

Hardness Indices for Free and Bonded Atoms

Ludwik Komorowski

Institute of Organic and Physical Chemistry, Technical University of Wrocław,
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

Quantitative measures for the hardness property of atoms are reviewed and critically discussed. Experimental as well as theoretical ways to describe the atomic hardness have not yet produced a consensus how much value such indices may possess for an experimental chemist. Possible applications emerging in this growing field of cooperation between the theory and the chemical practice are indicated.

1	Experimental Sources of Chemical Hardness	46
1.1	Polarizability	46
1.2	Atomic Radius and Volume	48
1.3	Charge Capacitance	49
1.4	Absolute Hardness	50
1.5	Chemical Approximation	52
2	Focusing on Bonded Atoms	53
2.1	Partition Dilemma	53
2.2	Definition Problem	54
3	Atomic Hardness from Calculations	55
3.1	Density Functional (DF) Theory Viewpoint	55
3.2	Quantumchemical Solution	56
3.3	Atom-in-Molecule Electronegativity and Hardness	57
4	Chemical Applications and Expectations	60
4.1	Charge Transfer	61
4.2	Charge Transfer Affinity	63
4.3	Pearson Principle (HSAB)	65
4.4	Pauling Electronegativity Scale	66
4.5	Reactivity and Substituent Effect	67
5	Conclusions	68
6	References	69

1 Experimental Sources of Chemical Hardness

The Pearson principle (Hard and Soft Acids and Bases) introduced in 1963 as a qualitative rule, has not changed its role over the years [1, 2]. The hard or soft character of reacting species, clearly exemplified by ionic Lewis acids/bases classified into groups as hard, soft or borderline, was assigned according to intuitive criteria, not to a uniform, measurable property. Efforts to create a scale of hardness were hampered by the verbal, not mathematical formulation of the Pearson principle which did not claim for a quantitative measure of hardness. (The very term was not given a formal definition until 1983). In contrast to electronegativity scale, originally based on bond dissociation energies, no uniform data body has ever been indicated to demonstrate the role of hardness. Interpretation of the heat of formation data was perplexed by the Pearson and Pauling paradox [3]. It has even been uncertain, if hard/soft properties, originally introduced for Lewis acids and bases, may also be attributed to molecules of any kind or parts thereof: chemical groups or bonded atoms.

The breakthrough made by Parr and Pearson in 1983 [4] by unifying electronegativity and hardness within the DF (Density Functional) theory, brought the old problem of scale into the light: is it possible and useful to define a uniform scale of hardness? Experimentally observable properties of atoms and molecules which can be related to hardness, provide a clue.

1.1 Polarizability

Acids and bases classified by Pearson as soft were invariably easy polarizable, thus supporting the term softness, indicating species amenable to deformations. Although softness was considered as a broader property [1], implying also the low ionization energy, large radius and low oxidation number, polarizability has been indicated as the simplest convenient property reflecting softness. Connections between the polarizing ability of bonding species and the covalent character of bonds which they form was investigated by Fajans, long before the notion of hardness appeared in the chemical literature [5, 6]. High polarizability of a partner results in more covalent bonds, as in AgCl compared to NaCl lattice. Pearson extended this conclusion, proving that soft acids tend to hold bases by covalent bonds, whereas ionic forces are responsible for the bond formation between hard partners.

Fajans and Pearson both understood that information contained in polarizability coefficient for chemical species reaches beyond its simple, electrostatic definition: $\mu_{\text{ind}} = \alpha E$. It was Jørgensen, however, who first discussed the implications of the polarizability function given by the perturbation analysis [7]:

$$\alpha = \frac{2}{3} \frac{(E_k - E_0) |\langle \Psi_0 | R | \Psi_k \rangle|^2}{(E_k - E_0)^2 - \hbar^2 \nu^2} \quad (1)$$

Contribution from the discrete states Ψ_k is emphasized by this formula, very much in the spirit of contemporary DF analysis of softness. The connection between softness measured by polarizability and low ionization energy was not overlooked in this work, however, Tl(III) was regarded as a counter-example: being a soft central atom it exhibits rather high ionization energy. The role of electron affinity, hardly available at that time, could not be included into consideration.

The measure of polarizability was provided by the abundant data on molecular, ionic and atomic refractions. Refractions in chemistry seem to be of historical importance today. Their long use and the sophisticated level they reached in chemistry provide important hints. Refraction has been recognized as a molecular volume, thus discussion of softness may be reduced to the level of molecular or atomic dimensions, as indeed it was later proposed (Sect. 1.2). Refractions have also been known to be additive, atomic refractions are transferable between molecules. This was but the first indication that atomic softness that should roughly parallel refractions (polarizability), may also be defined for bonded atoms. Examples of atomic and ionic refractions are given in Tables 1 and 2. The increasing order of refraction indeed reflects the expected hardness sequence, the borderline between soft and hard species can be drawn at ca. $2\text{--}3\text{ cm}^3/\text{mol}$.

Table 1. Ionic refractions (R_D) and corresponding hardness indices, $\eta_1 = (4\pi\epsilon_0 R_D^{1/3})^{-1}$ compared to ionic radii (r_i) and hardness parameters derived therefrom. $\eta_2 = (4\pi\epsilon_0 r_i)^{-1}$. After Ref. [14]

Ion	R_D (cm^3/mol)	η_1 (V/e)	r_i (nm) *	η_2 (V/e)
Li ⁺	0.074	46.7	0.090	16.0
Na ⁺	0.457	25.4	0.116	12.4
K ⁺	2.12	15.3	0.152	9.49
Rb ⁺	3.57	12.8	0.166	8.69
Cs ⁺	6.15	10.7	0.181	7.97
Be ²⁺	0.020	72	0.059	24.4
Mg ²⁺	0.238	31.4	0.086	16.8
Ca ²⁺	1.19	15.5	0.114	12.6
Ba ²⁺	3.94	12.4	0.149	9.68
Cu ⁺	1.08	19.1	0.091	15.8
Ag ⁺	4.33	12.0	0.129	11.2
Au ⁺	4.75	11.7	0.151	9.55
Zn ²⁺	0.72	21.9	0.088	16.4
Cd ²⁺	2.74	14.0	0.109	13.2
Hg ²⁺	3.14	13.4	0.116	12.4
H ⁻	25.65	6.65		
F ⁻	2.65	14.2	0.119	12.1
Cl ⁻	9.30	9.33	0.167	8.67
Br ⁻	12.14	8.54	0.182	7.92
I ⁻	18.08	7.48	0.206	7.00
O ²⁻	9.88	9.14	0.126	11.4
S ²⁻	26.0	6.62	0.170	8.48

* Crystalline ionic radii, coordination number 6

Table 2. Atomic refractions (R_D) and corresponding hardness indices, $\eta = (4\pi\epsilon_0 R_D^{1/3})^{-1}$. Van der Waals radii (r_w) and corresponding hardness indices $\eta = (4\pi\epsilon_0 r_w)^{-1}$ are also shown. After Ref. [14 and 15]

Atom	Molecule	R_D (cm^3/mol)	η_1 (V/e)	r_w (nm)	η_2 (V/e)
H	hydrocarbons	1.028	19.4	0.145	9.94
C sp^3	hydrocarbons	2.591	14.3	0.170	8.48
C sp^2	hydrocarbons	3.379	13.1		
C sp	hydrocarbons	3.579	12.9		
N sp^3	ΦNR_2	4.243	12.1	0.155	9.30
	ΦNHR	3.650	12.7		
	ΦNH_2	3.144	13.3		
	NR_3	2.744	14.0		
	HNR_2	2.582	14.3		
	H_2NR	2.378	14.7		
N sp^2	pyridin	2.252	15.0		
N sp	RCN	1.880	15.9		
O	R_2O	1.764	16.2	0.150	9.61
O	R(OR)_2	1.607	16.8		
O	R_2CO	1.134	18.8		
O	$\text{R}\Phi\text{CO}$	1.751	16.2		
S	RSH	7.729	9.94	0.180	8.01
S	R_2S	7.921	9.87		
S	ΦSH	8.132	9.73		
S	ΦSR	8.54	9.60		
S	$\Phi_2\text{S}$	9.05	9.42		
P	R_3P	9.01	9.42	0.185	7.79
F	RF	0.81	45.3	0.160	9.01
Cl	RCl	5.844	10.9	0.190	7.59
Br	RBr	8.741	9.54	0.200	7.21
I	RI	13.954	8.14	0.212	6.80

Polarizabilities, eagerly studied in the early days of the Pearson principle, have not been truly embraced by the DF theory. Vela and Gázquez demonstrated how the static dipole polarizability is related to global softness (S) and the Fukui function $f(r)$: $\alpha = S \int r^2 \cos^2\theta f(r) dr$, [8]. Collection of polarizability data α and the softness $S = I - A$ for neutral atoms shows a rather poor correlation coefficient of ca. 0.77.

