

Acidic and Basic Molecular Hardness in LCAO Approximation

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ABSTRACT

Hardness of a molecule has been formulated as an average of a set of terms representing various types of reactivity. Hardness parameters for molecules and bonded atoms have been calculated by the ab initio Hartree–Fock self-consistent field (HF SCF) method. An analysis has been presented of the correlation between the relative magnitude of contributions to the total hardness and experimentally observed acidic or basic reactivity of molecules. © 1997 John Wiley & Sons, Inc.

Introduction

The density functional theory has recently been successfully applied in theoretical chemistry and offered formal justification of purely experimental description of properties of chemical systems: electronegativity and hardness [1]. Parr and Pearson introduced, for the first time, a quantification of the hardness property [2] widely explored before as qualitative descriptor. The $\frac{1}{2}(I-A)$ has since been widely accepted as a measure of the hardness for isolated, neutral atoms and molecules. Attempts to quantify the hardness of bonded atoms-in-molecule, however, have not yet pro-

duced a clear picture of how the hardness parameters can be applied in studies of reactivity, a focus of chemistry-oriented studies (cf. Refs. [3, 4]).

This work is devoted to analysis of electronegativity and hardness in the framework of quantum-chemical LCAO molecular orbital (MO) methods based on the self-consistent-field (SCF) Hartree–Fock–Roothaan (HFR) Hamiltonian. The base for this analysis is the original solution of that problem offered by Komorowski and Lipiński [5–7].

The eigenvalue problem for the closed shell is formulated as

$$FC = SCE, \quad (1)$$

where F denotes the matrix of the HFR operator, S the overlap matrix, C the LCAO eigenvectors, and E the orbital energies. The elements of the energy matrix F for the closed-shell entity in the atomic

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orbitals (AO) representation are given by

$$F_{kl} = \sum_m \sum_n (H_{kl} + P_{mn} g_{kl, mn}). \quad (2)$$

Symbols in the above equations correspond to the standard labels commonly used in the literature. The electronic energy of the system is given by the expression:

$$\begin{aligned} E &= \sum_k \sum_l P_{kl} \left(H_{kl} + \frac{1}{2} \sum_m \sum_n P_{mn} g_{kl, mn} \right) \\ &= \frac{1}{2} \sum_k \sum_l P_{kl} (H_{kl} + F_{kl}). \end{aligned} \quad (3)$$

The orthonormalization condition for molecular orbitals in the system of N electrons reads

$$\sum_k \sum_l P_{kl} S_{kl} = N. \quad (4)$$

The first and second derivatives of the energy to P_{kl} are given by the expression:

$$\begin{aligned} \frac{\partial E}{\partial P_{kl}} &= F_{kl}, \\ \frac{\partial^2 E}{\partial P_{kl} \partial P_{mn}} &= g_{kl, mn}. \end{aligned} \quad (5)$$

Corresponding third and higher energy derivatives are identically zero.

Electronegativity

The energy of the electronic system is a function of the number of the electrons; the real values of the argument are limited to integral N . Perdew and co-workers showed that only left- and right-hand derivatives of $E(N)$ exist due to the discrete character of the argument N [8]. Since electronegativity is a negative derivative of energy, it can rigorously be calculated in the vicinity of N_0 , as proved in Ref. [8].

$$\chi = - \left(\frac{\partial E}{\partial N} \right)_V = \begin{cases} I & (N_0 - 1) < N < N_0 \\ A & N_0 < N < (N_0 + 1) \end{cases} \quad (6)$$

where N_0 is number of electrons in the neutral state of the system, I and A are ionization energy and electron affinity, respectively.

