MAXIMUM HARDNESS INDEX OF QUANTUM ACID-BASE BONDING

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Abstract

A unified picture of the hard-and-soft-acids-and-bases and maximum hardness principles was approached through introducing the maximum hardness index Y. It provides particular chemical hardness ranges where the chemical bonding behaves like hard-hard, soft-soft, and hard-soft or soft-hard acid-base interaction characters and furnishes the key to analytical classification of acids and bases in an intrinsic structural manner. The reliability of the present recipe and index was tested by the chemical hardness ordering predictability and chemical bond nature characterization on a particular series of molecular Lewis acids and bases within various computational and experimental atomic chemical hardness scales. Although a consistent chemical hardness principles and related-indices picture was furnished in all cases, considerable differences were noted with respect to the old-fashioned Pearson classification.

1. Introduction

There had been long recognized that acids and bases play a central role in any unified theory of chemical bond and bonding. In this regard, their characterization has always been a conceptual challenge for chemists, with a rich and exciting epistemological history [1, 2].

Recall the pioneering works of Lémery and Boyle (in the early XVIIth century) which introduced the Cartesian salt (or solubility) theory and the associate principle of reactivity driven by the "struggle between acids and alkali" as well. Next, the major contribution of Rouelle (the XVIIIth century), which consecrated the base concept as the complement of that

of an acid, and that of Black, with his pneumatic theory of reactions, being culminated by the Lavoisier's contribution according to which the oxygen is directly related to the acidic character of matter. Further insight was brought by the Volta, Gay-Lussac and Liebig physico-chemical experiments (at the beginning of the XIXth century) in elucidating the fact that acids have to contain hydrogen to be exchanged with a metal and a "radical" of different nature; they established the famous principle:

$$acid + base \leftrightarrow salt + water \tag{1}$$

The first unification of the acidic-basic character of a compound (or solution) was formulated by the Arrhenius, Van't Hoff, and Ostwald in the 1880's, leading to a picture where acids and bases release hydrogen and hydroxide ions, respectively, their interaction being responsible for the acid-base reactions. In the XX century, the acid and base definitions met considerable conceptual enlargement paralleling the newly emerging quantum theory of atoms and molecules. This was achieved in three steps, however not necessarily chronologically. As such, the foreground theory belongs to Brønsted and Lowry (1923), which assumes the proton as the particle, never free, which intermediates between an acid (the donor) and a base (the acceptor) compounds during chemical reactions. Within this framework the new acid-base interaction paradigm looks like:

$$acid\,1 + base\,2 \leftrightarrow acid\,2 + base\,1 \tag{2}$$
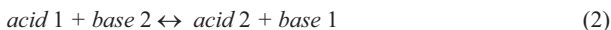
Although efficient, this theory excessively enhanced the role of proton; fortunately, due to the Lewis' intuition (1916) [3], the electron pair was soon recognized as a more general conceptual tool in defining acids, bases, and their chemical bonding. By considering acids and bases as chemical species susceptible to accept and to donate *a pair* of electrons, respectively, almost entire chemistry was reformulated in terms of these so-called Lewis compounds. Worth noting, the Lewis base definition seems to superimpose on the Brønsted-Lowry theory while the acidic Lewis definition covers more general cases.

Next, in the second half of the XX century, the acid-base theory was once more refined, on the ground of the molecular orbital theory, by Pearson [4-10].

In this context, the chemical bonding and reactions were described in two steps: one step regards the Coulomb interaction, being quantified by the electronegativity index χ, seen as the negative of the chemical potential of the interacting systems [11], and by the associated equalization principle [12]; in the second step, the stability of the newly formed chemical bond is regulated by the so called chemical hardness index η, seen as the second order effect, consequently defined as the chemical force (*i.e.*, the gradient of the chemical potential) acting on the bonding species [13-16]. In molecular orbital terms, the middle point of the HOMO-LUMO gap is associated to the chemical potential (*i.e.*, minus electronegativity), while the weight of the gap it taken as the double of the chemical hardness of that molecule. With these, the acids and bases are further classified as soft ("*s*") and hard ("*h*"): a soft species has electrons easy to be transferred in the vacant orbital (LUMO) whereas the chemical reactions are more favourable as the HOMO level of one species vertically approaches the LUMO of the other.

