

Hardness, softness, and the Fukui function in the electronic theory of metals and catalysis

(chemical reactivity/density functional theory/local softness/density of states)

WEITAO YANG AND ROBERT G. PARR

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514

Contributed by Robert G. Parr, June 3, 1985

ABSTRACT The concepts of hardness $\eta = (\partial^2 E / \partial N^2)$, and Fukui function $f(r) = [\partial \rho(r) / \partial N]_{v(r)}$, which have recently been associated with the theory of chemical reactivity in molecules, are extended to the theory of metals. It is shown that at $T = 0$, $1/\eta = g(\epsilon_F)$ and $f(r) = g(\epsilon_F, r)/g(\epsilon_F)$, where $g(\epsilon_F)$, and $g(\epsilon_F, r)$ are the density of states and the local density of states, at the Fermi energy ϵ_F . Softness S and local softness $s(r)$ are defined as $1/\eta$ and $Sf(r)$, respectively, and it is shown that

$$s(r) = \frac{1}{kT} [\langle \rho(r)N \rangle - \langle N \rangle \langle \rho(r) \rangle],$$

where the averages are over a grand canonical ensemble. It is pointed out that the postulate that $f(r)$ or $g(\epsilon_F, r)$ determines site selectivity for metals in chemisorption and catalysis is synonymous with the recent argument by Falicov and Somorjai [Falicov, L. M. & Somorjai, G. A. (1985) *Proc. Natl. Acad. Sci. USA* 82, 2207-2211] that such selectivity is determined by low-energy density fluctuations.

The behavior of an atom or a molecule often is characterized by some parameters that chemists have extracted from their experience and used for the prediction of chemical reactivity.

The electronegativity χ , defined by Mulliken (1) as the average of ionization potential I and electron affinity A , $\chi = \frac{1}{2}(I + A)$, is such a parameter; it is a useful measure of the tendency of a species to attract electrons. Another such conception is the idea of hardness or softness, introduced by Pearson (2, 3) in studying acid-base chemical reactions of the type $A + :B \rightarrow A:B$, where A , the acceptor of electrons, is the acid, B , the donor of electrons, is the base. Acids and bases are classified as hard or soft as shown below.

	<u>Hard</u>	<u>Soft</u>
Acids	high positive charge low polarizability small size	low positive charge high polarizability larger size
Bases	high electronegativity difficult to oxidize low polarizability	low electronegativity easily oxidized higher polarizability

The principle of hard and soft acids and bases (2, 3) states that hard acids prefer to react with hard bases and soft acids prefer to react with soft bases (both thermodynamically and kinetically). This principle has been valuable for classifying a wide variety of chemical facts.

Density functional theory (4-6) has extraordinary potential for quantifying chemical concepts and providing them with a theoretical basis. Thus the electronegativity χ has been identified (7) as the negative of the chemical potential

μ , which is the Lagrange multiplier in the Euler-Lagrange equation in density functional theory, and

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

where E is the total electronic energy, N is the number of electrons, and $v(r)$ is the external electrostatic potential an electron at r feels due to the nuclei. Mulliken's formula $-\frac{1}{2}(I + A)$ is no more than the finite-difference approximation for Eq. 1.

Similarly, the natural definition of the hardness, called η ,* has been shown (8) to be

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

which has the finite-difference approximation $I - A$. It is remarkable that chemists sensed the importance of the quantities χ and η before their quantitative definitions as first and second derivatives of the E versus N curve were realized. The hardness/softness/acid/base principle has been derived using Eq. 2 as the definition of hardness (8) and has been commented on (9).