1.2 Atomic Radius and Volume

Small size favors hardness, other things being equal. Early consideration of hard and soft acids and bases did not go far beyond this conclusion. Until the direct relation between electronegativity and hardness was discovered, the atomic radius was associated with electronegativity rather than with hardness. Gordy ($\chi \propto Z/r$ [9]) and Allred and Rochow ($\chi \propto Z/r^2$ [10]) and Sanderson $\chi \propto Z/r^3$ [11]) directly incorporated atomic or ionic radius into their electronegativity

definitions, and with considerable success. Other authors recently presented modifications of these concepts [11], including the atomic dimension as polarizability radius, ionic radius or covalent radius, by Nagle, Görlich, and Politzer et al. respectively.

Proportionality between internuclear distances in homonuclear diatomic molecules, and their $(I - A)^{-1}$ was discovered by the Parr group in 1979 [12]. At that time, the $(I - A)^{-1}$ value had already been recognized as the second derivative of energy in the parabolic approximation, d^2E/dN^2 , but had not yet been identified with hardness. Later, Gázquez and Ortiz derived the expected relation between atomic hardness and the reciprocal atomic radius $\langle r^{-1} \rangle$, [13]. Komorowski has shown that van der Waals radii, not covalent radii, provide a more reliable measure of atomic hardness [14]. The best correlations with the Parr and Pearson absolute hardness parameter was found for ionic radii derived from ionic refractions. The same method was successfully used for the evaluation of the hardness parameters for atoms bonded in organic molecules [15]. Typical features known as hardness inequalities were properly accounted for among the main group elements. Tables 1 and 2 show a collection of data of atomic and ionic radii. Neutral and ionic species can hardly be compared by this measure, as only the crude van der Waals radii are available for atoms, while more precise ionic radii are fairly reliable measure of ionic dimensions in crystals. Covalent radii were found inappropriate for measuring the atomic hardness.

1.3 Charge Capacitance

The electronegativity function, introduced by Iczkowski and Margrave, revealed the charge dependence of electronegativity [16]. This comes from the general expression for the energy of atoms, $E(N)$, assumed to be polynomial function of the number of electrons N , in order to reproduce a set of ionization energies; electronegativity was simply a derivative thereof: $\chi = dE/dN$. Sanderson assumed in his early work that electronegativity is a linear function of charge, he did not, however, pay much attention to the charge coefficient of this dependence [11]. The Iczkowski and Margrave $\chi(q)$ function becomes linear $\chi = a + bq$, for a parabolic energy curve. It was commonly built on three energy values: $E(0) = 0$, $E(1) = I$ and $E(-1) = A$; I and A being ionization energy and electron affinity, respectively. Then the charge capacitance becomes $b = (I - A)$, identical with what was later identified as absolute hardness. It was evaluated for atoms and chemical groups first by Huheey, becoming the precursor of the modern concept of hardness [17, 18].

The parabolic energy function, though widely used, has often been criticized as being to crude an approximation, even in the limited charge range of $\langle -1, 1 \rangle$. Huheey's charge capacitance was explored in calculation of atomic charges on bonded atoms and led to reasonable charge transfer or atomic charges in molecules [18]. The formalism broke down, though, when applied to ionic crystals e.g.: NaCl. Komorowski argued that the parabola should be

replaced by the binomial $E(q) = aq^4 + bq^3$ thus leading to $\chi(0) = 0$; a remarkable improvement of charge transfer calculated for a number of solid salts and complexes was achieved [19]. The charge capacitance method has only been applied to neutral atoms, there is no difficulty in extending it to molecules. Bonded atoms, however, could not be discerned, since the parabolic function assumes that the charge capacitance does not vary with charge.

1.4 Absolute Hardness

Parr and Pearson completed the hardness puzzle in 1983, by proposing the definition of hardness as the second derivative of energy, $\eta = d^2E/dN^2$, thus making a bridge between electronegativity and hardness [4]. Taking the Mulliken absolute electronegativities as a model, they proposed an index of absolute hardness: $\eta = 1/2(I - A)$, indirectly accepting the parabolic $E(N)$ dependence, at least locally, around the chosen oxidation state. This definition was successfully applied to neutral atoms, cations and molecules acting as Lewis acids. The authors escaped its rigorous application to anions (Lewis bases) arguing, that the variable curvature of $E(N)$ function becomes meaningless when the dependence flattens for $N - Z < -1$. Using the hardness parameter for appropriate Lewis acid was recommended instead, leading to identical hardness indices for e.g. F and F^- , Cl and Cl^- etc. (see Table 3, last column). A resolution of this inconsistency was proposed by Komorowski [14], who discussed the use of vertical, rather than adiabatic atomic energies, especially electron affinities, which makes the calculation of absolute hardness for anions strictly parallel to that for cations.

The general definition of atomic hardness as a derivative did not discern between the acidic and basic behavior of atoms, representing the curvature of $E(N)$ at $N = Z$ (neutral atom). Komorowski demonstrated that absolute hardness (and absolute electronegativity) cannot be regarded as actual energy derivatives but both may be obtained strictly by averaging the respective derivative over the range $N \langle Z - 1, Z + 1 \rangle$ [14, 20]. Pure acidic and basic properties of atoms cannot be reflected in the absolute electronegativity and/or hardness indices; only a mean average character of a species is shown. Acidic hardness (η_a) and basic hardness (η_b) have been introduced by averaging the derivative d^2E/dN^2 over the range $N \langle Z, Z + 2 \rangle$ and $N \langle Z - 2, Z \rangle$ respectively. Then:

$$\eta_a = 1/2 (I_1 - A_2) \quad \text{and} \quad \eta_b = 1/2 (I_2 - A_1) \quad (2)$$

where I_1 , I_2 , and A_1 , A_2 , stand for the first and the second ionization energy and vertical electron affinity, respectively. These indices are free of the inconsistency inherent to absolute hardness [4]. A review of data for acids and bases is given in Table 3. The η_a and η_b indices for neutral atoms suggest that the typical chemical behavior of an element is determined by the lower index of the two. For ions, η_a and η_b indices are in few cases significantly different from

Table 3. Acidic hardness (η_a) and basic hardness (η_b) indices as compared to absolute hardness, η . After Ref. [14 and 4]

Atom/ion	η_a (V/e)	η_b (V/e)	η (V/e)
<i>Neutral atoms</i>			
H	6.80	∞	6.42
Li	2.70	37.5	2.38
Na	2.57	23.4	2.30
K	2.17	15.6	1.92
Rb	2.09	13.9	1.85
Cs	1.90	11.8	1.71
F	8.77	19.2	7.01
Cl	6.50	10.1	4.70
Br	5.92	9.20	4.24
I	5.22	8.02	3.70
O	10.84	16.8	6.08
S	8.23	10.6	4.12
N	11.4	14.8	7.27
P	5.24	9.49	4.86
As	4.89	8.92	4.49
C	5.63	11.6	5.00
Si	4.08	7.48	3.38
Ge	3.97	7.34	3.35
<i>Cations (η_b is given only when appropriate)</i>			
Li ⁺	37.5		35.1
Na ⁺	23.4		21.1
K ⁺	15.5		13.6
Rb ⁺	13.5		11.7
Cs ⁺	11.3		9.6
Be ²⁺	72		67.8
Mg ²⁺	36.2		32.5
Ca ²⁺	22.4		19.7
Sr ²⁺	19.0		16.3
Ba ²⁺	15.1		12.8
Cu ⁺	9.53	14.6	6.9
Ag ⁺	10.1	13.6	6.9
Hg ⁺	9.4	11.9	4.2
Sn ²⁺	11.6	13.0	7.9
Pb ²⁺	7.1	13.1	8.5
Mn ²⁺	7.93	17.8	9.3
Fe ²⁺	11.4	19.3	7.3
Fe ³⁺	19.3		13.1
Co ²⁺	12.8	17.1	8.2
Co ³⁺	17.1		8.9
Ni ²⁺	13.8	18.4	8.5
Ni ³⁺	18.4		9.9
Tl ⁺	10.0	11.9	7.2
Tl ³⁺	15.1		10.5
<i>Anions (η_a has been omitted as inappropriate)</i>			
H ⁻		6.8	6.8
F ⁻		8.7	7.0
Cl ⁻		6.5	4.7
Br ⁻		5.9	4.2
I ⁻		5.2	3.7

the absolute hardness η , e.g. for Cu⁺, Ag⁺, Hg⁺, Tl⁺, Fe²⁺ etc. All these cations are moderately soft bases, while they can act as very soft acids; only the latter effect is roughly described by η .