From now on, the molecular systems are recognised as hard and soft acids and bases (HSAB), in the sense that each molecule can be seen as hard-hard, soft-soft, hard-soft or soft-hard bonding combinations between acids and bases. The associate HSAB principle of chemical reactivity was formulated as well, providing that "hard acids prefer hard bases and soft acids prefer soft bases" [17, 18]:

$$h_1 - s_1 + s_2 - h_2 \leftrightarrow h_1 - h_2 + s_2 - s_1 \qquad (3)$$

Despite the qualitative character [19-28] of the HSAB principle, an appropriate quantum index to smoothly distinguish between the soft and hard character of acids, bases, and their bonding, would switch HSAB towards a quantitative theory – which is just the main goal of the present work.

2. Maximum Hardness Index Υ

In quantum mechanical characterization of bonding, the chemical hardness appears to play the inner stabilization role, behaving as the main quantum influence (or force) [29]. However, its involvement takes place in two correlated stages: one stage regards the fulfillment of the HSAB principle, where adducts react according to their reciprocal strengths, see Eq. (3); the second stage in bonding accounts for the minimization of the quantum fluctuations around the energetic equilibrium of bond that corresponds to the so-called maximization of hardness (MH), from where the associated MH principle [30, 31].

Since the two chemical hardness stages and principles drive the quantum chemical bond, the quest for their linked description, both at the phenomenological and analytical levels, appears as a natural endeavor. In this respect, aiming to quantify "in one shoot" the chemical HSAB and MH principles, the so called *maximum hardness index* [32] was recently proposed:

$$Y = 1 - \frac{1}{2\eta^2} \tag{4}$$

The expression (4) was derived through considering also the chemical softness index as the inverse of the global chemical hardness [10]:

$$S = \frac{1}{2\eta} \tag{5}$$

quantifying the degree of electronic cloud polarizability (propensity to deformation), in competition with the chemical hardness, under the normalized form:

$$Y = \frac{\eta - S}{\eta} = \frac{\eta}{\eta} - \frac{S}{\eta}. \tag{6}$$

It is clear that the definition (6) emphases on how the chemical bond stability is related to the difference between the hard-hard (η/η) and soft-hard (S/η) ratios, transposing in an analytical manner the two equilibrium sides of bonding equilibrium in (3).

In the next, let's comment on some faces of the meaning of the maximum hardness index Y ((4) and (6)).

First, on the associate symbol, one could remark that the electronegativity index was historically assigned by "X" while the chemical hardness, which in above chemical bonding phenomenology follows the electronegativity equalization principle, should be identified by letter "Y". Other literal argument was offered elsewhere [32].

Second, the definition (6) incorporates the hard-hard (or soft-soft) and hard-soft (or soft-hard) contest of the chemical bond by means of η/η and S/η terms, respectively. As

such, the difference (6) measures the degree by which the equilibrium in (3) is broken to favor or not the stabilization of hard-hard and soft-soft bonds.

From the point of view of the values that Y acquire, two main states of bonding may be revealed. One is quantified by the values $Y \in [0,1]$, in which case the equilibrium in (3) is departed to its right side; however, as Y closely tends to 1, as the hard-hard bond is more favorable to the soft-hard state of adducts ($h - h \gg s - h$, or $\eta/\eta \gg S/\eta$).

The other accounts for the values of Y bellow to zero, that indicates the stabilization process is not yet completed, according to the HSAB principle; in other words, the equilibrium in (3) is shifted to its left side as $h - h$ bonding is less favorable, respecting $s - h$ one ($\eta/\eta < S/\eta$). Actually, the negative of Y means a sort of violation of maximum hardness requirement for chemical bond stabilization, that is achieved between 0 and 1 and is completed when $Y \rightarrow 1$.

Nevertheless, another interesting feature of the equations (4) and (6) yields when rewriting them in the equivalent form:

$$1 = \frac{S}{\eta} + Y .\tag{7}$$

The form (7) may be easily assimilated to both a conservation principle (of chemical bond from adducts) and a *probabilistic equation*. In fact, one can interpret the chemical bond formation by the competition between the hard-soft and maximum hardness (hard-hard) bonding probabilities. The probability character is crucial to certify the quantum character of the chemical hardness involved in bonding, not only phenomenologically but also analytically. Moreover, since the hard-soft term (S/η) in (7) basically express the emerging HSAB principle and Y values associates with MH quantum effects, the unified chemical hardness of bonding equation may be formulated as:

$$1 = \text{HSAB} + \text{MH} .\tag{8}$$

This equation may constitute the foreground relation for future quantum chemical kinetics of the chemical bond.

