EMPIRICAL EVALUATION OF CHEMICAL HARDNESS

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Two possible measures of hardness are proposed. An average chemical hardness is calculated separately for acidic and basic reactions of atoms. Differential hardnesses are derived from atomic radii.

1. Introduction

The concept of chemical hardness, first introduced by Pearson as a qualitative ordering property for the classification of Lewis acids and bases [1,2], has recently been successfully incorporated into density functional theory [3,4], which had previously provided useful theoretical support to the chemical concept of electronegativity.

Parr and Pearson have proposed a quantitative definition of atomic hardness as the second derivative of the atomic energy function $E(N)$: $\eta = \frac{1}{2}d^2E(N)/dN^2$. They presented an absolute hardness scale with indices $\frac{1}{2}(I-EA)$ [5]. Subsequent analysis disclosed attractive applications of hardness in the study of chemical reactivity [6–8].

There is a gap, however, between a coherent theoretical analysis and a practical indexing of atomic properties suitable for chemical use. Such a difficulty has already been encountered with electronegativity: absolute electronegativity is only a finite difference approximation to a rigorously defined function $\chi(N) = -dE(N)/dN$. Absolute electronegativity indices should be considered as the average of $\chi(N)$, ($N \in N_0-1$, N_0-1) rather than identified with any real chemical potential [9–11]. An absolute scale of chemical hardness suffers from a similar weakness: this has resulted from the adoption of the operational definition $\frac{1}{2}(I-EA)$ which is not compatible with the second energy derivative unless $E(N)$ is parabolic. An attempt has been made to show that absolute hardness constitutes an average of $d\chi/dN$ but

this was found to be the case only for homogeneous $E(N)$ and neutral atoms [11]. Two novel approaches to the concept of hardness are developed in this work: an average chemical hardness is obtained from absolute electronegativities, and, alternatively, differential hardness $(d\chi/dN)_{N=N_0}$ can be given a numerical value when a simple electrodynamical atomic model is considered.

2. Average chemical hardness

The equivalence between differential and absolute electronegativities has been demonstrated by the equation [10]

$$\bar{\chi} = \frac{\int_{N_0-1}^{N_0+1} \chi(N)\,dN}{e\int_{N_0-1}^{N_0+1} dN} = \frac{1}{2}e^{-1}(I+EA) \qquad (1)$$

($e>0$ is the elementary charge introduced explicitly in order to stress the units of $\bar{\chi}$: volt). For eq. (1) to be valid it is sufficient to require that $E(N)$ be continuous and differentiable between N_0-1 and N_0+1. This definition emphasizes the average character of absolute electronegativity.

An analogous equation can be formally applied to hardness:

$$\bar{\eta} = \frac{\int_{N_0-1}^{N_0+1} \eta(N)\,dN}{e\int_{N_0-1}^{N_0+1} dN}$$

$$= \frac{1}{2}e^{-1}[\chi(N_0+1) - \chi(N_0-1)] . \qquad (2)$$

It is not particularly informative, however, as long as

$\chi(N)$ remains unknown. From the chemical point of view, one is tempted to use appropriate absolute values $\bar{\chi}$ instead of $\chi(N)$ in eq. (2). Such a substitution is well motivated, as all chemical information is contained in $\bar{\chi}$ not in $\chi(N)$. The chemical hardness would appear as the average slope of $\bar{\chi}$. However, eq. (2) would lose its mathematical purity, as $\bar{\chi}$ is certainly not differentiable with respect to N at $N=N_0$, as shown by Perdew et al. [9]. The slope of $\bar{\chi}$ should then be considered separately for $N_0 \leqslant N \leqslant N_0 + 1$ and $N_0 - 1 \leqslant N \leqslant N_0$. Chemically, this corresponds to acidic (electron accepting) and basic (electron donating) behaviour. Hence, eq. (2) can be split into

$$\bar{\eta}_a = e^{-1}(\bar{\chi} - \bar{\chi}_-) = \tfrac{1}{2}e^{-2}(I_1 - EA_2) \qquad (3)$$

(acidic hardness), and

$$\bar{\eta}_b = e^{-1}(\bar{\chi}_+ - \bar{\chi}) = \tfrac{1}{2}e^{-2}(I_2 - EA_1) \qquad (4)$$

(basic hardness). Subscripts " $-$ " and " $+$ " refer to the increased and decreased number of electrons respectively; I_1, I_2, EA_1, EA_2 are first and second ionization energies and electron affinities. This definition of the hardness parameter is limited to integral charge only; free ions and molecules which are simple Lewis acids and bases conform to this requirement. Eqs. (3) and (4) reveal a conceptual difference between chemical hardness ($\bar{\eta}_a$, $\bar{\eta}_b$) and absolute electronegativity at a basic level. While $\bar{\chi}$ is defined for a given chemical entity, $\bar{\eta}_a$ and $\bar{\eta}_b$ are specified for a given type of behaviour, either acidic or basic. The need for separate definitions of hardness for acids and bases can be gleaned from the work of Parr and Pearson [5]. They found themselves compeled to admit non-uniform indices of hardness for neutral atoms, $\tfrac{1}{2}(I - EA)$, and for anionic bases, $\tfrac{1}{2}(I_2 - I_1)$. Eqs. (3) and (4) surmount this difficulty and even the factor of 1/2 introduced by Parr and Pearson for symmetry reasons has now been shown to be an inherent part of the definition.