1.5 Chemical Approximation

When the DF theory provided chemists with an unanimous and easy tractable definition of hardness, the older concepts of polarizability (1.1) or atomic dimensions (1.2) measuring hardness were put in the shade. However, the expertise gained by chemists in using polarizabilities, especially refractions, led to a formal unification of this measure of hardness with the new one, rigorously based on atomic energies. Refractions are the key to experimental hardness parameters for bonded atoms.

A conceptual solution of the problem was offered in the form of chemical approximation [15]. Electrodynamical analogy was proposed for atoms: atom as a metallic sphere of radius r , hence a link was open to the descriptive apparatus already existing in classical electrodynamics. Although applying electrodynamical equations to an atom is reasoning by analogy only, it proved useful for the unification purposes. The numerical value of polarizability α for atoms is reasonably well related to the cube of atomic radius, $\alpha = 4\pi\epsilon_0 r^3$, in the same way as it is known for a metallic sphere. The second derivative of energy versus charge of the metallic sphere (its hardness) is given by $\eta = (4\pi\epsilon_0 r)^{-1}$, only if the radius of the sphere is assumed not to change with ionization. The electrical capacity of the sphere, $\sigma = 4\pi\epsilon_0 r$ may then be identified with its softness. The energy function for a metallic sphere being a parabola, the model exhibits this expected feature when applied to atoms: $\eta = (4\pi\epsilon_0 r)^{-1} = (I - A)^{-1}$. The model correctly incorporates the Sanderson electronegativity equalization principle as the potentials of metallic spheres become equal, when the spheres are connected.

The hardness matrix is diagonal in the chemical approximation, its elements have the straightforward meaning of atomic hardness parameters ($\eta_{ii} = d^2E/dN_i dN_i$). Softness of the bonded atom (an analog of capacitance) is simply the inverse hardness ($\sigma_{ii} = \eta_{ii}^{-1}$), molecular softness is the sum thereof, $\sigma_M = \sum \sigma_{ii}$. This result was unexpected: other studies suggested that molecular softness may be an average rather than a sum of atomic softness' when the latter are identified with $(I_i - A_i)$ for free atoms [21]. The discrepancy between the two approaches unveils the limitation of the latter absolute hardness parameters in describing the properties of bonded atoms.

The chemical approximation also explained the question of units for hardness, $1 \text{ V/e} = 6.2418 \times 10^{18} \text{ F}^{-1}$, and opened a way to evaluation of atomic hardness from available chemical data of polarizability and atomic radii for free as well as for bonded atoms and ions: $\eta = (4\pi\epsilon_0)^{-1} R_D^{-1/3}$. The versatile properties of hardness parameters derived from atomic refractions are shown in Table 2. Chemical approximation made possible the transformation of the

refraction data and atomic/ionic radii into hardness units and thus their comparison. Agreement between the hardness indices for ions obtained from refraction (η_1 , Table 1) and absolute hardness or acidic hardness (η and η_a resp. in Table 3) is astonishing. The phenomenon is less satisfactory for atoms, but atomic refractions still cannot be rejected as a precise measure of atomic hardness, sensitive enough to reflect differences in the bonding state of the atom.

2 Focusing on Bonded Atoms

The chemical description of a molecule is invariably built upon a concept of the bonded atom, which is an observable and accessible reality for a chemist. Numerous experimental techniques have been developed that allow direct observation of features of a bonded atom; X-ray techniques, NMR and ESCA are but the most evident examples. Chemical reactions also provide an insight into the properties of a bonded atom, demonstrated through its interactions with other species external to the molecule, that eventually result in a chemical reaction involving that atom. Chemists are usually not concerned with a rigorous definition of a bonded atom, avoiding possible confusion by classifying atoms into groups according to their transferable properties. This relativity of chemical description of atoms is important source of flexibility of the chemical language. Confusions are avoided by relying upon expertise in chemistry which could hardly be framed into a formalism, but otherwise exhibits all features of a profound theory. Chemical predictions are by no means less reliable than the mathematical language of the physical sciences. It is important to realize, that the power of chemistry is built upon a concept of bonded atom, whose diversified properties chemists are able to describe, without going into its formal description as a definite part of a molecular system. No theoretical model has yet been able to reproduce all the subtle properties of a bonded atom that chemists can describe and predict.

2.1 Partition Dilemma

The first plausible method of partitioning a molecule into atoms is by cutting it into pieces: mapping the electron density in a molecule provides hints as to where borderline between vicinal atoms should be set [22]. Such a method does not fit a picture of nearly spherical atoms, an article of faith for chemist, but would reproduce the additivity of atomic volumes. The finest example of such geometrical methods has been elaborated by Bader, who offered general condition for the borderline between atoms as zero flux of electron density, $\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$ [23]. Quantum topology built upon this definition yields largely transferable atoms and molecular fragments of peculiar, nonconventional shape, and well defined volume matching atomic volumes from refractions.

An alternative picture of diffused and overlapping atoms has been introduced by the DF theory [24]. The molecular density is the sum of the atomic densities at every point of space within the system, chemical potentials of atoms are equal and atoms are minimally promoted from their ground states. Atoms are then defined by their cloud of electron density, they are not spherical but may have "aerodynamical" shapes easily acceptable to the chemist, and may bear nonintegral charges. Equalization of the chemical potential in the molecule, crucial for DF theory, is not very informative, as the difference between bonded atoms, obvious to a chemist, is lost in their electronegativity. An early analysis stimulated by the Thomas-Fermi statistical model of atom suggested even that electronegativity equalization leads to formally neutral bonded atoms [15]. Another shortcoming of the very general DFT concept of the bonded atom is the difficulty in producing exact, differential electronegativities for the molecule [25, 15]. The finite difference (absolute) electronegativities $1/2(I + A)$ are somewhat shaky ground for the partitioning procedure.

2.2 Definition Problem

From a very formal point of view, partitioning of the molecule is not a necessary precondition to finding the energy derivatives. Exact energy function and atomic populations may not be needed either, if only properties of atoms are properly identified with energy derivatives. Electronegativity poses little problem: differential electronegativities $\chi_i = dE/dN_i$ are all equal for atoms in the molecule, their common level being electronegativity of the molecule, $\chi_M = dE/dN$. Most contemporary studies stimulated by the DF theory admit χ_M to be equal to the absolute electronegativity $1/2(I + A)$, which is an article of faith rather than a rule. Since absolute electronegativity is not an actual derivative, but an average thereof (see Sect. 1.4 and Ref. [20]), its value depends on the $\chi(N)$ function which is not the same for a molecule and for individual atoms. Average (absolute) electronegativity for bonded atoms may not be identical to $1/2(I + A)$ for a molecule, and yet the Sanderson principle would hold for the derivatives: $dE/dN = dE/dN_i = dE/dN_j$, etc. Analysis of the average atomic electronegativities as descriptive and nonequalized indices for bonded atoms is given in Sect. 3.2.

Hardness parameters are even more challenging at the very level of their definition. Not only the average (absolute) character of the commonly used indices has to be emphasized, but also identification of the mathematical derivatives with the hardness property of bonded atom is controversial. The diagonal elements of hardness matrix are $\eta_{ii} = d^2E/dN_i^2$, the off-diagonal terms are $\eta_{ij} = d^2E/dN_i dN_j$. Within the chemical approximation [15] as well as in the $r_{ij} = \infty$ limit [26] the off-diagonal parameters vanish and η_{ii} may safely be taken as atomic hardness. Unfortunately, such circumstances physically mean non-interacting atoms, not a very interesting case for the chemist. The problem is profound and has not been addressed with the attention it

deserves, to the best of the author's knowledge. Nalewajski discussed it briefly [26], but tended to apply the diagonal η_{ii} elements for atomic hardness in his elaborate analysis of charge sensitivities for atom-in-a-molecule model [27, 28]. Nalewajski also elaborated the Normal Representation of the Electronegativity Equalization model, which results in diagonalization of the hardness matrix [29].