Under the HFR calculation scheme, the problem of discontinuity of $E(N)$ function is shifted to somewhat deeper level:

$$\left(\frac{\partial E}{\partial N} \right)_V = \sum_{kl} \frac{\partial E}{\partial P_{kl}} \frac{\partial P_{kl}}{\partial N} = \sum_{kl} F_{kl} \left(\frac{\partial P_{kl}}{\partial N} \right)_V. \quad (7)$$

The discontinuity of the derivatives is now hidden in $(\partial P_{kl}/\partial N)_V$. Following the scheme presented in [8], the right- and left-side derivatives are obtained under Koopmans restriction as:

$$\begin{aligned} \left(\frac{\partial P_{kl}}{\partial N} \right)_V^+ &= P_{kl}^+ - P_{kl} = c_k^{\text{LUMO}} c_l^{\text{LUMO}} = a_{kl}^+, \\ \left(\frac{\partial P_{kl}}{\partial N} \right)_V^- &= P_{kl} - P_{kl}^- = c_k^{\text{HOMO}} c_l^{\text{HOMO}} = a_{kl}^-. \end{aligned} \quad (8)$$

Hence

$$\begin{aligned} \chi^+ &= - \sum_{kl} F_{kl} a_{kl}^+ \\ &= - \sum_{kl} F_{kl} c_k^{\text{LUMO}} c_l^{\text{LUMO}} = -\varepsilon_{\text{LUMO}}, \end{aligned} \quad (9)$$

$$\begin{aligned} \chi^- &= - \sum_{kl} F_{kl} a_{kl}^- \\ &= - \sum_{kl} F_{kl} c_k^{\text{HOMO}} c_l^{\text{HOMO}} = -\varepsilon_{\text{HOMO}}, \end{aligned} \quad (10)$$

where the \pm sign denotes increasing (+) or decreasing (−) number of electrons; thus the right- and left-side derivatives at $N = N_0$. Electronegativity of a molecule may now only be obtained as an average of χ^+ and χ^- ; resulting value of χ_M will no longer represent the true derivative. The average, rather than differential character of the electronegativity has already been postulated in previous work [9].

$$\begin{aligned} \chi_M &= - \left(\frac{\partial E}{\partial N} \right)_V = \frac{1}{2} (\chi^+ + \chi^-) \\ &= - \frac{1}{2} \sum_{kl} (a_{kl}^+ + a_{kl}^-) F_{kl} \\ &= - \frac{1}{2} (\varepsilon^{\text{LUMO}} + \varepsilon^{\text{HOMO}}) = \frac{1}{2} (I + A). \end{aligned} \quad (11)$$

Hardness

The molecular hardness η_M , according to the quantitative definition by Parr and Pearson [2],

will be expressed as the second derivative of energy:

$$\eta_M = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right) = \sum_{kl} \left(\frac{1}{2} \frac{\partial F_{kl}}{\partial N} a_{kl} + F_{kl} b_{kl} \right) \\ = \sum_{kl} \left(\frac{1}{2} \sum_{mn} a_{kl} a_{mn} g_{klmn} + F_{kl} b_{kl} \right), \quad (12)$$

where $b_{kl} = \frac{1}{2}(\partial^2 P_{kl}/\partial N^2) = \frac{1}{2}(\partial a_{kl}/\partial N)$. Due to the discontinuities of the derivatives, the rigorous differential value of η_M at $N = N_0$ does not exist. The right- and left-side derivatives η^{++} and η^{-} may be used instead; they will be found using a_{kl}^+ and a_{kl}^- as introduced above.

Respective b^+ and b^- derivatives are identically equal to zero, as follows from Eq. (8). Hence,

$$\eta^{++} = \frac{1}{2} \sum_{kl} \sum_{mn} g_{kl, mn} a_{kl}^+ a_{mn}^+ \\ = \frac{1}{2} \sum_{kl} \sum_{mn} g_{kl, mn} c_k^{\text{LUMO}} c_l^{\text{LUMO}} c_m^{\text{LUMO}} c_n^{\text{LUMO}} \\ = \frac{1}{2} J_{\text{LUMO}} \quad (13)$$

and

$$\eta^{--} = \frac{1}{2} \sum_{kl} \sum_{mn} g_{kl, mn} a_{kl}^- a_{mn}^- \\ = \frac{1}{2} \sum_{kl} \sum_{mn} g_{kl, mn} c_k^{\text{HOMO}} c_l^{\text{HOMO}} c_m^{\text{HOMO}} c_n^{\text{HOMO}} \\ = \frac{1}{2} J_{\text{HOMO}}. \quad (14)$$

These hardness values have been identified before by Giambiagi et al. [10, 11] and by Julg [12] as possible measure of hardness of systems with odd number of electrons.