Going to the physico-chemical meaning of the maximum hardness, its probabilistic nature will be first justified. Although linear, the definition (4) may be immediately rearranged under exponential form, with the associate limiting points within the [0, 1] realm:

$$Y_e = \exp\left(-\frac{1}{2\eta^2}\right) = \begin{cases} 0 & ... \ \eta \to 0 \\ \dfrac{1}{\sqrt{e}} \cong 0.606531 & ... \ \eta = 1 \\ 1 & ... \ \eta \to \infty \end{cases} \qquad (9)$$

Worth noting, the above exponential maximum hardness index resembles the original hyperbolic one on the chemical hardness domain where $\eta > 1$, whereas the unfolded hyperbolic version covers in more detail the chemical bonding regions, as shown by the limits:

$$Y_h = 1 - \frac{1}{2\eta^2} = \begin{cases} -\infty & ... \ \eta \to 0 \\ 0 & ... \ \eta = \dfrac{1}{\sqrt{2}} \cong 0.707107 \\ 0.5 & ... \ \eta = 1 \\ 1 & ... \ \eta \to \infty \end{cases} \qquad (10)$$

and by the graphical representation in Figure 1.
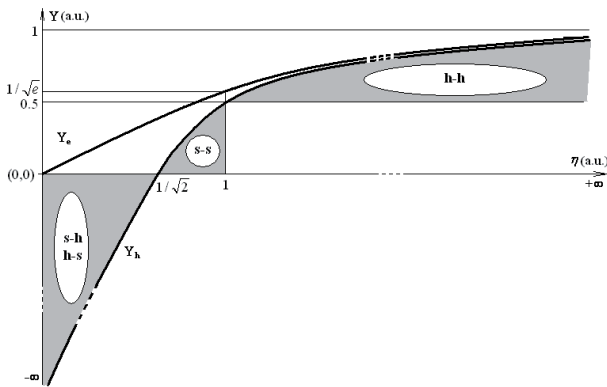
Figure 1. *Comparison between the hyperbolic maximum hardness index (10), with marked regions of the hard-hard (h-h), soft-soft (s-s), soft-hard (s-h), and hard-soft (h-s) natures of the chemical bonding in reaction (3), and the associate exponential form (9). Both scales are set in arbitrary units (a.u.).*

From the Figure 1, the almost complete superposition between the exponential and hyperbolic MH indices (9) and (10), is evident for values of chemical hardness exceeding unity, but the hyperbolic function covers considerably more cases than the always-positive exponential form, for values below unity. In fact, the hyperbolic MH index allows the quantum characterization of the chemical bonds as appears in the HSAB reaction (3). This is due to the dual positive and negative values of Y_h, a behavior that provides maximum structural information on the concerned bond.

Remarkably, the $Y_h(\eta)$ graph offers the chemical bonding partition in three correlated regions.

The first one corresponds to values of the chemical hardness higher than unity, a case in which Y_h holds values over 0.5 probability for the equilibrium in (3) flowing to its right side; as higher chemical hardness values of the bond are assessed as hard-hard binding frame is preferred.

The second region rises within the interval $1/\sqrt{2}<\eta<1$ in which the Y_h probability stands bellow 0.5 values, however, with positive nonzero figures, such that the chemical bond can be still formed as the soft-soft combination in the right side of Eq. (3).

The last region provides negative values for Y_h indicating the "hole" or anti-bonding character that can further be associated to an anti-binding entropy S of states with negative statistical probability $\exp(S/k_B)$, k_B being the Boltzmann constant; since the bonding states are restricted through the induced negative potential barrier, the equilibrium in (3) is driven to its left side and, consequently, assigned to the soft-hard (or hard-soft) bonding character of concerned molecules. Moreover, due to the negative probabilities assumed, the hard-soft (or soft-hard) bonding situation may link with the back-scattering framework of adducts in a velocity limiting step within the virtual (transition state) channels of reaction (3) respecting hard-hard and soft-soft rearrangements [33].