Komorowski and Lipiński presented a quantum chemical study in which they prove a relation for the atomic hardness η_i [30, 31]:

$$\eta_i = d\chi_M/dN_i = \sum_j \eta_{ij}(dN_j/dN) \quad (3)$$

Atomic hardness parameters can be derived for every hardness matrix if only the Fukui function indices dN_j/dN are known. (cf. Sect. 3.2).

3 Atomic Hardness from Calculations

Hardness parameters for free atoms became an easy target on the basis of DF theory; any formalism correctly reproducing first ionization energies and electron affinities could be used as a reliable source of $\eta = 1/2(I - A)$. A number of studies devoted to that topic presented hardness' parameters with various degree of refinement [32, 33, 34]. Studies concentrated on bonded atoms were not as abundant and considerably less conclusive in describing properties of the atom in the molecule.

3.1 Density Functional (DF) Theory Viewpoint

The beauty of the Density Functional theory and a source of its remarkable successes relies on the electron density function $\rho(\mathbf{r})$, as a basic variable of the theory. Electron density is of necessity a local value that does not distinguish between parts of a molecule, and decomposition of $\rho(\mathbf{r})$ into contributions from individual atoms has not been pursued. Instead, properties of the molecule are inspected through the local parameter of hardness, $\eta(\mathbf{r})$ and softness $s(\mathbf{r})$, introduced by Parr and Berkowitz [35, 36, 37], as opposed to the global quantities resulting in integration over the volume of the molecule. They turned their attention to the fact, that determining all properties of the system, i.e.: both the dependence on the number of electrons N and the local field $V(\mathbf{r})$ is possible by even more subtle parameters: hardness (or softness) kernels $\eta(\mathbf{r}, \mathbf{r}')$. Nalewajski explored this device in analysis of the protonation reaction path [28, 38].

Nalewajski also noticed the need for atomic hardness parameters for chemical reactivity studies and pursued a study of that problem [39]. A set of recursive combination rules for molecular hardness was presented, where a need for a "coarse-grained" atom-in-a-molecule analog of the global hardness has been stressed—the hardness parameters for bonded atoms. Effective atomic hardnesses are calculated in this study for a set of diatomic and triatomic molecules, conclusions are transferable to molecular fragments as well. The analysis is based on the consideration of a response of the molecule to perturbation dN_i at a chosen atomic site. A frozen system with only the i -th atom perturbed is considered first ($dN_i = dN$), then the system is allowed to relax by a charge flow in order to bring the chemical potentials (electronegativities (μ_i) to a common level. The resulting dependence between the effective atomic hardness (η_i) and the hardness matrix elements (η_{ij}) is not readily extendable to a larger molecule, unless its stepwise division into fragments is performed and the analysis repeated in a recursive manner for each step. A simplified analysis has also been offered for rigid and relaxed hardness parameters of molecular fragments [39].

3.2 Quantumchemical Solution

Quantumchemical methods have not been very successful in describing the properties rooted in the Density Functional theory. Early works typically concentrated on orbital electronegativities under the tyranny of the Sanderson electronegativity equalization principle [40–46]. An integral study resulting in electronegativity parameters for bonded atoms was made by Ponec [47].

More recent quantumchemical studies on hardness typically follow the Pearson hint, indicating the HOMO-LUMO gap as a readily available measure of molecular hardness [48, 49, 50]. Results reflect properly the known chemical features of small molecules and atoms [51, 52, 53]. The N -differentiability problem [54] that become a quandary for nonintegrally populated atoms in the molecule might have been a reason hampering calculations of quantum chemical atomic hardness.

An original and complete solution of that problem has been offered by Komorowski and Lipiński [30, 31]. Their analysis is based on the resolution of the Hartree-Fock eigenproblem for a molecule on the basis of atomic orbitals. If F_{kl} denote elements of the energy matrix, S_{kl} are overlap integrals and P_{kl} stand for the elements of the bond order matrix. the following results for atomic electronegativity and hardness are obtained.

Electronegativity and hardness for bonded atom are by definition:

$$\chi_A = - \left[\frac{\partial E}{\partial N_A} \right]_{N_B \neq A} \quad \text{and} \quad \eta_A = \frac{1}{2} \left[\frac{\partial \chi_M}{\partial N_A} \right]_{N_B \neq A} \quad (4)$$

They represent rigid parameters for atom A in molecule M and may be found

from the following identities:

$$\chi_A = \frac{\sum_{k \in A} \sum_l F_{kl} a_{kl}}{\sum_{k \in A} \sum_l S_{kl} a_{kl}} \quad (5)$$

$$\eta_A = \frac{\sum_{k \in A} \sum_l F_{kl} b_{kl}}{\sum_{k \in A} \sum_l S_{kl} a_{kl}} \quad (6)$$

a_{kl} and b_{kl} indices appearing in Eqs. 5 and 6 play a crucial role in the analysis. By definition, they are derivatives of the bond order matrix elements after the total number of electrons.

$$a_{kl} = \frac{dP_{kl}}{dN} \quad \text{and} \quad b_{kl} = \frac{1}{2} \frac{d^2 P_{kl}}{dN^2} \quad (7)$$

Determination of a_{kl} and b_{kl} was proposed on the ground of Koopman's theorem, which leads to following mean values:

$$\bar{a}_{kl} = \frac{1}{2} (C_k^{\text{LUMO}} C_l^{\text{LUMO}} + C_k^{\text{HOMO}} C_l^{\text{HOMO}}) \quad (8)$$

$$\bar{b}_{kl} = \frac{1}{2} (C_k^{\text{LUMO}} C_l^{\text{LUMO}} - C_k^{\text{HOMO}} C_l^{\text{HOMO}}). \quad (9)$$

The very fundamental problem for this analysis is apparent violating the Sanderson principle, since the resulting electronegativities for bonded atoms are not equalized. This should not be a problem: atomic electronegativities calculated using \bar{a}_{kl} and \bar{b}_{kl} (Eqs. 8 and 9) have the meaning of absolute quantities that parallel $1/2(I + A)$ for free atoms. Absolute electronegativities are not true derivatives, but rather the mean values thereof, when averaging is done between the number of electrons in the system $N_o + 1$ and $N_o - 1$ [31]. These average quantities need not be equalized even when the Sanderson principle holds for the corresponding derivatives dE/dN_A , which, unfortunately, have not been accessible so far.

3.3 Atom-in-Molecule Electronegativity and Hardness

Electronegativities χ_A calculated according to the above quantum chemical scheme are given in Table 4. They include the overall effect of three factors that determine the chemical potential of a bonded atom:

(1) some inherent original property of the atom fixed by its atomic number Z ;

Table 4. Quantum chemical electronegativity and hardness indices for atoms bonded in diatomic molecules. Absolute electronegativity and hardness of molecules, calculated by the same method, is also shown. After Ref. [31]

Molecule	Atom	Charge transfer q	χ_A (V)	η_A (V/e)	χ_M (V)	η_M (V/e)
H ₂	H	0.0	7.18	12.24	7.18	12.24
F ₂	F	0.0	10.26	6.94	10.26	6.94
Cl ₂	Cl	0.0	7.68	5.05	7.68	5.05
Br ₂	Br	0.0	7.53	4.58	7.53	4.58
I ₂	I	0.0	7.19	4.03	7.19	4.03
HF	H	0.333	-3.00	3.00	6.88	9.87
	F		11.81	13.31		
HCl	H	0.197	-0.93	0.93	6.15	7.08
	Cl		9.18	9.71		
HBr	H	0.161	-0.48	0.48	6.03	6.50
	Br		8.69	8.97		
HI	H	0.087	0.46	-0.46	6.03	5.57
	I		8.11	7.82		
ClF	Cl	0.247	9.17	6.98	8.19	5.52
	F		5.10	0.95		
BrF	Br	0.323	8.84	6.40	7.99	5.04
	F		4.67	-0.21		
IF	I	0.441	8.61	5.49	8.04	4.46
	F		5.31	-0.47		
BrCl	Br	0.072	8.00	5.39	7.61	4.78
	Cl		7.07	3.90		
ICl	I	0.194	7.86	4.95	7.53	4.37
	Cl		6.93	3.33		
IBr	I	0.119	7.55	4.40	7.45	4.22
	Br		7.32	3.50		
LiH	Li	0.562	2.40	0.71	4.80	3.76
	H		8.42	8.38		
LiF	Li	0.848	-0.05	0.25	5.15	5.30
	F		10.26	10.27		
LiCl	Li	0.702	0.50	-0.18	5.39	5.04
	Cl		10.16	10.14		
LiBr	Li	0.685	0.45	-0.12	5.20	4.91
	Br		9.83	9.81		
LiI	Li	0.604	0.58	-0.18	4.86	4.49
	I		8.98	8.95		
NaH	Na	0.714	1.13	0.58	3.55	3.24
	H		6.71	6.70		
NaF	Na	0.961	-0.18	0.31	4.17	4.41
	F		8.50	8.50		
NaCl	Na	0.870	-0.05	0.15	4.47	4.57
	Cl		8.85	8.85		
NaBr	Na	0.852	-0.12	0.24	4.34	4.52
	Br		8.66	8.66		
NaI	Na	0.790	-0.10	0.28	4.03	4.22
	I		7.99	8.00		

- (2) the actual state of an atom which may be described by its charge;
- (3) its interaction with neighbors, either ionic or covalent.