Both χ and η are global properties in the sense that they characterize the species as a whole. On the other hand, the frontier electron densities proposed by Fukui (10, 11) are local properties that depend on r ; they differentiate one part of a molecule from another and serve as reactivity indices. The density functional expression of this idea is the Fukui function defined by Parr and Yang (12, 13), the local quantity

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} = \left(\frac{\delta \mu}{\delta v(r)} \right)_N. \quad [3]$$

For a finite system such as a molecule, the derivative in Eq. 3 depends on whether one is adding or subtracting an electron (12). When the molecule is accepting electrons, one has $f^+(r)$, the index for nucleophilic attack; when the molecule is donating electrons, one has $f^-(r)$, the index for electrophilic attack; the average $f^0(r) = (f^+(r) + f^-(r))/2$ is the index for radical attack (12). The frontier-electron theory of chemical reactivity (10, 11) transcribes into the postulate that $f(r)$ determines site selectivity in chemical reactions.

Chemical catalysis is a problem in chemical reactivity, and so we well may expect the same principle to apply. In the present paper we demonstrate that it does, at least for the catalytic activity of metals. We use a formula relating $(\partial \rho(r) / \partial \mu)_{T,v}$ in a grand canonical ensemble to a certain fluctuation and we lean heavily on a recent argument by Falicov and Somorjai (14) that local fluctuations are determinative for catalysis. First we extend the concepts of hardness and

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "advertisement" in accordance with 18 U.S.C. §1734 solely to indicate this fact.

*In ref. 8 a factor of $\frac{1}{2}$ was included in the definition of η , which we here drop.

fukui function to metals (where they are in fact simpler than for molecules because the discontinuities just mentioned do not occur). Then we give the proof of our claim. Finally, we state the result in its most general form.

Hardness and Fukui Function for Metals

In the Kohn–Sham (15) formulation of finite-temperature density functional theory, one has the self-consistent equations

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) - \mu \right] \psi_i = \varepsilon_i \psi_i, \quad [4]$$

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 f(\varepsilon_i - \mu), \quad [5]$$

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta F_{xc}[\rho]}{\delta \rho(\mathbf{r})}, \quad [6]$$

where $f(\varepsilon_i - \mu)$ is the Fermi function,

$$f(\varepsilon_i - \mu) = \frac{1}{1 + \exp[\beta(\varepsilon_i - \mu)]} \quad [7]$$

and the $\psi_i(\mathbf{r})$ are the normalized Kohn–Sham orbitals. $F_{xc}[n]$ is the exchange-correlation free-energy functional.

From Eq. 5 one has

$$N = \int d\mathbf{r} \rho(\mathbf{r}) = \sum_i f(\varepsilon_i - \mu) = \frac{2V}{(2\pi)^3} \int d\mathbf{k} f[\varepsilon(k) - \mu], \quad [8]$$

where the discrete sum has been replaced by an integral; a sum over the band index is assumed here and later in the formulas below. Alternatively,

$$N = \int d\varepsilon g(\varepsilon) f[\varepsilon - \mu], \quad [9]$$

where $g(\varepsilon)$, the density of states at energy ε , is given by

$$g(\varepsilon) = \sum_i \delta(\varepsilon_i - \varepsilon) = \frac{2V}{(2\pi)^3} \int d\mathbf{k} \delta[\varepsilon(k) - \varepsilon]. \quad [10]$$

At $T = 0$, μ is equal to the Fermi energy ε_F and

$$f(\varepsilon_i - \mu) = \begin{cases} 1 & \varepsilon_i < \mu \\ 0 & \varepsilon_i > \mu. \end{cases} \quad [11]$$

At $T = 0$ we therefore have

$$N = \int_0^\mu d\varepsilon g(\varepsilon) \quad [12]$$

and hence

$$\left(\frac{\partial N}{\partial \mu} \right)_{T,V} = \frac{1}{\eta} = g(\varepsilon_F), \quad [13]$$

where V is the volume and the lattice structure remains unchanged in the differentiation here and later. For a metal at absolute zero, the reciprocal of the hardness is the density of states at the Fermi level.