Resuming, the maximum hardness index helps in prescribing the hard and soft nature of the acid-base chemical bonding against the domains of chemical hardness as follows:

$$\left.\begin{array}{c} hard-hard \\ soft-soft \\ hard-soft(soft-hard) \end{array}\right\} \begin{array}{c} ACID-BASE \\ BONDING \end{array} \begin{cases} Y_h \geq 0.5 & ...\ \eta \geq 1 \\ 0 \leq Y_h < 0.5 & ...\ 1/\sqrt{2} \leq \eta < 1 \\ Y_h < 0 & ...\ 0 < \eta < 1/\sqrt{2} \end{cases} \qquad (11)$$

Additionally, the soft-to-hard classification of acids and bases can in any case be established through identifying on the $Y(\eta)$ diagrams the soft, borderline, and hard detached "islands" of Y values respecting η range. All these aspects should leave with quantum elucidation of the chemical bond and bonding nature via maximum hardness index Y.

3. Molecular Chemical Hardness Implementation

The molecule can be seen as a collection of atoms [34], thus, its global quantum properties - in general, and that of chemical hardness and softness - in particular, can be computed as additive contributions of atomic components. In this respect, the molecular softness is written as:

$$S_M = \sum_A S_A \ ,$$
(12)

since it progressively accounts for the electronic cloud deformations of atoms in molecules [28]. To describe the molecular hardness, also a frontier partition correction factor is necessary, *e.g.*, the so-called atomic Fukui function [35],

$$f_A(r) = \left(\frac{\partial \rho_A(r)}{\partial N_A} \right)_{V_A(r)} = - \left(\frac{\delta \chi_A}{\delta V_A(r)} \right)_{N_A} \ ,$$
(13)

which account for the atomic density ρ_A or electronegativity χ_A variation respecting the total number of electrons N_A or that of the bare potential V_A in atoms, respectively; consequently it can be re-written as:

$$\eta_M = \sum_A f_A \eta_A$$
(14)

Therefore, an operational atoms-in-molecules chemical hardness expression is to be achieved once the Fukui function is determined. This goal may be elegantly achieved since the Fukui function also applies at the softness level in a reciprocal manner than it links the atoms in molecules for chemical hardness, namely:

$$S_A = f_A S_M \tag{15}$$

Now, combining the expressions (12) and (15), the atomic Fukui function gets out as:

$$f_A = \frac{S_A}{\sum\limits_A S_A} \tag{16}$$

while by further accounting of the chemical hardness-softness relationship (5) it provides the global atomic containing molecular chemical hardness:

$$\eta_M = \frac{n^{AIM}}{\sum\limits_A \dfrac{n^A}{\eta_A}} \tag{17}$$

which depends on the total number of atoms in molecule and the number of identically atoms, n^{AIM} and n^A , respectively.

This way, the remaining issue is to asses the atomic chemical hardness a computational recipe. As such worth recognizing that the chemical hardness roots on electronegativity throughout an analytical hierarchy, visible also from the combined relations (13) and (14) [36]. However, a systematic derivation of chemical hardness based on various electronegativity sources was recently reported and expresses the atomic chemical hardness in terms of the linear-response function [12, 37]:

$$L(r) = -\frac{\nabla\rho(r)\cdot\nabla V(r)}{[\nabla V(r)]^2} \tag{18}$$

appearing in the so-called reactivity softness indices [12]

$$a \equiv \int L(r)dr \ , \tag{19}$$

$$b \equiv \int L(r)V(r)dr , \tag{20}$$

and in the chemical action functional [32]

$$C_A \equiv \int \rho(r)V(r)dr \tag{21}$$

through the functionals listed in Table I [38].

Table I. *Systematic chemical hardness density functionals derived from the associate hierarchy of electronegativity expansions by means of charge and potential variations [38], in terms of atomic valence number of electrons N_v, of the softness related indices from eqs. (19) and (20), and of the chemical action (21), respectively.*