The role of each of these factors may be determined independently (see Ref. [31]). The meaning of the χ_A index is the same as in the classical Pauling definition: a power to attract electrons by a bonded atom whilst it is engaged in a molecular environment. χ_A should not be confused with electronegativities for free atoms, neutral or charged, which never include the interaction effect and are known to be a linear function of charge. Similar electronegativities can also be extracted from quantumchemical analysis as standard electronegativities $\chi^\circ(q)$. They show expected linear dependence on atomic populations q_A , (Mulliken) given by the same Hartree-Fock analysis.

$$\chi_A^\circ(q_A) = \bar{\chi}_A + q_A \bar{\eta}_A \quad (10)$$

This relationship is a source of two additional parameters: $\bar{\chi}_A$ standard average electronegativity (intercept) and $\bar{\eta}_A$, standard average hardness (slope). The $\bar{\chi}_A$ and $\bar{\eta}_A$ indices describe inherent properties of an atom manifested through its bonding to a variety species, Table 5. This point of view was first proposed by Huheey [18], who used the equation $\chi = \chi_v + bq$ for the valence state electronegativities of the free atom. Results of this work on the bonded atom are compared to Huheey's on the free atom in Table 5. The common feature of $\bar{\eta}$ and Huheey's b factor is their independence from atomic charge.

Table 5. Inherent electronegativity ($\bar{\chi}$) and hardness ($\bar{\eta}$) for atoms as compared to Huheey's valence state electronegativity (χ_v) and corresponding charge capacitance for atoms (b)

Atom	Free atom [18]		Bonded atom [31]	
	χ_v [V]	b [V/e]	$\bar{\chi}$ [V]	$\bar{\eta}$ [V/e]
H	7.17	12.85	7.18	6.40
Li	3.10	4.57	2.07	3.00
Na	2.80	4.67	1.18	3.23
F	12.18	17.36	16.87	12.80
Cl	9.38	11.30	12.73	8.15
Br	8.40	9.40	11.58	7.27
I	8.10	9.15	10.22	6.88
O	9.65 ^a	15.27 ^a	13.15	11.21
Nall	7.39 ^a	13.10 ^a	10.06	8.99
Nsp ³	11.54	14.78	11.61	9.68
Nsp	15.68	16.46	10.58	12.32
Csp ³	7.98	13.27	9.21	8.41
Csp ²	8.79	13.67	6.09	7.57
Csp ^{2b}	8.79	13.67	6.34	8.37
Csp	10.39	14.08	6.74	7.55

^a p valence state; ^b five-member rings

For univalent atoms, where details concerning the choice of the valence state do not obscure the picture, the role of bonding is clearly seen, Table 5. Atoms are considerably softer when bonded; fluorine is still the hardest, lithium and sodium are the softest. Bonded hydrogen appears to be slightly softer than iodine, while free H is harder than chlorine. The electronegativity of bonded halogens is remarkably higher than that of the corresponding free atoms. The latter effect was anticipated in earlier work [15].

The effect of chemical environment on the hardness of bonded atoms may be observed on η_A indices in Table 4. Bonded atoms may show hardness much different from their free state, e.g., $\eta_{Cl} = 4.70$, $\eta_{Cl/HCl} = 9.70$, $\eta_{Cl/ICl} = 3.33$. Though η_A depends on how the atom is bonded, no direct relation to atomic charge was determined. In some instances η_A is quite surprising: fluorine in HF is very hard (13.31), while in ClF it is soft (0.94), the charge transfer being similar 0.333 and 0.247, respectively. The atom, which otherwise would be predicted to be hard by a chemist (e.g. hydrogen in HX) is soft, its partner being much harder than the corresponding free atom. Atoms seem to borrow hardness from a partner; this effect is striking in alkali halides, where halide anions become very hard.

Such symbiosis is also observed on the inherent atomic hardnesses that are not included in Table 5. When considered separately, CF₃ carbon ($\bar{\eta} = 38.04$) is much harder than CH₃ carbon ($\bar{\eta} = 17.91$) the latter being more electronegative. Both CF₃ and CH₃ seem to become much softer, when bonded to an aromatic ring ($\bar{\eta} = 8.8$). Value $\bar{\eta} = 8.43$ is the mean average value for all types of C(sp³). The phenomenon of symbiosis has been observed experimentally and described in many situations [18].

4 Chemical Applications and Expectations

Electronegativity and hardness which are challenges to the DF theory are both rooted deeply in the chemical experiment. They are products of chemists' attempts to contain a variety of properties of the chemical species into a single index (electronegativity) and to order the experimental observations according to a selective rule (hardness). This way of thinking will probably be followed by chemists until some general theory of chemical interactions emerges. Such a theory should not only offer a quantitative description to chemical reactivity but must also operate in a language that chemist could perceive and appreciate. It is by no means certain, that such a concept will ever be realized, but at least the current development of chemical theories stimulated by the methodology and successes of experimental physics is pointing in that direction. So far, experimental chemists rely upon indexing the properties and trends, of which electronegativity, reactivity indices, or Hammett-type constants are the most typical examples. While this may be indeed a necessary first step to quantification of the

chemical observations, the next step is much harder to accomplish: to offer quantitative rules (formulas!) that will explore existing indices and scales in quantitative predictions, beyond the area from which the indices were derived. Selected achievements built upon electronegativity and hardness are discussed below.

4.1 Charge Transfer

Electronegativity was built upon the observations of bond ionicity of simple compounds [55]. Pauling did not go so far as to recommend using electronegativities for the calculation of atomic charges, but that was done by many of his followers [56]. With the advent of the DF theory, after the classical achievements of Iczkowski and Margrave, it became evident that both charge transfer and the bonding energy may be formally estimated from electronegativity and hardness indices for free atoms.

Parr and Pearson considered the simplest case of two noninteracting atoms exchanging electrons until their electronegativities are equal [4]. Then the charge transfer ΔN is:

$$\Delta N = \frac{(\chi_A - \chi_B)}{2(\eta_A + \eta_B)} \quad (11)$$

Nalewajski completed this picture by introducing the core polarization energy [57]:

$$\Delta N = \frac{(\chi_A - \chi_B) + 2(\alpha_B \Delta Z_B - \alpha_A \Delta Z_A)}{2(\eta_A + \eta_B)} \quad (12)$$

Pearson explored Klopman's earlier suggestion of including not only the Coulomb interaction but also the covalent bonding expressed by the two-center, one-electron exchange integral β [58, 59]:

$$\Delta N = \frac{2(\chi_A - \chi_B)}{(\eta_A + \eta_B) - 1/R - 2\beta/(N_A N_B)^{1/2}} \quad (13)$$

Komorowski considered the Coulomb polarization and induction interaction between atoms located at the distance equal to the sum of their atomic radii, and used identities offered by the chemical approximation. A simple expression was suggested [60]:

$$\Delta N = \frac{\left(\frac{\chi_A}{\eta_B} - \frac{\chi_B}{\eta_A}\right)}{\left(\frac{\eta_A}{\eta_B} + \frac{\eta_B}{\eta_A}\right)} \quad (14)$$

All these approaches were formally based on the absolute electronegativity and absolute hardness indices used as derivatives of the energy function $E(N)$.