The focus of this present work is to propose an average hardness as a natural extension of the average electronegativity given by Eq. (11). This will be done by using average values of \bar{a}_{lk} and \bar{b}_{kl} derivatives rather than simply averaging the η^{++} and η^{--} .

Let

$$\bar{a}_{kl} = \frac{1}{2}(a_{kl}^+ + a_{kl}^-) \\ = \frac{1}{2}(c_k^{\text{LUMO}} c_l^{\text{LUMO}} + c_k^{\text{HOMO}} c_l^{\text{HOMO}}). \quad (15)$$

The average value of \bar{b}_{kl} around $N = N_0$ will be

found for the entire range $N \in (N_0 + 1, N_0 - 1)$ using finite difference approximation to the derivative $b_{kl} = (\partial a_{kl}/\partial N)$.

$$\bar{b}_{kl} = \frac{a_{kl}^+ - a_{kl}^-}{2} = \frac{1}{2}(c_k^{\text{LUMO}} c_l^{\text{LUMO}} - c_k^{\text{HOMO}} c_l^{\text{HOMO}}). \quad (16)$$

The average value of molecular hardness around $N = N_0$ may now be found as [cf. Eq. (12)]:

$$\eta_M = \sum_{kl} \left(\frac{1}{2} \sum_{mn} g_{kl, mn} \bar{a}_{kl} \bar{a}_{mn} + F_{kl} \bar{b}_{kl} \right) \\ = \sum_{kl} \left[\frac{1}{8} \sum_{mn} g_{kl, mn} (a_{kl}^+ a_{mn}^+ + a_{kl}^- a_{mn}^- + a_{kl}^+ a_{mn}^- \\ + a_{kl}^- a_{mn}^+) + F_{kl} \bar{b}_{kl} \right] \\ = \frac{1}{4} [\frac{1}{2} J_{\text{LUMO}} + (2J_{\text{LUMO, HOMO}} - K_{\text{LUMO, HOMO}}) \\ + \frac{1}{2} J_{\text{HOMO}}] + \sum_{kl} F_{kl} \bar{b}_{kl} \\ = \frac{1}{4} (\eta^{++} + 2\eta^{+-} + \eta^{--}) + \eta^{\text{val}}. \quad (17)$$

The above result for the average molecular hardness appears as natural combination of the terms whose meaning have been already known. The last term has been analyzed in detail in previous work and proved to be identical with $\frac{1}{2}(\text{I-A})$ under Koopmans restriction. It has been denoted the valence hardness [5]:

$$\eta^{\text{val}} = \sum_{kl} F_{kl} \bar{b}_{kl}. \quad (18)$$

The formula for η^{+-} has been first analyzed by Giambiagi and de Giambiagi [10]; the authors claimed it to be proper measure for the hardness of closed-shell systems. For an entire molecule or free atom $\eta^{+-} = \eta^{-+}$ always.

$$\eta^{+-} = \frac{1}{2} \sum_{kl} \sum_{mn} g_{kl, mn} a_{kl}^+ a_{mn}^- \\ = \frac{1}{2} \sum_{kl} \sum_{mn} g_{kl, mn} c_k^{\text{LUMO}} c_l^{\text{LUMO}} c_m^{\text{HOMO}} c_n^{\text{HOMO}} \\ = \frac{1}{2} (2J_{\text{LUMO, HOMO}} - K_{\text{LUMO, HOMO}}) \quad (19)$$

Atom in Molecule

Electronegativity and hardness for bonded atom are by definition [5–7]:

$$\chi_A^{\text{def}} = - \left(\frac{\partial E}{\partial N_A} \right)_{N_{B \neq A}}, \quad (20)$$

$$\eta_A = \frac{1}{2} \left(\frac{\partial \chi_M}{\partial N_A} \right)_{N_{B \neq A}}. \quad (21)$$

