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Improved hardness parameters for molecules

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Abstract. It is shown that molecular hardness can be expressed as the geometric mean of the hardness values for constituent atoms. Using this principle the hardness values for several molecules have been calculated from the pertinent atomic data obtained through a five-point finite difference formula. Finally, gradation of several acids and bases into hard, border-line and soft categories has been made on the basis of their calculated hardness values.

Keywords. Molecular hardness; geometric mean principle; five-point finite difference formula.

1. Introduction

Of late, there has been an upsurge of interest in providing rigorous theoretical foundations (Iczkowski and Margrave 1961; Parr *et al* 1978; Parr 1983, 1989; Parr and Pearson 1983; Nalewajski 1984; Berkowitz *et al* 1985; Giambiagi *et al* 1988; Nalewajski *et al* 1988; Pearson 1988; Goycoolea *et al* 1989; Parr and Chattaraj 1991) for certain popular chemical concepts like electronegativity (Pauling 1960; Sen and Jørgensen 1987) and hardness (Pearson 1963; Huheey 1983). Density-based theories of many-electron systems have been found to be especially useful in this regard. In the density functional theory the electronegativity (χ) and the hardness (η) are defined as follows (Parr *et al* 1978; Parr and Pearson 1983).

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_v \simeq \frac{I+A}{2}, \tag{1}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v \simeq I - A, \tag{2}$$

where v is the external nuclear potential, and E, I and A are respectively the total energy, ionization potential and electron affinity of an N-electron system.

The concept of hardness was originally introduced by Pearson (1963) in order to rationalize the stability of various ligand–metal ion complexes. Since then it has been established (Parr 1989; Parr and Chattaraj 1991) as a very useful index for interpreting a wide variety of chemical phenomena. This concept has been quantified through (2), and experimental values for molecular hardness can be estimated from the pertinent I (Rosenstock *et al* 1977) and A (Janousek and Brauman 1979) values. The expression for η as given by (2) has been obtained using a three-point finite

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difference formula for the second derivative. In earlier work, the geometric mean (GM) principle (Parr and Bartolotti 1982; Sanderson 1983) for molecular chemical potential ($\mu = -\chi$) and the arithmetic mean (AM) principle (Yang *et al* 1985) for molecular softness ($S = 1/\eta$) have ben advocated. In this paper we have shown that the GM principle for η is a consequence of the same principle for μ, and the assumption, $\eta_j = \gamma\mu_j$ (γ is a constant) made for atoms leads automatically to the corresponding assumption, $\eta = \gamma\mu$, made (Yang *et al* 1985) for molecules. Using the GM principle η values for several molecules have been calculated from the pertinent atomic data obtained through a five-point finite difference formula for $(\partial^2 E/\partial N^2)$. The η values thus calculated are referred to as 'improved' ones since they are obtained by using a better approximation for the second derivative. It was shown by Parr and Pearson (1983) that an acid will readily react with a base if they have similar η values, which is a quantitative statement of the well-known HSAB (hard and soft acid-base) principle (Pearson 1963). Based on this and other empirical principles acids and bases have been classified (Huheey 1983) into three categories, namely, hard, border-line and soft. We have categorized some of these compounds on the basis of their improved η values.

2. Theoretical background

Since $\chi = -\mu$, it follows from (1) and (2) that

$$\eta = \left(\frac{\partial \mu}{\partial N}\right). \tag{3}$$

If the molecule contains P atoms and $\{\mu_j, j = 1, 2, \ldots, P\}$ denote the corresponding chemical potentials, then according to the GM-principle

$$\mu = \left(\prod_{j=1}^{P} \mu_j\right)^{1/P}. \tag{4}$$

Substituting (4) in (3) and making use of the following definition for atomic hardness,

$$\eta_j = \frac{\partial \mu_j}{\partial N_j} = \frac{\partial \mu_j}{\partial N}\left(\partial \sum_{j=1}^{P} N_j/\partial N_j\right) = \frac{\partial \mu_j}{\partial N}, \tag{5}$$

we get,

$$\eta = \frac{\mu}{P}\left[\sum_{j=1}^{P} \eta_j/\mu_j\right], \tag{6}$$

Now, following Yang *et al* (1985) if we assume that

$$\eta_j = \gamma\mu_j, \tag{7}$$

then (6) yields

$$\eta = \gamma\mu. \tag{8}$$

Now substituting (7) and (8) in (4) one gets

$$\eta = \left(\prod_{j=1}^{P} \eta_j\right)^{1/P}, \tag{9}$$

which shows that the GM principle for molecular hardness follows automatically from the corresponding principle for molecular chemical potential. The atomic hardness parameters, η_j, required for the calculation of η have been evaluated using the following five-point finite difference formula.