Results were encouraging: the charge transfer obtained by the formulas was reasonable from the chemical point of view, except in the exotic case for a chemist: charge transfer within the crystalline lattice [19]. The success may be somewhat superficial. It is due to the very definition of electronegativity, given by Pauling. If Pauling's ionic contribution to the dissociation energy of a diatomic molecule (Δ) is considered to be purely coulombic, (q^2/R), then the charge transfer $q \simeq (R\Delta)^{1/2} = (\chi'_A - \chi'_B)R_{AB}^{1/2}$ is determined by the electronegativity difference, the driving factor in more elaborate treatments summarized by Eqs 11–14, Table 6.

Expressions for the charge transfer, even though all are apparently successful, do not lead to identical physical predictions. The condition for zero charge transfer implied by Eq. 14 is different from the rest.

$$\chi_A \eta_A = \chi_B \eta_B \quad (15)$$

χ and η are absolute indices for free atoms. Zero charge transfer, obvious for a homonuclear bond, is not excluded for a heteronuclear bond. There is a neat illustration for this effect: the C-H bond, is only ionic to a very small degree, despite the $\simeq 1$ V difference in the electronegativities of carbon and hydrogen. A review of calculated charge transfer data is given in Table 6.

Compared to a chosen set of "reasonable", quantumchemical charge transfer values in diatomic molecules, it is surprising how well are they reproduced by the Pauling electronegativities (column 1). The Parr and Pearson equation

Table 6. Charge transfer ΔN (in electrons) calculated from approximate formulas for a selection of bonds and molecules. Absolute electronegativity and hardness data as in Ref. [4]

Molecule/bond	Pauling* ($\chi'_A - \chi'_B$)/ $R_{AB}^{1/2}$	Parr and Pearson Eq. 11	Komorowski Eq. 14	Quantum-chemical (INDO) Ref. 29
HF	0.480	0.492	0.728	0.333
HCl	0.268	0.006	0.184	0.197
HBr	0.219	0.020	0.233	0.161
HI	0.100	-0.020	0.383	0.087
ClF	0.336	0.132	0.581	0.247
BrF	0.419	0.125	0.607	0.323
IF	0.583	0.170	0.763	0.441
BrCl	0.077	-0.016	0.054	0.072
ICl	0.241	0.033	0.261	0.194
IBr	0.166	0.053	0.228	0.119
LiH	0.366	0.237	0.830	0.562
LiF	0.983	0.394	1.201	0.848
LiCl	0.749	0.304	0.981	0.702
LiBr	0.699	0.347	1.061	0.685
LiI	0.570	0.309	0.923	0.604
NaH	0.434	0.247	0.849	0.714
NaF	1.108	0.406	1.220	0.961
NaCl	0.850	0.318	1.015	0.870
NaBr	0.792	0.363	1.103	0.852
NaI	0.651	0.326	0.972	0.790

* From Ref. [60]; R is the bond length

(Eq. 11) is hardly an acceptable source of the charge transfer. The novel formula, Eq. 14, produces very reasonable charge values. The set of absolute electronegativity and hardness parameters was identical in all calculations, and was quite arbitrary, given the discussion on hardness parameters in Sect. 1. Equation 14 may be reliably used for charge estimation purposes, it seems.

4.2 Charge Transfer Affinity

Absolute electronegativities are not true derivatives of energy. They are average mean values, sometimes called the finite difference values, and as such are indices rather than derivatives. Consequently, either the charge transfer, or the interaction energy calculated from such indices will have a meaning of an index rather than a real energy. Komorowski proposed, that the negative of the interaction energy between two atoms be called the Charge Transfer Affinity (CTA), using thermodynamical language [60]. Charge Transfer Affinity provides strictly the same information as given by the original Pauling work: ionic stabilization energy due to the charge flow between interacting partners. Expressions for CTA corresponding to the approximations for the discussed charge transfer are summarized below, respectively.

Pauling [55]:

$$\Delta = (\chi'_A - \chi'_B)^2 \text{ in electronvolts}$$

$$\text{or } \text{CTA} = a(\chi_A - \chi_B)^2, \quad (16)$$

where χ' and χ are Pauling and Mulliken electronegativities, respectively, and $a = 0.101 \div 0.122$.

Parr and Pearson [4]:

$$\text{CTA} = \frac{(\chi_A - \chi_B)^2}{4(\eta_A + \eta_B)} \quad (17)$$

Nalewajski [57]:

$$\text{CTA} = \frac{\frac{1}{2}(\chi_A - \chi_B)^2 - (\chi_A - \chi_B)(\alpha_B \Delta Z_B - \alpha_A \Delta Z_A)}{(\eta_A + \eta_B)} - (V_A \Delta Z_A + V_B \Delta Z_B) \quad (18)$$

where α stands for polarizability and V is electron-nuclear attraction per unit charge.

Pearson [58]:

$$\text{CTA} = \frac{(\chi_A - \chi_B)^2}{4(\eta + \eta - 1/R + 2\beta)} \quad (19)$$

where β is two-center, one-electron exchange integral.

Komorowski [60]:

$$\text{CTA} = \frac{1}{2R} \frac{\left(\frac{\chi_A}{\eta_B} - \frac{\chi_B}{\eta_A} \right)^2}{\left(\frac{\eta_A}{\eta_B} + \frac{\eta_B}{\eta_A} \right)} \quad (20)$$

where R is the sum of atomic radii.

Charge Transfer Affinity in the units of energy may be more convenient than the simple electronegativity difference as a measure of the prospective charge transfer interaction between two chemical species for two reasons:

- (1) it includes the effect of hardness of both partners;
- (2) it provides a measure in readily understandable units of energy, thus removing the long-lasting inconsistency concerning possible units of electronegativity.

Examples of the numerical results for CTA are given in Table 7. The Pauling Δ value was included in Table 7 as the experimentally available benchmark for the ionic energy, which CTA is supposed to reproduce. Departures from these experimental values are evident, even for the CTA based on true Pauling electronegativities; it is well known, that Δ only served as a guide to construction

Table 7. Charge Transfer Affinity calculated by various approaches for selected pairs of atoms in diatomic molecules. Absolute electronegativity and hardness parameters as in Ref. [4]

Molecule	Pauling ($\chi'_A - \chi'_B$) ²	Charge Transfer Affinity in electronvolts		
		Parr and Pearson Eq. 17	Komorowski ($R = \eta_A^{-1} + \eta_B^{-1}$) in Eq. 20	Pauling Δ (experiment)
HF	3.61	0.195	0.300	2.79
HCl	0.81	0.012	0.097	0.96
HBr	0.49	0.004	0.151	0.53
HI	0.09	0.004	0.398	0.054
ClF	1.00	0.205	0.894	0.58
BrF	1.44	0.175	1.100	0.81
IF	2.56	0.311	1.709	1.30
BrCl	0.04	0.002	0.006	0.006
ICl	0.36	0.009	0.145	0.137
IBr	0.16	0.022	0.103	0.062
LiH	1.21	0.494	1.833	
LiF	9.0	1.462	4.211	4.49
LiCl	4.0	0.656	1.885	3.17
LiBr	3.24	0.799	2.010	2.86
LiI	1.96	0.581	1.357	2.04
NaH	1.44	0.535	1.921	
NaF	9.61	1.53	4.353	3.68
NaCl	4.41	0.710	2.016	2.59
NaBr	3.61	0.862	2.165	2.37
NaI	2.25	0.637	1.496	2.28

of the electronegativity scale. Equation 20 provides results largely equivalent to the Pauling formula and which are reasonable. Equation 17 cannot be recommended for estimation of the ionic energy.

4.3 Pearson Principle (HSAB)

Translation of the Hard and Soft Acids and Bases principle into a readily applicable formal expression has never been achieved. Huheey suggested, that the driving force to the HSAB rule is a strong hard-hard interaction only, in a set of an acid/base exchange reaction [18]. Nalewajski presented a thorough discussion of that topic [57] and summarized older concepts. Soft-soft interaction is predominantly covalent, whereas hard-hard interaction occurs through ionic forces. The classical formula for energy (Eq. 17) explains why a soft-soft interaction is favored over a soft-hard one; the favorable hard-hard situation cannot be accounted for by Eq. 17.