Electronegativity Source	Chemical Hardness Functionals
$d\chi = d\chi[dN]$	$\eta_A^{[1]} = \dfrac{1}{2\sqrt{a}}\left[\arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right)\right]$
$d\chi = d\chi[dN, dNdN]$	$\eta_A^{[2]} = \dfrac{1}{4\sqrt{a}}\left\{\arctan\left(\dfrac{N_v-2}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v+2}{\sqrt{a}}\right) - 2\left[\arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right)\right]\right\}$
$d\chi = d\chi[dN, \delta V(r)]$	$\eta_A^{[3]} = \dfrac{1}{2}\left\{\dfrac{2\left[C_A\left(1+a-N_v^2\right)-2bN_v\right]}{(1+a)^2 + 2(a-1)N_v^2 + N_v^4} + \dfrac{1}{\sqrt{a}}\left[\arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right)\right]\right\}$
$d\chi = d\chi[dN, dNdN, \delta V(r)]$	$\eta_A^{[4]} = \dfrac{1}{4}\left\{\dfrac{4\left[C_A\left(1+a-N_v^2\right)-2bN_v\right]}{(1+a)^2 + 2(a-1)N_v^2 + N_v^4} + \dfrac{1}{\sqrt{a}}\left[\arctan\left(\dfrac{N_v-2}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v+2}{\sqrt{a}}\right)\right] - \dfrac{2}{\sqrt{a}}\left[\arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right)\right]\right\}$

From Table I, it is obvious that the chemical action occurs only when the chemical hardness derivation is based on electronegativity explicit variation respecting the external potential of the valence electrons N_v, while the appearance of the potential is also present in the rest of cases through the reactivity softness indices (19) and (20). Nevertheless, since in chemical action the electronic potential and density are together convoluted, it is expected to contribute together at driving the chemical bonding to the minimum energetic state, as described by the density functional Hohenberg-Kohn theorems [11], recently unified within the associate *chemical action principle* [32]:

$$\delta C_A = 0. \tag{22}$$

Finally, the atomic chemical hardness systematic expressions of Table I become workable once further specification of atomic properties are implemented. This last step can be achieved by considering the valence electrons on the n quantum indexed shell evolving under the effective radial atomic core potential, $-Z_{eff}/r$, and displaying a valence electronic Slater density (STO), with the valence orbital exponents ξ. In these conditions, the linear response and the chemical action indices of equations (19)-(21) may be evaluated between infinite- until the atomic- radii contributions, with the atomic radius (R) approaching the small-range expansion around the atomic center, with respective results [37]:

$$a(R) \equiv \left(\int_{\infty}^{R} L(x)dx \right)\Big|_{R \to 0}$$

$$= \frac{2\pi \left(2n\Gamma[2+2n, 2R\xi] - \Gamma[3+2n, 2R\xi] \right)}{Z_{eff}\, \xi\, (2n)!}\Big|_{R \to 0}$$

$$\cong \frac{2\pi}{Z_{eff}\, \xi\, (2n)!} \left\{ \begin{array}{l} 4(R\xi)^{2(1+n)}\left(\dfrac{2^{1+2n}\, R\xi}{3+2n} - \dfrac{2^{2n}\, n}{1+n} \right) \\ + 2n\Gamma[2+2n] - \Gamma[3+2n] \end{array} \right\}, \tag{23}$$

$$b(R) \equiv \left(\int_{\infty}^{R} L(x)V(x)dx \right)\Big|_{R \to 0}$$

$$= \frac{4\pi \left(-2n\Gamma[1+2n, 2R\xi] + \Gamma[2+2n, 2R\xi] \right)}{(2n)!}\Big|_{R \to 0}$$

$$\cong \frac{4\pi}{(2n)!} \left\{ \begin{array}{l} \dfrac{(2R\xi)^{1+2n}}{(1+n)(1+2n)}\left[2n^2 - R\xi + 2n(1-R\xi) \right] \\ - 2n\Gamma[1+2n] + \Gamma[2+2n] \end{array} \right\}, \tag{24}$$

$$C_A(R) \equiv \left(\int_{\infty}^{R} 4\pi x^2 \rho_{STO}(x)V(x)dx \right)\Big|_{R \to 0}$$

$$= \frac{8\pi Z_{eff}\, \xi\, \Gamma[2n, 2R\xi]}{(2n)!}\Big|_{R \to 0}$$

$$\cong \frac{4\pi Z_{eff}\, \xi \left[2n\Gamma[2n] - (2R\xi)^{2n} \right]}{n(2n)!} \tag{25}$$

with Γ being the Euler's Gamma function.

Since this procedure is specific for correlating the density functional electronegativity (DFE) with the atomic radii scales, it is appropriately of being implemented also in chemical hardness computation.

This way, all atomic basic ingredients are considered in the molecular evaluation of chemical hardness which should be reflected in the soft and hard character of chemical bonding through the maximum hardness index Y.