Electronegativity of the molecule can now be decomposed:

$$\chi_M^{+/-} = - \sum_A \left(\frac{\partial E}{\partial N_A} \right)^{+/-} \frac{dN_A}{dN} = \sum_A \chi_A^{+/-} K_A^{+/-} \quad (22)$$

where K_A 's are Fukui function indices [1] and the \pm signs denote the left- and right-side derivatives, respectively. In the AO basis

$$K_A^{+/-} = \left(\frac{dN_A}{dN} \right)^{+/-} = \sum_{k \in A} \sum_l S_{kl} a_{kl}^{+/-} \quad \text{and} \quad \sum_A K_A^{+/-} = 1. \quad (23)$$

By combining with Eqs. (8) and (9), the electronegativity of bonded atom becomes

$$\chi_A^{+/-} = - \frac{\sum_{k \in A} \sum_l F_{kl} a_{kl}^{+/-}}{\sum_{k \in A} \sum_l S_{kl} a_{kl}^{+/-}}. \quad (24)$$

In this same way we have the orbital electronegativity

$$\chi_k^{+/-} = - \frac{\sum_l F_{kl} a_{kl}^{+/-}}{\sum_l S_{kl} a_{kl}^{+/-}}. \quad (25)$$

Under Koopmans theorem the orbital and atomic electronegativity conform to the electronegativity equalization.

$$\chi_k^{+/-} = \chi_A^{+/-} = \chi_M^{+/-} = -\varepsilon_{\text{LUMO/HOMO}} \quad (26)$$

The same holds for average electronegativity as defined by Eq. (11). Decomposition of the molecu-

lar hardness into atomic contributions can be, in principle, performed in similar manner [5–7]:

$$\eta_M = - \sum_A \left(\frac{\partial \chi_M}{\partial N_A} \right) \frac{dN_A}{dN} = \sum_A \eta_A K_A. \quad (27)$$

The average molecular hardness, as given by Eq. (17) may now be obtained using average \bar{a}_{kl} from Eq. (15) to calculate the average Fukui index K_A from Eq. (23). Adopting for the η^{++} , η^{+-} , η^{-+} , and η^{--} the same summation rules as for $\eta_M^{\text{val}} = \sum_A \eta_A^{\text{val}} K_A$, atomic hardness can be decomposed into terms identical as in Eq. (17) for the molecular hardness.

$$\eta_A = \frac{1}{4} (\eta_A^{++} + \eta_A^{+-} + \eta_A^{-+} + \eta_A^{--}) + \eta_A^{\text{val}}. \quad (28)$$

However, the η_A^{+-} and η_A^{-+} are no longer identical, as demonstrated by their defining equations below:

$$\begin{aligned} \eta_A^{++} &= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} a_{kl}^+ a_{mn}^+ g_{kl, mn}}{\sum_{k \in A, l} S_{kl} a_{kl}^+} \\ &= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} c_k^{\text{LUMO}} c_l^{\text{LUMO}} c_m^{\text{LUMO}} c_n^{\text{LUMO}} g_{kl, mn}}{\sum_{k \in A, l} S_{kl} c_k^{\text{LUMO}} c_l^{\text{LUMO}}}, \end{aligned} \quad (29)$$

$$\begin{aligned} \eta_A^{+-} &= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} a_{kl}^+ a_{mn}^- g_{kl, mn}}{\sum_{k \in A, l} S_{kl} a_{kl}^+} \\ &= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} c_k^{\text{LUMO}} c_l^{\text{LUMO}} c_m^{\text{HOMO}} c_n^{\text{HOMO}} g_{kl, mn}}{\sum_{k \in A, l} S_{kl} c_k^{\text{LUMO}} c_l^{\text{LUMO}}}, \end{aligned} \quad (30)$$