Tables 1–3 present values of $\bar{\eta}_a$ and $\bar{\eta}_b$ indices for various atoms and atomic ions and comparisons with Parr and Pearson's index η_P.

3. Differential hardness

In contrast to $\bar{\chi}$, the $\chi(N)$ function based on a purely speculative but continuous $E(N)$, is not

expected to show singularities at integral N. The derivative $(d\chi(N)/dN)_{N=N_0}$ is rigorously defined even if numerically inaccessible. A physical meaning may be attributed to differential hardness on the grounds of "chemical approximation" [11]. Since atoms can be considered as metallic spheres with polarizability $\alpha \approx r^3$, the question of their atomic capacitance may be raised. The capacitance of a metallic sphere is simply $\sigma = 4\pi\epsilon_0 r$. At the atomic level the "proper name" for the capacitance is softness or inverse hardness [6,12]. Such a trivial electrodynamical analogy leads to the simple formula

$$\eta(N) = \frac{1}{\sigma} = \frac{1}{4\pi\epsilon_0} \frac{1}{r(N)} . \qquad (5)$$

This equation finds interesting support in the quantum-chemical work of Gasques and Ortiz [13], who have established the relationship $\eta \propto \langle r^{-1} \rangle$ for the radial part of the wavefunction. With eq. (5) differential hardness becomes as accessible as the atomic or ionic radii themselves. Various values of atomic radii $r(N)$ are given in tables 1–3.

4. Discussion

This work has unveiled a peculiar feature of chemical hardness [‡]: it will be an atomic property only in the $\Delta N \rightarrow 0$ limit. The alternative differential hardness η (eq. (5)) shows a limited predictive capability. The acidic or basic character of an atom is unlikely to significantly influence η since the effect of atomic charge is only indirectly included in the definition. Consequently $\bar{\eta}_a$ and $\bar{\eta}_b$, not η, should be used for classification of acids and bases. Examination of tables 1–3 lead to the following conclusions:

(a) In general, $\bar{\eta}_a \leqslant \eta \leqslant \bar{\eta}_b$ is observed for atoms which is consistent with known features of $E(N)$ curves (table 1).

(b) Van der Waals radii, not covalent radii, provide a more reliable measure of atomic hardness, as compared to chemical hardness parameters (table 1). Since interatomic distances in a number of homonuclear single bonds are close to the van der Waals

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‡ Note that the name hardness as the resistance to deformation has also been used for $C(\text{Å}^{-1})$ in the atomic repulsion energy term $B\exp(-Cr)$ [16].

Table 1

Hardness parameters for atoms: η', derived from R_{XX}, the single homonuclear bond distance; η'', derived from van der Waals radii r; $\bar{\eta}_a$, $\bar{\eta}_b$, acidic and basic chemical hardness, eqs. (3) and (4); η_P, Parr and Pearson absolute hardness

Atom	R_{XX} [a] (nm)	η' (V/e)	r [a] (nm)	η'' (V/e)	I_1 [a] (eV)	$\bar{\eta}_a$ [b] (V/e)	I_2 [a] (eV)	EA_1 [a] (eV)	$\bar{\eta}_b$ (V/e)	η_P [c] (eV)
H	0.0742	19.4	0.145	9.94	13.59	6.80	–	0.75	–	6.42
Li			0.155 [d]	9.30	5.39	2.70	75.64	0.62	37.5	2.38
Na			0.190 [d]	7.59	5.14	2.57	47.38	0.55	23.4	2.30
K			0.235 [d]	6.15	4.34	2.17	31.62	0.50	15.6	1.92
Rb			0.248 [d]	5.81	4.18	2.09	27.29	0.49	13.9	1.85
Cs			0.267 [d]	5.40	3.89	1.90	23.11	0.47	11.8	1.71
F	0.1418	10.16	0.160	9.01	17.42	8.77	34.97	3.40	19.2	7.01
Cl	0.1988	7.24	0.190	7.59	13.01	6.50	23.81	3.62	10.1	4.70
Br	0.2284	6.30	0.200	7.21	11.84	5.92	21.76	3.36	9.20	4.24
I	0.2666	5.40	0.212	6.80	10.45	5.22	19.13	3.06	8.02	3.70
O	0.148	9.73	0.150	9.61	13.61	10.84	35.12	1.46	16.8	6.08
S	0.205	7.02	0.180	8.01	10.46	8.23	23.33	2.08	10.6	4.12
N	0.145	9.93	0.155	9.30	14.53	11.4	29.60	0	14.8	7.27
P	0.221	6.52	0.185	7.79	10.48	5.24	19.72	0.75	9.49	4.86
As	0.243	5.92			9.78	4.89	18.63	0.80	8.92	4.49
C	0.154	9.35	0.170	8.48	11.26	5.63	24.38	1.27	11.6	5.00
Si	0.235	6.13	0.210	6.87	8.15	4.08	16.34	1.38	7.48	3.38
Ge	0.241	5.98			7.94	3.97	15.93	1.24	7.34	3.35

