

LETTERS

Philicity: A Unified Treatment of Chemical Reactivity and Selectivity

Pratim Kumar Chattaraj,* Buddhadev Maiti, and Utpal Sarkar

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

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A generalized concept of philicity is introduced through a resolution of identity, encompassing electrophilic, nucleophilic, and radical reactions. Locally, a particular molecular site may be more prone to electrophilic attack or another may be more prone to nucleophilic attack, but the overall philicity of the whole molecule remains conserved. Local philicity is by far the most powerful concept of reactivity and selectivity when compared to the global electrophilicity index, Fukui function, local softness, or global softness because it contains information about almost all of the known global and local descriptors of chemical reactivity and selectivity.

In this letter, the concept of by far the most powerful and general reactivity and selectivity index, the philicity, is introduced. It contains almost all information obtainable from hitherto known different global and local reactivity and selectivity descriptors, in addition to the information regarding electrophilic/nucleophilic power of a given atomic site in a molecule.

Global reactivity parameters such as electronegativity (χ),¹⁻³ hardness (η),⁴⁻⁷ and electrophilicity index (ω)⁸ and local reactivity indices such as Fukui function ($f(\vec{r})$)^{9,10} and local softness¹¹⁻¹³ have been introduced into the chemical literature, which eventually obtained legitimacy within density functional theory (DFT).¹⁴ For an N -electron system with total energy E , electronegativity³ and hardness⁵ have been defined as the following first- and second-order derivatives:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \quad (1)$$

$$\eta = \left(\frac{1}{2}\right)\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \left(\frac{1}{2}\right)\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} \quad (2)$$

where μ and $v(\vec{r})$ are chemical and external potentials, respec-

tively. On the basis of a previous idea by Maynard et al.,⁸ Parr et al.⁸ have introduced the electrophilicity index as

$$\omega = \frac{\mu^2}{2\eta} \quad (3)$$

Local quantities such as Fukui function and local softness define the reactivity/selectivity of a specific site in a molecule. The Fukui function¹⁰ or the frontier function forms the background of local reactivity/selectivity theories in the spirit of Fukui's frontier orbital theory⁹ and is defined as¹⁰

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\delta \mu}{\delta v(\vec{r})}\right)_N \quad (4)$$

Discontinuities in the $\rho(\vec{r})$ versus N plot provide three different types of Fukui functions,¹⁰ namely,

$$f^+(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}) \quad \text{for nucleophilic attack} \quad (5a)$$

$$f^-(\vec{r}) = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}) \quad \text{for electrophilic attack} \quad (5b)$$

$$f^0(\vec{r}) = (\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r}))/2 \quad \text{for radical attack} \quad (5c)$$

where $\rho_M(\vec{r})$ is the electron density of the M -electron species.

* To whom correspondence should be addressed. E-mail: pkc@chem.iitkgp.ernet.in.

Corresponding condensed-to-atom variants are written^{15–17} in terms of the respective electron populations (q_k) on the atomic site k of the molecule (in place of the associated electron densities as in eq 5) as follows

$$f_k^\alpha; \quad \alpha = +, -, \text{ and } 0 \quad (6)$$

where $\alpha = +, -, \text{ and } 0$ refer to nucleophilic, electrophilic, and radical reactions, respectively.

The local softness is related to Fukui function as follows:¹⁴

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu} \right)_{v(\vec{r})} = \left(\frac{\partial \rho(\vec{r})}{\partial N} \right)_{v(\vec{r})} \left(\frac{\partial N}{\partial \mu} \right)_{v(\vec{r})} = f(\vec{r})S \quad (7a)$$

where S is the global softness given as¹⁴

$$S = \frac{1}{2\eta} = \int s(\vec{r}) d\vec{r} \quad (7b)$$

stemming from the normalization of the Fukui function,¹⁴ namely,

$$\int f(\vec{r}) d\vec{r} = 1 \quad (7c)$$

Three different types of local softness associated with the corresponding Fukui function (cf eq 5) can be defined as follows:

$$s^\alpha(\vec{r}) = f^\alpha(\vec{r})S \quad (8)$$

Related condensed-to-atom quantities are given as:

$$s_k^\alpha = f_k^\alpha S \quad (9)$$

When two molecules react, which one will behave as an electrophile (nucleophile) will depend on which has a higher (lower) electrophilicity index. This global trend originates from the local behavior of the molecules or precisely the atomic site that is prone to electrophilic (nucleophilic) attack. A relative electrophilicity index has been defined¹⁸ as s_k^-/s_k^+ the usefulness of which has been, however, questioned in recent times.¹⁹ A somewhat different local electrophilicity is also known.²⁰ In the present work, we describe a generalized treatment of both global and local electrophilicity, as well as nucleophilicity, by resolving the identity associated with the normalization of the Fukui function.¹⁴

Considering the existence of a local electrophilicity index ($\omega(\vec{r})$) that varies from point to point in an atom, molecule, ion, or solid, we may define it as follows:

$$\omega = \int \omega(\vec{r}) d\vec{r} \quad (10)$$

Obviously one of the best choices of $\omega(\vec{r})$ can be obtained by the resolution of the identity given in eq 7c, namely,

$$\omega = \omega \int f(\vec{r}) d\vec{r} = \int \omega f(\vec{r}) d\vec{r} = \int \omega(\vec{r}) d\vec{r} \quad (11a)$$

where

$$\omega(\vec{r}) = \omega f(\vec{r}) \quad (11b)$$

It may be noted that $\omega(\vec{r})$ contains information on $f(\vec{r})$ (eq 11b), in addition to that on ω (eq 10) but $f(\vec{r})$ cannot provide $\omega(\vec{r})$ without an explicit knowledge of ω . An additional knowledge of the chemical potential allows $\omega(\vec{r})$ to provide $s(\vec{r})$, S , and η . Alternatively, put eqs 7a,b in eq 3 to obtain eq 11.