$$\begin{aligned} \eta_A^{-+} &= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} a_{kl}^- a_{mn}^+ g_{kl, mn}}{\sum_{k \in A, l} S_{kl} a_{kl}^-} \\ &= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} c_k^{\text{HOMO}} c_l^{\text{HOMO}} c_m^{\text{LUMO}} c_n^{\text{LUMO}} g_{kl, mn}}{\sum_{k \in A, l} S_{kl} c_k^{\text{HOMO}} c_l^{\text{HOMO}}}, \end{aligned} \quad (31)$$

$$\eta_A^{--} = \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} a_{kl}^- a_{mn}^- g_{kl, mn}}{\sum_{k \in A, l} S_{kl} a_{kl}^-}$$

$$= \frac{1}{2} \frac{\sum_{k \in A, l} \sum_{mn} c_k^{\text{HOMO}} c_l^{\text{HOMO}} c_m^{\text{HOMO}} c_n^{\text{HOMO}} g_{kl, mn}}{\sum_{k \in A, l} S_{kl} c_k^{\text{HOMO}} c_l^{\text{HOMO}}}$$
(32)

Results and Discussion

The formulas for molecular and atomic hardness derived in the preceding section have been used in calculation performed by the ab initio method. Results of a single SCF run were sufficient for calculation. Basis set used for Br, Li, I, K, and Na was 3-21 G; for O, S, B, N, and H was 4-31 G; and for Cl and F was 6-31 G. All calculations were performed by using the MICROMOL program on the workstation IBM RS/6000/AIX. Hardness for a selection of molecules has been presented in Tables I to III.

Tables I and II provide illustrations of the relative ratio of components contributing to the total molecular hardness in diatomic molecules. The valence hardness is in most cases the most important component of η ranging up to 70% (in H_2 and N_2). On the other hand the valence hardness is only ca. 16% of η in Br_2 and I_2 , the leading component being the total radical hardness ($\eta^{+-} + \eta^{-+}$), ca. 50%. The radical contribution is only

slightly less pronounced in Cl_2 and O_2 (ca. 40%). For bonded atoms, a striking low valence hardness for Li in halides should be noted, as opposed to sodium in its respective halides and also to LiH.

Results for atomic hardness in Table II show very clearly how the acidic or basic properties of the diatomic molecule are associated with one end (one atom in molecule) only. The η^{++} and η^{--} contributions to the hardness of the molecule are practically dominated by the cation and anion, respectively. Although the molecules listed in Table II do not show either acidic or basic properties as a whole, the acidic properties of cations and basic character of anions is well established in practice. The same is observed for NH_3 and BF_3 molecules. Results for the latter two molecules tend to suggest that the most common property of a molecule is the one characterized with the highest hardness contribution. Elucidation of this question needs further effort.

The interesting result of this work is in deriving an expression for the average hardness that includes all previously separately introduced measures of hardness. Four terms contribute to the total average hardness parameter: (i) the valence hardness, equivalent to the I-A concept; (ii) acidic hardness η^{++} , appropriate for the process of gaining electrons; (iii) basic hardness η^{--} appropriate for the process of losing electrons; and (iv) radical hardness η^{+-} . Acidic and basic terms were of special focus for this study. Of particular interest is an intriguing possibility of discovering if the prevailing type of reactivity of a molecule or bonded atom can be deduced from the relative contributions to the total hardness. While this task needs further study, some interesting hints are born from this present work: (i) when a specific contribution to hardness of a molecule is dominated by one atom only, the atom tends to dominate the properties of the whole molecule with respect to this type of reactivity; (ii) valence hardness alone does not reproduce any specific reactivity of a molecule but rather it determines the global hardness on the system.

TABLE I
Calculated hardness indices for homonuclear molecules (hardness in V/e).

Molecule	η	η^{val}	η^{++}	η^{+-}/η^{-+}	η^{--}
H_2	15.75	11.31	2.62	5.35	4.45
F_2	17.64	10.37	4.64	8.19	8.07
Cl_2	5.68	2.03	2.53	4.69	2.70
Br_2	3.90	0.66	2.26	4.17	2.38
I_2	3.33	0.60	1.92	3.50	1.99
O_2	8.77	3.07	4.02	7.33	4.15
S_2	7.07	3.81	2.27	4.18	2.41
N_2	15.41	10.64	3.24	5.95	3.91
Li_2	4.19	2.59	1.02	1.91	1.58

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TABLE II
Calculated hardness indices for diatomic molecules (hardness in V / e).