$$\eta_j = (1/6)[8(I_j - A_j) + (\chi_j^- - \chi_j^+)] \tag{10}$$

where χ_j^+ and χ_j^- are the electronegativity values of the monopositive and mononegative ions of the jth atom. It is worthwhile to recall that the three-point finite-difference approximation yield $\eta_j = I_j - A_j$, which differs considerably from (10).

3. Results and discussion

The hardness values for several atoms constituting the molecules considered herein, as obtained from three-point and five-point finite difference formulas, are compared in table 1. For the estimation of η_j, the value of I_j, A_j and χ_j^- are taken from the self-interaction corrected and correlated density functional calculation by Goycoolea *et al* (1989), while those of χ_j^+ are numerically extrapolated from the data given therein. As can be seen from table 1, the improved η_j values are always lower than those obtained by the $I_j - A_j$ approximation. In a few cases like *C*, *O* and *F* the two sets of values differ by as much as 0·5 eV.

Figure 1 depicts the variation of geometrically averaged η values with the corresponding experimental values for the molecules considered by Yang *et al* (1985). Both sets of values for η refer to the three-point approximation. The rms deviation of the calculated values from experiment has been found to be 1·17 eV. The regression analysis for the least-squares fit to a straight line passing through the origin indicates that the slope of the line, the standard deviation, the standard error of estimate (with respect to the fitted line) and the regression coefficient are 1·037, 1·75 eV, 1·10 eV and 0·99 respectively. For the sake of comparison the linear regression analysis was carried

Table 1. Calculated hardness values η_j (eV) of some atoms.

	η_j	
Atom	Three-point	Five-point
H	12·84*	
C	9·38	8·86
N	13·08	12·84
O	11·38	10·92
F	13·44	12·86
S	7·62	7·40
Cl	8·82	8·56
P	9·06	9·08
Br	7·96	7·80
I	6·96	6·84