The local density of states $g(\varepsilon, \mathbf{r})$ is defined by

$$\begin{aligned} g(\varepsilon, \mathbf{r}) &= \sum_i |\psi_i(\mathbf{r})|^2 \delta(\varepsilon_i - \varepsilon) \\ &= \frac{2V}{(2\pi)^3} \int d\mathbf{k} |\psi_k(\mathbf{r})|^2 \delta[\varepsilon(k) - \varepsilon]. \end{aligned} \quad [14]$$

At absolute zero temperature we therefore have, in analogy with Eq. 12,

$$\rho(\mathbf{r}) = \int_0^\mu d\varepsilon g(\varepsilon, \mathbf{r}). \quad [15]$$

Consequently, using Eq. 13, we find from Eq. 3

$$\begin{aligned} f(\mathbf{r}) &= \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{T,V} = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{T,V} \left(\frac{\partial \mu}{\partial N} \right)_{T,V} \\ &= \eta g(\varepsilon_F, \mathbf{r}) = \frac{g(\varepsilon_F, \mathbf{r})}{g(\varepsilon_F)}. \end{aligned} \quad [16]$$

The fukui function is the normalized local density of states at the Fermi level; the normalization $\int f(\mathbf{r}) d\mathbf{r} = 1$ corresponds to $\int g(\varepsilon_F, \mathbf{r}) d\mathbf{r} = g(\varepsilon_F)$.

Softness and Local Softness

It is now natural to define, for any species, the *global softness* S as the inverse of global hardness,

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})}, \quad [17]$$

and the *local softness* $s(\mathbf{r})$ by the formula

$$s(\mathbf{r}) = S f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{T,v(\mathbf{r})}. \quad [18]$$

Then

$$S = \int d\mathbf{r} s(\mathbf{r}). \quad [19]$$

For metals at $T = 0$ we have

$$S = g(\varepsilon_F), \quad [20]$$

$$s(\mathbf{r}) = g(\varepsilon_F, \mathbf{r}). \quad [21]$$

The fukui function may therefore be thought of as a normalized local softness.

With these definitions, molecules and infinite systems are described in a unified way. Note that different metals have different softnesses, all large, but not infinite as would be implied by use of the finite-difference approximation $\eta = I - A$.

Softness and Fluctuations in a Grand Ensemble

Consider our system of interest, be it metal or molecule, as a member of a grand canonical ensemble of equivalent systems at the same T , V , and μ . Denote averages over the ensemble with symbols $\langle \rangle$. Then N in the foregoing formulas is $\langle N \rangle$, and there is a textbook formula for $\langle N^2 \rangle - \langle N \rangle^2$,

$$S = \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{1}{kT} [\langle N^2 \rangle - \langle N \rangle^2]. \quad [22]$$

Large softness and large number fluctuations go together!

There is an even more interesting local fluctuation formula, however, derived in the *Appendix* starting from the formula for $\langle \rho(\mathbf{r}) \rangle$ in a grand ensemble. Namely,

$$s(\mathbf{r}) = f(\mathbf{r})S = \frac{1}{kT} [\langle \rho(\mathbf{r})N \rangle - \langle N \rangle \langle \rho(\mathbf{r}) \rangle]. \quad [23]$$

Local softness or the Fukui function measures the local fluctuations in $\rho(\mathbf{r})$, as they vary with \mathbf{r} ! The fluctuations in Eqs. 22 and 23 both depend linearly on T as $T \rightarrow 0$.