Molecule	Atom	Charge	η	η^{val}	η^{++}	η^{+-}	η^{-+}	η^{--}
HF			17.56	11.44	2.89	5.42	5.42	10.73
	H	0.48	7.39	5.71	2.83	3.88	0.00	0.00
HCl			13.20	8.77	2.58	4.49	4.49	6.16
	H	0.19	8.85	4.63	2.94	2.86	5.77	5.30
HCl			17.35	11.59	1.07	11.36	4.49	6.16
	Cl	-0.19	11.29	7.79	2.52	4.17	4.17	3.15
HBr			13.71	9.61	1.76	7.32	4.17	3.15
	Br	-0.05	7.59	4.16	2.90	2.60	5.73	2.46
HI			9.81	6.70	2.24	3.76	3.76	2.65
	H	-0.07	6.26	3.07	2.85	2.47	5.38	2.09
LiH			11.29	8.00	1.58	5.19	3.76	2.65
	I	0.07	6.35	4.12	1.43	2.13	2.13	3.24
NaH			11.05	8.01	0.96	5.59	2.09	3.52
	H	-0.27	11.74	8.47	3.02	3.24	3.24	3.62
LiF			14.21	10.80	3.08	3.13	4.68	2.74
	Na	0.89	9.68	6.00	0.46	7.44	3.16	3.67
LiF			8.96	6.14	1.42	2.11	2.11	5.66
	Li	0.72	2.70	0.49	1.42	2.10	2.37	2.94
LiCl			19.60	12.26	1.14	20.36	2.10	5.77
	F	-0.72	7.17	5.00	1.46	1.92	1.92	3.37
LiCl			2.04	0.07	1.47	1.89	2.26	2.25
	Li	0.63	16.91	10.26	-1.10	22.37	1.91	3.41
LiBr			6.54	4.50	1.46	1.87	1.87	2.96
	Li	0.47	2.12	0.24	1.47	1.83	2.21	2.01
LiI			12.41	9.18	0.71	7.34	1.85	3.01
	Br	-0.47	6.00	4.12	1.47	1.78	1.78	2.51
LiI			1.88	0.08	1.48	1.73	2.17	1.80
	Li	0.44	11.47	8.50	0.32	7.28	1.76	2.55
NaF			14.31	10.49	3.07	3.18	3.18	5.82
	Na	0.89	14.40	10.97	3.09	3.01	4.38	3.25
NaCl			16.75	10.03	1.25	16.63	3.17	5.84
	F	-0.89	13.06	9.44	2.80	2.89	2.89	5.90
NaCl			13.21	9.71	2.91	2.58	4.34	4.15
	Na	0.92	13.28	9.22	1.78	5.68	2.88	5.91
NaBr			11.56	8.77	2.92	2.61	2.61	3.05
	Na	0.90	12.62	9.68	2.99	2.43	4.26	2.07
NaI			11.28	7.92	1.24	6.55	2.60	3.06
	Br	-0.90	10.91	8.31	2.71	2.55	2.55	2.57
NaI			11.82	9.03	2.85	2.28	4.27	1.78
	Na	0.91	10.57	7.74	1.64	4.56	2.54	2.57

TABLE III
Calculated hardness indices for NH_3 and BF_3 (hardness in V / e).

Molecule	Atom	Charge	η	η^{val}	η^{++}	η^{+-}	η^{-+}	η^{--}
NH_3			12.36	8.59	2.00	4.32	4.32	4.48
	N	-0.91	14.76	13.05	0.87	-2.98	4.29	4.56
BF_3			8.83	6.99	1.78	2.92	5.38	1.34
	H	0.30	15.58	11.75	2.80	4.66	4.66	3.20
BF_3			9.29	5.73	2.95	4.20	3.80	3.27
	B	1.43	21.09	16.59	1.61	8.46	4.65	3.25
BF_3								
	F	-0.48						

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