* Experimental (I–A) value

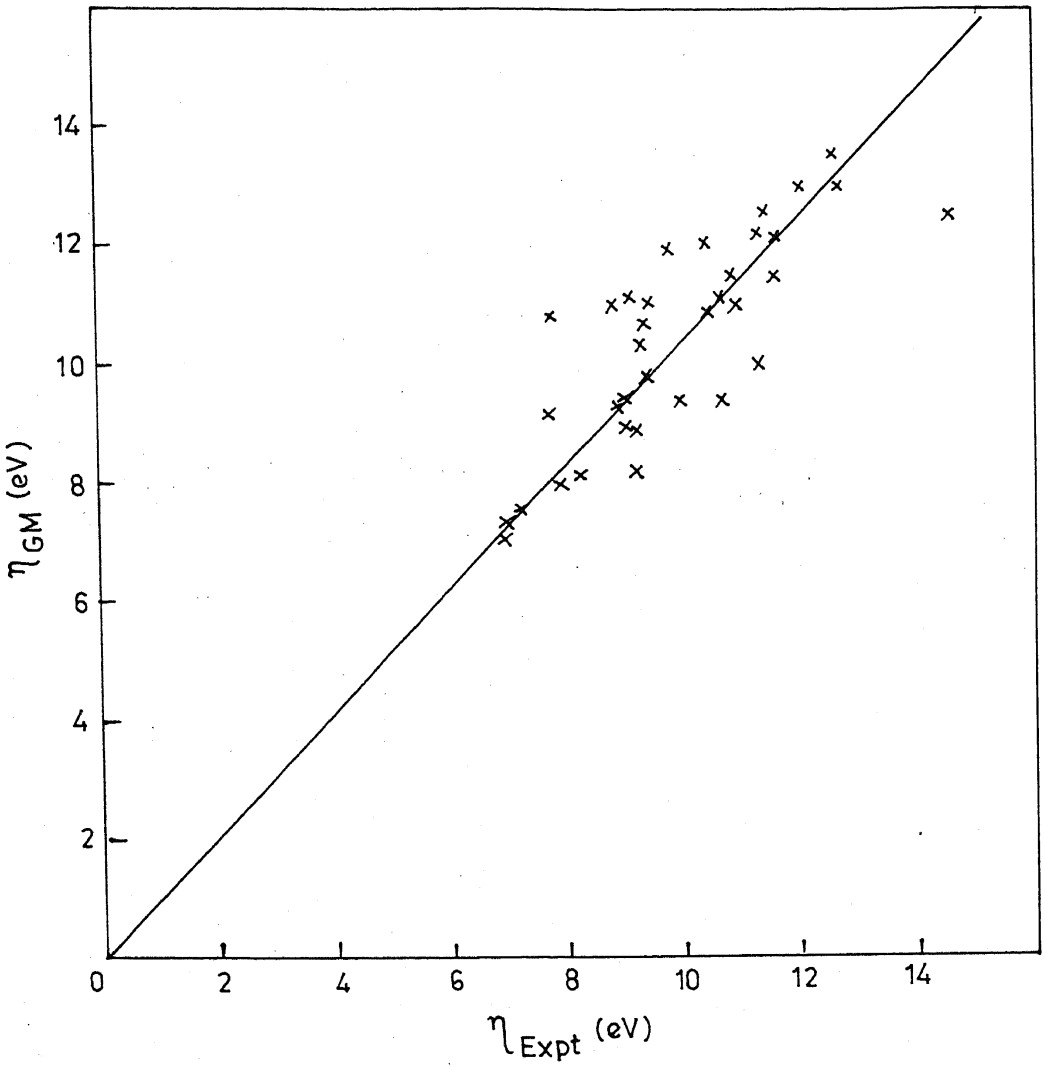

Figure 1. Comparison of geometrically averaged (η_{GM}) and experimental η values. (Both sets of data are taken from table 2 and correspond to the three-point level of approximation.)

out also for the AM principle of molecular hardness, and the values for the above quantities were found to be 1·22 eV, 1·046, 1·77 eV, 1·13 eV and 0·99 respectively.

Similar analysis with the five-point η values could not be made because of nonavailability of the corresponding experimental values. However, we have presented in table 2 both GM and AM η values for several molecules obtained at three-point and five-point levels of approximation, and compared them with the three-point experimental values. As expected, the five-point values are always lower than the corresponding three-point values. The discrepancy between the two sets of calculated values is quite pronounced in the case of S_2, SO, C_2, O_2, F_2, COS, SO_2, O_3, SO_3, CF_3I, CF_3Br and $C_6H_4O_2$. Since the five-point GM approximation is theoretically more rigorous than its three-point counterpart, the former calculated values are recommended in chemical applications of molecular hardness.

Finally, we have calculated the η values (table 3) for a number of acids and bases using the five-point GM approximation and classified them as hard, border-line and soft depending upon their η values. For the sake of comparison the classifications

Table 2. Comparison of geometrically averaged η_{GM}(eV) and arithmetically averaged η_{AM}(eV) values of some molecules obtained at three-point (I) and five-point (II) levels of approximation.