4. Application to Molecular Lewis Acids and Bases

According to Pearson, classification of acids and bases as hard and soft needs the recourse to the concept of strength although little insight this way is given since further appeal to the experimental enthalpy of reaction is involved [5, 10].

Even the consideration of the ionic and covalent bonding contributions, as appeared in the well known four-parameter equation of Drago and Wayland [39], helps not so much in quantifying HSAB principle, albeit a famous scientific debate was produced on the issues whether or not they may constitute viable quantum measures for the strength and softness, respectively [17]. In short, the main problem states that: having a given molecule or a bond, its chemical hardness may be evaluated by some experimentally or computationally based methods to establish the hard and soft nature of the bond itself, and even more, to precise, if possible, the hard and soft nature of the bonding components.

There was further conjectured that if a sort of universal soft-to-hard scale of molecular strength is produced, and each time confirmed or never invalidated, then the HSAB principle itself will be consecrated among the chemical universal principles. The fact that such universal classification was still not produced, it does not mean that the HSAB principle is not applicable. Contrarily, in our opinion, both epistemological (the postulates' need) and structural energetically arguments (see the last part of introduction), lead us, in a reverse way, to assume the HSAB as valid principle in any circumstances and to apply it in order to establish the specific hard and soft character of a particular chemical bond or molecular strength.

The actual maximum hardness index Y was introduced on the ground of assumed HSAB as true principle, resulting in a consistent picture of the HSAB-MH chemical bonding. Within this picture, specific chemical hardness ranges were defined to asses the type of hard

and soft bond (as a global character) and bonding (as an interaction character) without any other artifacts.

In this context, the actual hard and soft classification scheme is in the next compared and discussed against the traditional Pearson classification for a limited, however representative, series of molecular Lewis acids and bases as displayed in the Table II and III, respectively.

Table II. *Qualitative Pearson classification of Lewis acids tested in this work [4, 10].*

Soft			Borderline			Hard		
CH_2	$GaCl_3$	BH_3	SO_2	GaH_3	$B(CH_3)_3$	SO_3	$AlCl_3$	BCl_3
A1	*A2*	*A3*	*A4*	*A5*	*A6*	*A7*	*A8*	*A9*

Tables III. *Qualitative Pearson classification of Lewis bases tested in this work [4, 10].*

Soft			Borderline			Hard		
CH_3SH	CO	C_6H_6	N_2	C_5H_5N	$C_6H_5NH_2$	H_2O	N_2H_4	NH_3
B1	*B2*	*B3*	*B4*	*B5*	*B6*	*B7*	*B8*	*B9*

In order to compute the associate chemical hardness of the molecules of Tables II and III, the previously exposed atoms-in-molecules methodology is here implemented. However, for completeness, various theoretical ways of computing atomic hardness are also considered. Since, ultimately, the atomic chemical hardness depends on the atomic radii, two different sets of values were here implemented, and namely those based on the density functional electronegativity (DFE) [37] and on the Ghosh-Biswas (GB) scale [40], respectively. Moreover, for the benchmark considerations, the atomic hardness will be implemented in relation to the vertical ionization potential (IP) and the electronic affinity (EA) as well. That is further made in two distinct ways. One is to simply use the finite difference (FD) approximation to the standard differential energetic definition of hardness [11, 13, 32]:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E_N}{\partial N^2}\right)_{V(r)} \cong \frac{E_{N+1} - 2E_N + E_{N-1}}{2} = \frac{IP - EA}{2} \tag{26}$$

when the IP and EA experimental atomic scales are employed [41].

The other approach is based on the Pearson charge conducting sphere model of atomic systems in which, by considering the classical electrostatic expression for the total energy, $q^2 Z_{eff}/(4\pi\varepsilon_0 R)$, the specialization of the relation (26) will yield another practical expression for the chemical hardness:

$$\eta = \frac{Z_{eff}}{2R}(a.u.) \tag{27}$$

The index (27) will be recognized as softness based chemical hardness (η^S) on the ground of close similitude with the reciprocal relation (5) according to which the softness will appear directly proportional to the atomic radius.