We note in passing that boson systems are softer than fermion systems. With the upper sign for fermions, the lower sign for bosons, one has

$$\langle N \rangle = \sum_i \frac{1}{1 \pm \exp[\beta(\epsilon_i - \mu)]}, \quad [24]$$

and Eq. 22 gives

$$S = \frac{1}{kT} \left\{ \langle N \rangle \mp \sum_i \left(\frac{1}{1 \pm \exp[\beta(\epsilon_i - \mu)]} \right)^2 \right\}. \quad [25]$$

Reactivity in Chemisorption and Catalysis

Metals in general are soft (16), with large $g(\epsilon_F)$. Chemisorption and catalytic reactions on metal surfaces can then be thought of as soft-soft chemical reactions. Transition metals are particularly active because of their high $g(\epsilon_F)$. One may reasonably then suppose that the same principle will hold as for molecules (12), that $f(\mathbf{r})$, in this case $g(\epsilon_F, \mathbf{r})$, measures the site reactivity for metal surface reactions. For magnetic materials, the spin density functional theory will be required, and the necessary generalizations will be the spin Fukui functions

$$f_{\uparrow}(\mathbf{r}) = \left(\frac{\partial \rho_{\uparrow}(\mathbf{r})}{\partial N} \right)_{\nu}, \quad f_{\downarrow}(\mathbf{r}) = \left(\frac{\partial \rho_{\downarrow}(\mathbf{r})}{\partial N} \right)_{\nu}, \quad [26]$$

Not the entire metal surface is catalytically reactive, as was first pointed out by Taylor (17).

Falicov and Somorjai (14) recently have argued that the catalytic activity in transition metals is associated with low-energy electronic fluctuations. Eq. 23 above shows that their postulate is akin to ours: large $f(\mathbf{r})$ means large fluctuations and vice versa, or for magnetic systems f_{\uparrow} and f_{\downarrow} . It is equivalent to say that the preferred sites on a metal surface for chemisorption and catalysis are those for which the initial changes in work function on adsorption are the biggest (12).

Discussion

We have demonstrated that the Fukui function $f(\mathbf{r})$ and/or the local softness $s(\mathbf{r})$ are valid quantitative indications for chemical reactivity, for metals as well as for molecules. In metals at $T = 0$, $s(\mathbf{r})$ is the local density of states at the Fermi level, the quantity usually called $g(\epsilon_F, \mathbf{r})$. Strong confirmatory evidence comes from the similarity to the postulate of Falicov and Somorjai (14) about the importance of fluctuations in charge, our Eq. 23.

Support also is provided by the calculation of Feibelman and Hamann (18), for sulfur adsorbed on the Rh (001) surface. These authors show that $g(\epsilon_F, \mathbf{r})$ changes at and propagates from just the site at which sits the poisoning atom.

We have featured the local softness $s(\mathbf{r})$ in this paper, but it would also be possible to work with a local hardness $\eta(\mathbf{r})$ (19, 20). For a metal, $s(\mathbf{r})$ appears to be more convenient.

For a metal at $T = 0$, from $g(\epsilon_F, \mathbf{r})$ one can obtain $g(\epsilon_F)$ by

quadrature and $f(\mathbf{r})$ by then taking a quotient; the information in $g(\epsilon_F, \mathbf{r})$ is equivalent to the information in $g(\epsilon_F)$ and $f(\mathbf{r})$. The extent to which $f(\mathbf{r})$ by itself suffices to predict reactivity is uncertain at present, though clearly it carries all information about relative site preferences within a given species.

We have no reason not to suppose that our conclusions are not universally valid.

APPENDIX

Eq. 23 in the text is here derived within the theory of the classical grand canonical ensemble. The same conclusion remains true in quantum systems.

The interaction potential of the N -particle system is given by

$$V_N(1, \dots, N) = \sum_i^N \phi(i) + \sum_i^N \sum_{i < j}^N V(i, j). \quad [A1]$$

The grand partition function is

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \prod_{i=0}^N Z^*(i) \prod_{i < j}^N e(i, j) \, di, \dots, dN, \quad [A2]$$

where

$$Z^*(1) = \exp(\beta(\mu - \phi(1))) \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}, \quad [A3]$$

with $\beta = 1/kT$ and

$$e(1, 2) = \exp(-\beta V(1, 2)). \quad [A4]$$

Then

$$\langle \rho(1) \rangle = \frac{1}{\Xi} Z^*(1) \frac{\delta \Xi}{\delta Z^*(1)} = \frac{\delta \ln \Xi}{\delta \ln Z^*(1)}. \quad [A5]$$

