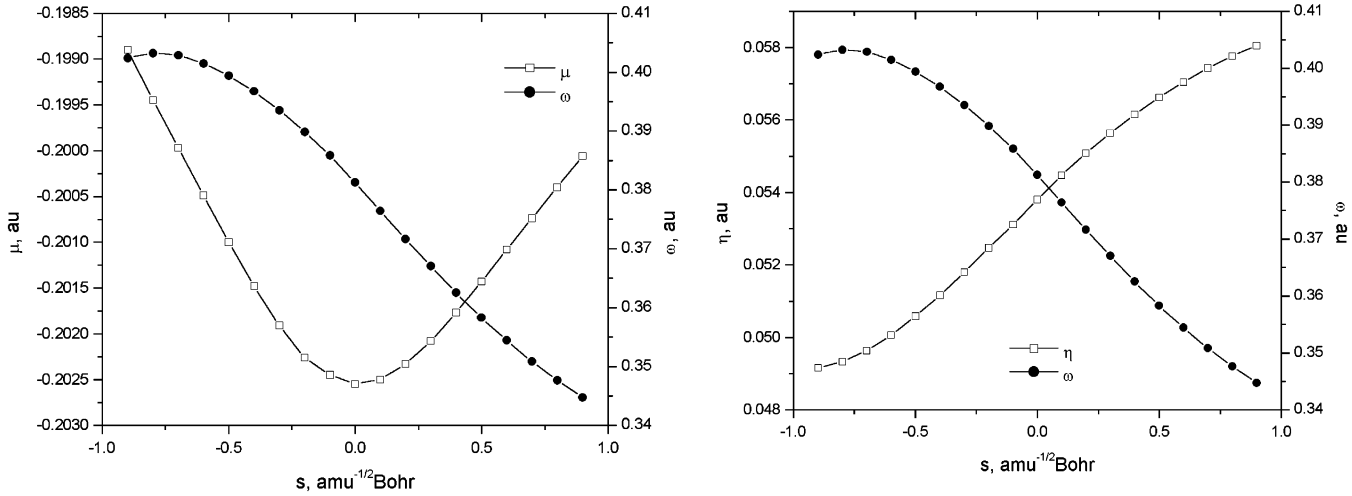


**Figure 4.** Change in the chemical potential, hardness, and electrophilicity at the B3LYP/6-311+G(d,p) level of theory along the IRC pathway corresponding to the sulphur to oxygen proton transfer in the *H***S**—C(═**O**)—C(═S)—OH system. Negative values of *s* correspond to the evolution of the **S**═C(—**O***H*)—C(═S)—OH species toward the asymmetric TS ($s = 0$), and the positive ones to their transformation toward the isomeric *H***S**—C(═**O**)—C(═S)—OH system.

maxima for $\omega$ are at atomic numbers corresponding to the halogen atoms instead of the noble gas atoms, as expected from chemical experience. Because the $\gamma$ values are small, the variation of $\omega$ with respect to $N$ resembles the values of $\mu$.

Figure 2 depicts the variation of chemical potential, hardness, and electrophilicity indexes along the rearrangement of HCN to CNH. The extremals for $\omega$ appears on the IRC path at *s* values close to $-1.75$, $-0.5$, and $+0.75$ amu$^{-1/2}$ bohr. For $-1.75$ and $-0.5$, $\mu$ and $\eta$ show also an extremal, whereas at 0.75 amu$^{-1/2}$ bohr, $\mu$ and $\eta$ show opposite slopes (eq 3). We can also note that hardness is not a minimum at the transition state but the three indexes are rapidly varying near this stationary point.

From Figure 3 we observe the change of global reactivity indexes along the IRC path for the oxygen to oxygen symmetric proton-transfer reaction in the *H***O**—C(═**O**)—C(═S)—OH system. This picture exemplifies the trivial case of eq 3 where $\omega$ is going to be maximal at the TS position, and where $\mu$ and $\eta$ also show extremals at this particular point. The sulfur to oxygen intramolecular proton-transfer reaction in the *H***S**—C(═**O**)—C(═S)—OH system, constitutes an interesting case because it is an example for a non trivial asymmetric reaction process.[20] From Figure 4 the changes in the $\mu$, $\eta$, and $\omega$ quantities along the IRC path of this reaction exemplify the general conclusions drawn above.

The present analysis furthermore explains and generalizes the results obtained by Chattaraj et al.[11] for intramolecular rearrangement reactions, who showed that $\mu$, $\eta$, and $\omega$ are respectively maximum, minimum, and minimum at the TS for the (trans)-$N_2H_2$ → (cis)-$N_2H_2$ reaction whereas they are respectively minimum, minimum, and maximum at the TS for the $F_2S_2$ → FSSF reaction as would have been predicted by eqs 3 and 12.

## V. Concluding Remarks

In the present work, we have explored the exact conditions for which the electrophilicity index, $\omega = \mu^2/2\eta$, will experience an extremum along an arbitrary reaction path. Some relationships in the framework of an approximated, but commonly used, finite difference operational scheme have been explicitly developed and related with the MHP. We found that under the conditions for the existence of a MHP, i.e., constants $\mu$, and $v(\mathbf{r})$, there will also be a *minimum electrophilicity principle*. Indeed, it is clear from the above framework that the global changes in the electrophilic power will be directed by the sites where the Fukui function for nucleophilic attacks is important (eq 16). Some general reacting systems have been used to test these general principles.

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