[a] Ref. [14].

[b] $EA_2 = 0$ assumed except: -8.08 eV for O, -6.11 eV for S and -8.29 for N [14].

[c] Ref. [5].   [d] Metallic radius, coordination number 12; ref. [14].

radii of their respective atoms, R_{XX} data of high accuracy may be used as a reliable source of hardness parameters for free atoms.

(c) The η' parameter derived from refraction seems to be more appropriate for cations than η'' calculated from crystalline ionic radii (table 2); η'' are too small compared to $\bar{\eta}_a$.

(d) The borderline between hard and soft acids can be drawn at $\bar{\eta}_a = 15$ V/e; typical soft acids display $\bar{\eta}_a \lesssim 10$ V/e (table 2). The classification of cations is consistent with the known chemical classification of acids [1]. Free atoms all appear to be soft acids, although some are quite hard as bases (table 1).

(e) The Parr and Pearson absolute hardness η_P, in all cases where reasonable comparisons can be made, is close to the acidic hardness $\bar{\eta}_a$. This is not unexpected, as the dominant component of both is I_1, the first ionization energy; EA_1 and EA_2 play only a minor role. This explains very clearly why η_P was found appropriate for acids and gave rather poor hardness values for bases [5].

(f) $\bar{\eta}_b$ for typical bases is close to the modified Parr and Pearson index, $\frac{1}{2}(I_2 - I_1)$ [5] (table 3). This again is readily understood, as the second ionization energy I_2 is dominant in both definitions. The $\bar{\eta}_b$ index is free of intuitive argumentation that has motivated a choice of η_P for bases.

The data in tables 1 and 3 suffer from a lack of reliable electron affinities except EA_1 for atoms. Parr and Pearson and other authors have argued that the $E(N)$ curve flattens out as the amount of negative charge on an atom increases [5,17]; this would suggest $EA_2 \approx 0$ and discussion of the hardness parameter would be considerably simplified. However, the above argument holds only for an adiabatic energy $E(N)$; in that case ΔE goes quickly to zero for negative ΔN. Vertical values of the second and higher electron affinities will be negative for most atoms, as can be seen from table 3 for O, S, and N. The need for vertical electron affinities can be understood when it is realized that the energies $E(N)$ involved are, at least conceptually, for atoms in a given chemical environment which provides a degree of external stabilization for an otherwise unstable ion. Negative ions

Table 2

Hardness parameters for free cations: η', derived from ionic refractions R_D, η $(V/e) = 19.6\,R_D^{-1/3}$ $(cm^3\,mol^{-1})$ [11], η'', derived from ionic radii r; $\bar{\eta}_a$, acidic chemical hardness, eq. (3) (basic chemical hardness $\bar{\eta}_b$ is given when appropriate only); η_P, Parr and Pearson absolute hardness