	η_{AM}		η_{GM}		
Molecule	I	II	I	II	η_{expt}*
I_2	6·96	6·84	6·96	6·84	6·98
IBr	7·46	7·32	7·44	7·30	7·24
S_2	9·06	7·40	9·06	7·40	7·74
Br_2	7·96	7·80	7·96	7·80	7·96
Cl_2	8·82	8·56	8·82	8·56	9·08
P_2	9·06	9·08	9·06	9·08	8·95
SO	9·50	9·16	9·31	8·98	8·87
C_2	9·38	8·86	9·38	8·86	9·06
CH	11·11	10·84	10·97	10·66	9·40
CN	11·23	10·84	11·08	10·66	10·68
O_2	11·38	10·92	11·38	10·92	11·62
OH	12·11	11·88	12·09	11·84	11·35
NH	12·96	12·84	12·96	12·84	12·72
F_2	13·44	12·86	13·44	12·86	12·62
CS_2	8·21	7·88	8·17	7·86	9·08
COS	9·46	9·06	9·33	8·94	10·72
SO_2	10·13	9·74	9·96	9·60	11·29
O_3	11·38	10·92	11·38	10·92	10·85
NH_2	12·92	12·84	12·92	12·84	12·02
N_2O	12·51	12·20	12·49	12·16	11·42
PBr_3	8·24	8·12	8·22	8·10	8·25
PCl_3	8·88	8·68	8·88	8·68	9·11
$POCl_3$	9·38	9·14	9·33	9·10	10·00
CH_3I	10·97	10·84	10·67	10·52	9·34
SO_3	10·44	10·04	10·29	9·90	9·30
CF_3I	11·33	10·86	10·96	10·52	8·83
C_2H_2	11·11	10·84	10·97	10·66	10·98
CF_3Br	11·53	11·04	11·26	10·80	10·91
CH_3	11·98	11·84	11·87	11·70	9·76
HNO_3	12·01	11·68	11·99	11·66	10·46
SF_6	12·61	12·08	12·39	11·88	14·60
$C_6H_5NO_2$	11·17	10·86	11·05	10·70	9·16
$C_6H_4O_2$	10·87	10·52	10·76	10·38	7·78

* These are experimental I–A values.

made by Huheey (1983) are also indicated in table 3. These have been made (Huheey 1983) on the basis of apparent preference for hard and soft reactants in the equilibrium,

$$BH^+ + CH_3Hg^+ \rightleftharpoons CH_3HgB^+ + H^+,$$

where H^+ and CH_3Hg^+ are respectively the reference hard and soft acids. As can be seen in 14 out of 26 cases identical prediction can be made about their degree of hardness. One should, however, note that it is not possible to draw a sharp line of demarcation between different acids and bases on the basis of their η values. For

Table 3. Classification of some acids and bases into hard (I), border-line (II) and soft (III) categories on the basis of their η_{GM}(eV) values.

		Classification	
Molecule	η_{GM}	Present*	Huheey (1983)
Acids			
BF_3	11·06	I	I
BCl_3	8·15	II	I
$Al(CH_3)_3$	10·90	I	I
AlH_3	9·98	I	I
$Be(CH_3)_2$	11·42	I	I
SO_2	9·60	II	II
$B(CH_3)_3$	11·25	I	II
GaH_3	10·08	I	II
BH_3	11·05	I	III
$Ga(CH_3)_3$	10·94	I	III
$GaCl_3$	7·44	III	III
$GaBr_3$	6·94	III	III
Bases			
N_2H_4	12·84	I	I
NH_3	12·84	I	I
H_2O	12·17	I	I
CH_3OH	11·75	I	I
$C_6H_5NH_2$	10·95	II	II
C_5H_5N	10·85	III	II
N_2	12·84	I	II
C_2H_4	11·35	II	III
C_6H_6	10·67	III	III
CO	9·84	III	III
$(CH_3)_3As$	11·42	II	III
$(CH_3)_3P$	11·48	II	III

*In the present classification an acid is said to be hard when $\eta > 9{\cdot}75$, border-line when η lies between 7·5 and 9·75 and soft when $\eta < 7{\cdot}5$. For the bases the corresponding figures are $> 11{\cdot}5$, 11·0–11·5 and $< 11{\cdot}0$ respectively.

example, according to Huheey (1983) N_2H_4 is a harder base than N_2 which does not tally with our prediction.

4. Concluding remarks

In the present investigation we have obtained an alternative working expression for chemical hardness. We have shown that the GM principle of molecular μ leads automatically to the same principle for η. Moreover, the η values calculated by GM and AM principles do not differ significantly. The present study also shows that it is not necessary to use the softness parameters for the calculation of atomic or molecular hardness, as it has been done by Yang *et al* (1985).

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