The great value of Pearson principle for chemists would certainly benefit from a quantification. A number of hardness indices available now from various sources would gain a great deal of interest from chemists, if they were employed in a formal description of HSAB. A potential solution has been offered in the form of Eq. 20, or its more elaborate version, Eq. 21, [60]

$$CTA = \frac{1}{2R} \frac{\left(\frac{\chi_A}{\eta_B} - \frac{\chi_B}{\eta_A}\right)^2}{\left(\frac{\eta_A}{\eta_B} + \frac{\eta_B}{\eta_A}\right) - p} \quad (21)$$

$$\text{where } p = \left(1 + \frac{\eta_B}{\eta_A}\right)^{-3} + \left(1 + \frac{\eta_A}{\eta_B}\right)^{-3}$$

Charge Transfer Affinity (CTA) is at a maximum for equal hardness indices, other circumstances being equal. This is exactly in accord with Pearson's suggestion [2]: "The HSAB principle is really stating that there is an extra stabilization in a hard-hard or a soft-soft combination". Equations 20 and 21 may not be claimed as a formulation of the Pearson principle. They only indicate, how this extra stabilization occurs and how it might interplay with other properties. It also offers a convenient starting point for the search for the "strength" of acids and bases as a parameter involving in some way electronegativity and hardness, both of which play a role in the interaction, and their effects cannot be separated. Observation of a pure hardness effect is never possible: variable hardness will be accompanied by variable electronegativity, and in principle the effects might cancel. The competing effect between electronegativity and hardness in the ionic exchange reactions is known as the Pauling-Pearson paradox [18]. Equations 20 and 21 show how the two overlapping effects of electronegativity and hardness may cumulate to produce the rule of thumb, known as the Pearson principle.

4.4 Pauling Electronegativity Scale

The list of energy expressions (CTA) presented in Sect. 4.2 (Eqs. 16, 17, 18, 19, 20) puts the traditional Pauling formula (Eq. 16) into new perspective. It seems to be a product of an illuminated guess for the ionic interaction energy, long before the hardness concept was ever conceived. Difficulties in setting a uniform scale of electronegativity on the basis of Eq. 16 are well known. The formula was used as a guide only, the actual electronegativity scale by Pauling was subject to extensive polishing over the years. The source of difficulty becomes evident by comparing Eqs. 16–20; important variable parameters of hardness were missing in the Pauling formula. Hence, Pauling electronegativities have a built-in effect of hardness in some average form, appropriate for a variety of typical chemical situations. This may well be the reason for their success. Chemists frequently consider the Pauling scale as the most appropriate measure of electronegativity. It cannot be expected that such a scale be strictly in a linear relation to pure Mulliken values. Discrepancies from the linear relation are well described in the literature [66] and apparently come from neglecting the hardness parameters.

Numerically, the Pauling scale has been arbitrary from its foundation, $\chi^{\text{Pauling}}(\text{Fluorine}) = 4.0$ has been accepted for practical reasons. The electronegativity differences, however, have been directly related to the ionic energies and were not affected. Coefficient a in Eq. 16 comes from replacing Pauling electronegativities with Mulliken values, using a common linear relation between both:

$$\Delta\chi^{\text{Mulliken}} = f\Delta\chi^{\text{Pauling}}, \quad f = 2.86 \div 3.15 \quad [\text{ref. 66, 67, 68}] \quad (22)$$

Where $a = f^{-2}$ in Eq. 16.

Little attention has ever been paid to the units of Pauling electronegativity. The only acceptable unit of electronegativity according to the DF theory is volt, the unit inherent to Mulliken absolute electronegativity. Conversion factor f between Mulliken scale (volts) and Pauling electronegativities formally in the units of $(\text{eV})^{1/2}$, finds an interesting explanation on the basis of Eqs. 17 and 20. When the effect of hardness is neglected in the widely accepted Eq. 17 by setting $\eta_A = \eta_B = \eta$, and if the chemical approximation is used, following relations result:

$$CTA = \left[\frac{4\pi\epsilon_0}{8} \right] (R/2)(\chi_A - \chi_B)^2 \quad \text{from eq. 17 or 20} \quad (23)$$

$$CTA = \left[\frac{4\pi\epsilon_0}{7} \right] (R/2)(\chi_A - \chi_B)^2 \quad \text{from eq. 21} \quad (24)$$

Since $[4\pi\epsilon_0/7] = 0.100 \text{ eV}\cdot\text{nm} \cong a$ (cf. Eq. 16), and Eq. 21 is more accurate by having all interaction affects included, transformation to the Pauling scale (χ') is justified by means of this theoretical parameter rather than by an experimental factor (Eq. 16 and following remark):

$$CTA = (R/2)(\chi'_A - \chi'_B)^2 \quad \text{or} \quad \Delta^{\text{Pauling}} = \frac{CTA}{R/2} \quad (25)$$

This interesting result discloses the nature of the relationship between Pauling electronegativities (χ') and Mulliken electronegativities (χ) in CTA and is not surprising (see discussion following Eq. 14 in Sect. 4.1).

The f factor (Eq. 22) now finds an elegant formal justification:

$$f = \left[\frac{7}{4\pi\epsilon_0} \right]^{1/2} = 3.174 \text{ (eV} \cdot \text{nm)}^{-1/2} \quad (26)$$

R, the sum of atomic radii plays important role in this formalism. As demonstrated in Sect. 1.5, equivalence between the absolute atomic hardness and atomic radius is best for van der Waals or ionic radii. Thus, the R distance may be much larger than the normal bond in the AB molecule. For the purpose of this analysis, however, $R/2 = R_{AB}$ as a working approximation might be used, which is strictly valid for van der Waals radii and homonuclear diatomic molecules. Another choice is to follow the chemical approximation and use some available hardness parameters to estimate R as: $R = (r_A + r_B) = (\eta_A^{-1} + \eta_B^{-1})$.

The relationship between CTA and Δ^{Pauling} , Eq. 25, has been tested on a collection of bonds and molecules. Linear function (ΔR) vs CTA was confirmed [60], and included even the hydrides never properly accounted for by the Pauling method. However, the non-zero intercept for a group of considerably ionic halides indicated, that CTA and Δ^{Pauling} may differ by some additive excess contribution [60]. Further study is needed in order to disclose the hidden beauty of the Pauling scale.

4.5 Reactivity and Substituent Effects

The potential to describe the chemical reaction path is emerging from the DF theory. Pearson [69] and Parr et al. [70] have proposed a principle of maximum hardness: stable molecules arrange themselves as to be as hard as possible. Zhou and Parr introduced the activation hardness parameter for the electrophilic aromatic substitution [71]. The same authors have shown a correlation between the absolute hardness of a molecule and aromaticity [72]. Nalewajski et al. studied the protonation reaction and described the relation between the interaction energy and charge sensitivities: hardness, softness, Fukui function [28, 38].

There is an abundant field of chemical data waiting for exploration by the DF theory based approaches: the substituent effect, a classical problem in chemical reactivity. A recent quantumchemical study by Komorowski and Lipiński [30, 31] opened the long needed route to theoretical hardness indices for bonded atoms which might be confronted with a variety of substituent indices known in organic chemistry. Two preliminary qualitative conclusions emerged from this study. First, electrophilic substitution in the benzene ring occurs at the hardest ring carbon, Table 8. Second, the relative sensitivity of the ring carbons to the substitution finds its measure in the interatomic hardness index $\eta_{AB} = 1/2(\partial^2 E / \partial N_A \partial N_B)$. It translates into numbers what had been

Table 8. Hardness parameters for the ring carbons in mono-substituted benzenes (in volt/electron). η_M is hardness of the molecule

Molecule	$\eta_{\text{C-ortho}}$	$\eta_{\text{C-meta}}$	$\eta_{\text{C-para}}$	η_M
ϕCH_3	2.96	2.23	11.10	5.46
ϕBr	2.31	1.02	11.28	5.30
ϕCl	2.60	1.38	11.38	5.35
ϕF	2.98	1.79	11.48	5.38
ϕOH	3.06	1.84	11.20	5.36
ϕNH_2	3.04	0.76	10.32	5.02
ϕCHO	3.44	4.90	5.18	5.18
ϕCOOH	4.33	6.32	4.11	5.26
ϕCN	4.40	5.85	5.16	5.20
ϕNO_2	8.32	11.29	- 2.05	5.14
benzene	5.54	5.54	5.54	5.54

Table 9. Intercarbon hardness parameters η_{AB} in mono-substituted benzenes between the ipso carbon (substituted) and three other ring carbons: *ortho*-, *meta*- and *para*- to the substituent

Molecule	$\eta_{AB} \text{ (V/e)}$ <i>C-ortho</i>	<i>C-meta</i>	<i>C-para</i>
ϕCH_3	15.46	- 0.78	4.42
ϕBr	18.86	- 0.79	6.71
ϕCl	17.66	- 0.78	5.58
ϕF	16.77	- 0.82	4.61
ϕOH	16.58	- 0.84	4.71
ϕNH_2	22.72	- 0.89	7.62
ϕCHO	25.66	1.14	3.32
ϕCOOH	21.78	1.30	3.51
ϕCN	29.67	- 0.11	2.56
ϕNO_2	23.04	0.60	9.36
benzene	19.32	0.00	2.86

deduced from valence structures of the benzene ring: the *meta* carbon is least sensitive to the substitution, Table 9. Reactivity of small molecules can also be described by the atom-in-molecule hardness parameters [31].