Using Eqs. A3 and A4, we obtain

$$\begin{aligned} \frac{\partial \langle \rho(1) \rangle}{\partial \mu} &= \int \frac{\delta \langle \rho(1) \rangle}{\delta Z^*(2)} \cdot \frac{\partial Z^*(2)}{\partial \mu} \, d\mathbf{r}_2 \\ &= \int \frac{\delta}{\delta Z^*(2)} \left(\frac{\delta \ln \Xi}{\delta \ln Z^*(1)} \right) \cdot Z^*(2) \cdot \beta \, d\mathbf{r}_2 \\ &= \beta \int d\mathbf{r}_2 \frac{\delta^2 \ln \Xi}{\delta \ln Z^*(2) \delta \ln Z^*(1)} \\ &= \beta \int d\mathbf{r}_2 (\langle \rho(2) \cdot \rho(1) \rangle - \langle \rho(2) \rangle \langle \rho(1) \rangle) \\ &= \beta \{ \langle N \cdot \rho(1) \rangle - \langle N \rangle \langle \rho(1) \rangle \}. \end{aligned} \quad [A6]$$

Discussions with Professor Max Berkowitz have been very helpful. W.Y. acknowledges with thanks the award of a Limited Service Assistantship from the Graduate School of the University of North Carolina. This research has been made possible by research grants from the National Science Foundation and the National Institutes of Health.

1. Mulliken, R. S. (1934) *J. Chem. Phys.* 2, 782-793.
2. Pearson, R. G. (1963) *J. Am. Chem. Soc.* 85, 3533-3539.
3. Pearson, R. G. (1966) *Science* 151, 172-177.
4. Hohenberg, P. & Kohn, W. (1964) *Phys. Rev. B* 136, 864-871.
5. Kohn, W. and Sham, L. J. (1965) *Phys. Rev. A* 140, 1133-1138.
6. Parr, R. G. (1983) *Annu. Rev. Phys. Chem.* 34, 631-656.
7. Parr, R. G., Donnelly, R. A., Levy, M. & Palke, W. E. (1978) *J. Chem. Phys.* 68, 381-387.
8. Parr, R. G. & Pearson, R. G. (1983) *J. Am. Chem. Soc.* 105, 7512-7516.

9. Nalewajski, R. F. (1984) *J. Am. Chem. Soc.* **106**, 944.
10. Fukui, K. (1973) *Theory of Orientation and Stereoselection* (Springer, Berlin).
11. Fukui, K. (1982) *Science* **217**, 747-784.
12. Parr, R. G. & Yang, W. (1984) *J. Am. Chem. Soc.* **106**, 4049-4050.
13. Yang, W., Parr, R. G. & Pucci, R. (1984) *J. Chem. Phys.* **81**, 2862-2863.
14. Falicov, L. M. & Somorjai, G. A. (1985) *Proc. Natl. Acad. Sci. USA* **82**, 2207-2211.
15. Kohn, W. & Vashishta, P. (1983) in *Theory of Inhomogeneous Electron Gas*, Lundquist, S. & March, N. H. (1973) (Plenum, New York), pp. 79-147.
16. Pearson, R. G. (1973) *Hard and Soft Acids and Bases* (Dowden, Hutchinson and Ross, Stroudsburg, PA), p. 3536.
17. Taylor, H. S. (1925) *Proc. R. Soc. London Ser. A* **108**, 105-111.
18. Feibelman, P. F. & Hamann, P. R. (1984) *Phys. Rev. Lett.* **52**, 61-64.
19. Ghosh, S. & Berkowitz, M. (1985) *J. Chem. Phys.* **83**, 2976-2983.
20. Berkowitz, M., Ghosh, S. & Parr, R. G., *J. Am. Chem. Soc.*, in press.