Cation	R_D [a] (cm^3/mol)	η' (V/e)	r [b] (nm)	η'' (V/e)	I_1 [c] (eV)	EA_2 [c] (eV)	$\bar{\eta}_a$ (V/e)	$\bar{\eta}_b$ (V/e)	η_P [d] (eV)
Li^+	0.074	46.7	0.090	16.0	75.64	0.620	37.5		35.1
Na^+	0.457	25.4	0.116	12.4	47.28	0.546	23.4		21.1
K^+	2.12	15.3	0.152	9.49	31.62	0.502	15.5		13.6
Rb^+	3.57	12.8	0.166	8.69	27.29	0.486	13.5		11.7
Cs^+	6.15	10.7	0.181	7.97	23.11	0.471	11.3		9.6
Be^{2+}	0.020	72	0.059	24.4	154.9	9.32	72		67.8
Mg^{2+}	0.238	31.7	0.086	16.8	80.14	7.64	36.2		32.5
Ca^{2+}	1.19	15.5	0.114	12.6	50.91	6.11	22.4		19.7
Sr^{2+}			0.132	10.9	43.63	5.7	19.0		16.3
Ba^{2+}	3.94	12.4	0.149	9.68	35.5	5.21	15.1		12.8
Cu^+	1.08	19.1	0.091	15.8	20.29	1.23	9.53	14.6	6.9
Ag^+	4.33	12.0	0.129	11.2	21.49	1.30	10.1	13.6	6.9
Au^+	4.75	11.7	0.151	9.55	20.52	2.3	9.1		5.7
Hg^+			0.133	10.8	18.76	0	9.4	11.9	4.2
Cu^{2+}			0.087	16.6	36.68	7.73	14.5		8.3
Zn^{2+}	0.72	21.9	0.088	16.4	39.72	9.39	15.2		10.8
Cd^{2+}	2.74	14.0	0.109	13.2	37.48	8.99	14.2		10.3
Hg^{2+}	3.14	13.4	0.116	12.4	34.20	10.4	11.9		7.1
Sn^{2+}					30.50	7.34	11.6	13.0	7.9
Pb^{2+}					21.57	7.42	7.1	13.1	8.5
Mn^{2+}			0.081	17.8	23.30	7.43	7.93	17.8	9.3
Fe^{2+}			0.075	19.2	30.65	7.87	11.4	19.3	7.3
Fe^{3+}			0.069	20.9	54.8	16.2	19.3		13.1
Co^{2+}			0.079	18.2	33.49	7.86	12.8	17.1	8.2
Co^{3+}			0.068	21.2	51.3	17.0	17.1		8.9
Ni^{2+}			0.083	17.4	35.16	7.64	13.8	18.4	8.5
Ni^{3+}			0.070	20.6	54.9	18.2	18.4		9.9
Tl^+			0.164	8.8	20.42	0.31	10.0	11.9	7.2
Tl^{3+}			0.102	14.1	50.7	20.4	15.1		10.5

[a] After L. Pauling, see ref. [15].   [b] Crystalline ionic radius for coordination number 6 [14].   [c] Ref. [14].   [d] Ref. [5].

Table 3

Hardness parameters for free anions: η', derived from ionic refraction R_D (see table 2); η'', derived from ionic radii r; $\bar{\eta}_b$, basic chemical hardness, eq. (4); η_P, Parr and Pearson absolute hardness

Anion	R_D [a] (cm^3/mol)	η' (V/e)	r [b] (nm)	η'' (V/e)	I_2 [c] (eV)	$\bar{\eta}_b$ [d] (V/e)	η_P [e] (eV)
H^-	25.65	6.65			13.59	6.8	6.8
F^-	2.65	14.2	0.119	12.1	17.42	8.7	7.0
Cl^-	9.30	9.33	0.167	8.63	13.01	6.5	4.7
Br^-	12.14	8.54	0.182	7.92	11.84	5.9	4.2
I^-	18.08	7.48	0.206	7.00	10.45	5.2	3.7
O^{2-}	9.88	9.14	0.126	11.4	1.46		
S^{2-}	26.0	6.62	0.170	8.48	2.08		
Se^{2-}	26.8	6.56	0.184	7.84	2.02		
Te^{2-}	35.6	5.96	0.207	6.97	1.97		

[a] After L. Pauling, see ref. [15].   [b] Crystalline ionic radius for coordination number 6 [14].
[c] Ref. [14].   [d] $EA_1 = 0$ assumed.   [e] Ref. [5].

may then be handled in the same way as cations: spontaneous electron loss prevents an experimental study but should not obviate theoretical considerations.

The scales of chemical hardness $\bar{\eta}_a$ and $\bar{\eta}_b$ given in tables 1, 2 and 3 demonstrate an additional important property: Hardness indices for acids and bases span roughly the same numerical range, at least for the ions for which reliable data are available. This has been claimed by Parr and Pearson as a conditio sine qua non for application of the hard and soft acid and bases rule (HSAB) [5]. The authors have been unable to achieve this goal via their index of absolute hardness $\eta_P = \frac{1}{2}(I - EA)$. The relationship between that index and the chemical hardness $\bar{\eta}_a$ and $\bar{\eta}_b$ proposed here can be demonstrated by considering two extreme situations. The first is trivial: for a bulk metal $I_1 = I_2 = EA_1 = EA_2$ thus $\bar{\eta}_a = \bar{\eta}_b = \eta_P = 0$. The second is idealized: Had Koopmans' theorem rigorously held for a closed shell then $I_1 = I_2$ and $EA_1 = EA_2$ and consequently $\bar{\eta}_a = \bar{\eta}_b = \eta_P$. The indices of chemical hardness, $\bar{\eta}_a$ and $\bar{\eta}_b$, given here appear as a natural extension to Parr and Pearson's ideas of absolute hardness which, in addition, are not subject to the limiting assumption of parabolic behaviour for $E(N)$.

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