5 Conclusions

Contemporary chemistry, abundant in experimental observations collected over the years, is becoming more and more concerned with a possible general explanation of chemical interactions. The legend of electronegativity and hard-

ness has grown from this desire. The Density Functional Theory provided much needed support to the chemical way of describing chemical species by indexing atoms with parameters derived from experimental observation. Interactions between atoms, molecules, ions, may be described by these parameters, if they only contain sufficient potential for generalization. Hardness (and electronegativity) is constantly revealing its predictive power. It will certainly grow, with the expected development of descriptive methods, based on the available theoretical achievements, producing the simplified apparatus needed for applications in chemical practice. Quantification of hardness is a formidable example and a promising starting point for further studies.

This work has been sponsored under project KBN 203229101.

6 References

- Pearson RG (1963) *J Am Chem Soc* 85: 3533
- Pearson RG (1990) *Coord Chem Rev* 100: 403
- Smith DW (1990) *J Chem Educ* 67: 611
- Parr RG and Pearson RG (1983) *J Am Chem Soc* 105: 7512
- Fajans K and Joos G (1924) *A Physik* 23: 1
- Fajans K (1941) *J Chem Phys* 9: 281
- Jørgensen CK (1966) *Struct Bond* 1: 234
- Vela A and Gázquez JL (1990) *J Am Chem Soc* 112: 1490
- Gordy W (1946) *Phys Rev* 69: 604
- Allred AL and Rochow EG (1958) *J Inorg Nucl Chem* 5: 264
- Sanderson RT (1960) *Chemical periodicity*. Reinhold, New York
- Nagle JK (1990) *J Am Chem Soc* 112: 4741
- Gorlich E (1990) *Z Phys Chem* 271: 169
- Politzer P, Parr RG and Murphy DR (1983) *J Chem Phys* 79: 3859
- Ray NK, Samuels L and Parr RG (1979) *J Chem Phys* 70: 3680
- Gázquez JL and Ortiz E (1984) *J Chem Phys* 81: 2741
- Komorowski L (1987) *Chem Phys Lett* 134: 536
- Komorowski L (1987) *Chem Phys* 114: 55
- Iczkowski RP and Margrave JL (1961) *J Am Chem Soc* 83: 3547
- Huheey JE (1971) *J Org Chem* 36: 204
- Watts JC and Huheey JE (1972) *Chem Phys Lett* 14: 89
- Huheey JE (1983) *Inorganic chemistry: principles of structure and reactivity*, Harper and Row, New York
- Komorowski L (1983) *Chem Phys* 76: 31
- Komorowski L (1983) *Chem Phys Lett* 103: 201
- Yang W, Lee C and Ghosh SK (1985) *J Phys Chem* 89: 5412
- Smith VH Jr (1977) *Physica Scripta* 15: 147
- Bader RFW, Anderson SG and Duke AJ (1979) *J Am Chem Soc* 101: 1389
- Parr RG (1984) *Int J Quant Chem* 26: 687
- Katriel J, Parr PG and Nyden MR (1981) *J Chem Phys* 74: 2397
- Nalewajski RF, Korchowiec J and Zhou Z (1988) *Int J Quant Chem (Quant Chem Symp)* 22: 349
- Nalewajski RF and Koniński M (1988) *Acta Phys Polon* 74: 255
- Nalewajski RF and Korchowiec J (1989) *Acta Phys Polon* 76: 747
- Nalewajski RF (1991) *Int J Quant Chem* 40: 265
- Komorowski L, Lipiński J, Misiak P and Pyka MJ (1988) *Sci Pap Inst Inorg Chem Tech U Wrocław*, 57, Ser Conf 12: 54
- Komorowski L and Lipiński J (1991) *Chem Phys* 157: 45
- Komorowski L, Lipiński J and Pyka MJ, *J Phys Chem* in press.
- Bohm MC and Schmidt PC (1986) *Ber Bunsenges Phys Chem* 90: 913
- Goyocoolea C, Barrera M and Zuloaga F (1989) *Int J Quant Chem* 36: 455
- Todd J and Whitehead MA (1989) *J Mol Struct* 202: 99
- Orsky AR and Whitehead MA (1987) *Can J Chem* 65: 1970
- Robles J and Bartolotti L (1984) *J Am Chem Soc* 106: 3723
- Berkowitz M, Gosh SK and Parr RG (1985) *J Am Chem Soc* 107: 6811
- Yang W and Parr RG (1985) *Proc Natl Acad Sci USA* 82: 6723
- Berkowitz M and Parr RG (1988) *J Chem Phys* 88: 2554
- Nalewajski RF and Korchowiec J (1989) *Croat Chim Acta* 62: 603
- Nalewajski RF (1989) *J Phys Chem* 93: 2658
- Nalewajski RF (1990) *Acta Phys Polon* 77: 817
- Magnusson E (1988) *Aust J Chem* 41: 827
- Reed J (1981) *J Phys Chem* 85: 148
- Voigt B and Dahl JP (1972) *Acta Chem Scand* 26: 2923
- Voigt B (1974) *Acta Chem Scand* 28: 1043, 1068
- Whitehead MA, Baird MA and Kaplansky M (1965) *Theor Chim Acta* 3: 135
- Baird NC, Sichel JM and Whitehead MA (1968) *Theor Chim Acta* 11: 38
- Mortier WJ, van Genechten K and Gasteiger J (1985) *J Am Chem Soc* 107: 829
- Ponec R (1980) *Theoret Chim Acta* 59: 629
- Pearson RG (1986) *Proc Natl Acad Sci USA* 83: 8440
- Pearson RG (1988) *Inorg Chem* 27: 734
- Pearson RG (1989) *J Org Chem* 54: 1423
- Jorge FE, Batista AB and Machado LC (1989) *An Acad bras Ci* 61: 1
- Giambiagi M and de Giambiagi MS (1988) *Chem Phys Lett* 152: 222
- Vinayagam SC and Sen KD (1988) *Chem Phys Lett* 144: 178
- Gázquez JL, Galvan M and Vela A (1990) *Theochem* 69: 29
- Pauling L (1932) *J Am Chem Soc* 54: 3570
- Batsanov SS (1990) *Sov Sci Rev B Chem* 15: 1-79 and references therein
- Nalewajski RF (1984) *J Am Chem Soc* 106: 944
- Pearson RG (1985) *J Am Chem Soc* 107: 6801
- Klopman G (1964) *J Am Chem Soc* 86: 1461
- Komorowski L (1987) *Z Naturforsch* 42a: 767
- Gordy W and Orville-Thomas WJ (1956) *J Chem Phys* 24: 439
- Nethercot AH Jr (1974) *Phys Rev Lett* 33: 1088
- Poole RT, Williams DR, Riley JD, Jenkin JG, Liesegang J and Letkey RCG (1975) *Chem Phys Lett* 36: 401
- Chen ECM, Wentworth WE and Ayala JA (1977) *J Chem Phys* 67: 2642
- Alonso JA and Girifalco LA (1979) *Phys Rev B* 19: 3889
- Pritchard HO and Skinner HA (1955) *Chem Rev* 55: 745
- Hinze J and Jaffe HH (1961) *J Am Chem Soc* 84: 540
- Nethercot AH Jr (1974) *Phys Rev Lett* 33: 1088
- Pearson RG (1987) *J Chem Educ* 64: 561
- Parr RG and Chattaraj PK (1991) *J Am Chem Soc* 113: 1854
- Zhou Z and Parr RG (1990) *J Am Chem Soc* 112: 5720
- Zhou Z and Parr RG (1989) *J Am Chem Soc* 111: 7371