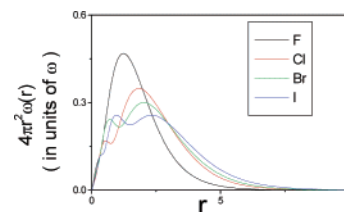


Figure 1. Radial distribution of philicity in the ground states of halogen atoms (F, Cl, Br, and I).

Three different types of $\omega(\vec{r})$ (henceforth, we call it local philicity index because it takes care of all types of reactions) can be readily defined as

$$\omega^\alpha(\vec{r}) = \omega f^\alpha(\vec{r}) \quad (12)$$

where again $\alpha = +, -, \text{ and } 0$ refer to nucleophilic, electrophilic, and radical attacks, respectively. Related condensed-to-atom variants for the atomic site k can be written as

$$\omega_k^\alpha = \omega f_k^\alpha \quad (13)$$

which in turn highlight the strength of the Fukui function¹⁰ and the frontier orbital theory per se.^{9,21} A very special case of this general treatment was given in ref 20.

Radial distributions of local philicity of halogen atoms are presented in Figure 1, and those of He atom in various electronic states and in different complexes of a two-state ensemble are given as Supporting Information. Atomic shell structure is conspicuous, and the philicity is positive everywhere. With electronic excitation, the “reactivity domain” or the “sphere of influence”²² increases drastically. To analyze the condensed philicities, we fall back upon the original paper of Yang and Mortier.¹⁵ The relative philicity patterns of various atomic sites of formaldehyde molecule, evaluated¹⁵ using an ab initio STO-6-311G theory are as follows: ω^+ , $H < O < C$; ω^- , $C < H < O$; ω^0 , $C < H < O$. It is clear from the trends that although the sum of any type of philicity (ω_k^α) over all atoms is constant and equal to the global electrophilicity index (ω) of Parr et al.,⁸ some site is better equipped for the electrophilic (nucleophilic) attack than the other. This site specificity is at the heart of the reaction mechanisms and is very important in understanding chemical reactions. It may be noted that a global nucleophilicity index would be superfluous because in comparison a system with lower electrophilicity will be more nucleophilic in character. The propensity of electrophilic/nucleophilic/radical attack will vary from point to point (atom to atom) in a molecule, but the overall propensity for all types of attacks (considering all sites) is conserved. Global electrophilicity of a molecule may remain undisturbed though the electrophilic (nucleophilic) power of a particular site may increase by a physico-chemical process with a corresponding decrease in other sites and a particular reaction with a nucleophile (electrophile) at that site becomes favored, a fact that highlights the strength of this local philicity over its global counterpart. This local philicity contains information about the global electrophilicity, Fukui function and an additional knowledge of electronegativity also provide the local softness and global softness, as well as the hardness and hence all of the known global and local descriptors of chemical reactivity and selectivity. It may also be noted that when one compares the relative reactivity and selectivity of two different molecules or between two sites of the same molecule it must be done in the condition of same electronegativity.²¹ In these situations, an a priori knowledge of chemical potential (electronegativity) is not mandatory.

The new concepts pertaining to chemical reactivity and selectivity developed in the present work may be summarized as follows: (1) Between the two molecules, the one with larger electrophilicity, a la Parr et al.,⁸ will prefer a reaction with an electrophile in comparison to the other, and the situation will be reversed in case of a reaction with a nucleophile. (2) A generalized concept of philicity is introduced via an identity resolution. There will be a distribution of electrophilic (nucleophilic) power in various atomic sites of a molecule keeping the overall philicity conserved. (3) Atomic shell structure is conspicuous in the radial philicity of atoms in ground and excited electronic states, as well as in a two-state ensemble. This quantity is always positive. (4) There is no need of an additional nucleophilicity index. (5) Local philicity is a more powerful quantity than the global electrophilicity because the former contains the information of the latter in addition to the site selectivity of a molecule toward electrophilic, nucleophilic, or radical attacks. The propensity of an atomic site toward electrophilic/nucleophilic/radical attack may be enhanced with a commensurate decrease in other sites even without any change in the global electrophilicity index. Local philicity provides the Fukui function, but the converse is not true because the latter does not have information about the global electrophilicity index. Because the global electrophilicity of two different molecules are different, best sites of two different molecules for a given reaction can be explained only in terms of the philicity and not the Fukui function. Local and global softness, as well as global hardness, can also be obtained from the local philicity provided one knows the electronegativity of the system. This information is not required when one compares the reactivity/selectivity of two systems or two different sites of the same system. (6) The present definition is mathematically exact in the sense that it depends on a generalized partitioning of the global electrophilicity without resorting to any specific definition of an atom in a molecule.

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Supporting Information Available: Radial distributions of philicity of He atom in various electronic states and in different complexions of a two-state ensemble. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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