Table IV. *Hardness values of the atomic species used in this work, computed both by considering density functional electronegativity (DFT) [37] and Ghosh-Biswas (GB) [40] atomic radii in relations (20)-(22) for the working chemical hardness functionals of Table I, respectively. The finite-difference (FD) definition based on vertical ionization energy (IP) and electron affinity (EA) scales [41], eq. (26), was added for experimental assessment. For comparison, the softness based chemical hardness values based on sphere-charged model of Pearson [10], eq. (27), is also included. In all cases the atomic values were computed upon hydrogen calibration to its experimental 6.45 eV value. All values are in electron-volts.*

Atomic Species	$\eta^{[1]}_{DFE}$	$\eta^{[1]}_{GB}$	$\eta^{[2]}_{DFE}$	$\eta^{[2]}_{GB}$	$\eta^{[3]}_{DFE}$	$\eta^{[3]}_{GB}$	$\eta^{[4]}_{DFE}$	$\eta^{[4]}_{GB}$	η^{S}_{DFE}	η^{S}_{GB}	η_{FD}
H	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45	6.45
B	9.43	6.02	10.45	6.28	53.06	122.72	53.17	123.24	14.34	10.97	4.06
C	16.76	10.03	21.99	11.24	174.22	372.6	175.07	374.2	22.67	17.1	4.99
N	28.29	15.68	37.54	19.94	593.97	958.9	595.75	962.91	32.52	24.69	7.59
O	53.8	24.2	44.99	55.25	3157.6	2521.7	3172.9	2530.5	44.44	33.81	6.14
Al	6.71	0.86	7.46	0.83	35.51	87.26	35.58	87.66	14.08	8.8	2.81
S	27.76	2.17	27.66	2.17	920.54	520.65	924.71	523.1	33.87	21.41	4.16
Cl	68.22	2.77	56.44	2.8	17059.7	934.87	17140.1	939.2	42.56	26.73	4.68
Ga	8.18	0.15	10.16	0.14	86.49	116.12	86.68	116.66	19.21	10.89	2.81

For the atomic chemical hardness functionals of Table I together with the FD and softness based forms (26) and (27), both the considered atomic DFE and GB radii scales are employed to evaluate the chemical hardness. It was computed for all atoms involved in the molecules of Tables II and II, in all possible variants, in Table IV, while for the molecules themselves the respective hardness and maximum hardness η and Y values are reported in the Tables V-VIII.

Table V. *Hardness values (eV) of the molecular Lewis acids tested in this work, computed upon atomic values of Table IV by the molecular chemical hardness formula (17).*

Lewis Acids	$\eta^{[1]}_{DFE}$	$\eta^{[1]}_{GB}$	$\eta^{[2]}_{DFE}$	$\eta^{[2]}_{GB}$	$\eta^{[3]}_{DFE}$	$\eta^{[3]}_{GB}$	$\eta^{[4]}_{DFE}$	$\eta^{[4]}_{GB}$	η^{S}_{DFE}	η^{S}_{GB}	η_{FD}
BCl₃	26.66	3.20	26.87	3.25	210.28	352.19	210.72	353.72	28.53	19.67	4.51
AlCl₃	20.72	1.78	21.37	1.76	141.16	272.68	141.44	273.94	28.27	17.71	4.01
SO₃	43.58	6.84	38.9	7.77	1964.2	1286.03	1973.43	1291.48	41.22	29.53	5.49
B(CH₃)₃	7.74	6.99	7.99	7.14	9.08	9.21	9.08	9.21	8.14	7.82	5.8
GaH₃	6.81	0.56	7.1	0.53	8.39	8.44	8.39	8.44	7.73	7.18	4.87
SO₂	40.98	5.52	37.22	6.04	1744.5	1105.5	1752.6	1110.3	40.25	28.34	5.3
BH₃	7.	6.34	7.13	6.41	8.27	8.45	8.27	8.45	7.48	7.19	5.62
GaCl₃	24.96	0.52	26.39	0.49	340.78	338.39	341.54	339.96	32.64	19.6	4.01
CH₂	8.11	7.32	8.44	7.52	9.5	9.59	9.5	9.59	8.47	8.14	5.88

Table VI. *Hardness values (eV) of the molecular Lewis bases tested in this work, computed upon atomic values of Table IV by the molecular chemical hardness formula (17).*

| Lewis Bases	$\eta^{[1]}_{DFE}$	$\eta^{[1]}_{GB}$	$\eta^{[2]}_{DFE}$	$\eta^{[2]}_{GB}$	$\eta^{[3]}_{DFE}$	$\eta^{[3]}_{GB}$	$\eta^{[4]}_{DFE}$	$\eta^{[4]}_{GB}$	η^{S}_{DFE}	η^{S}_{GB}	η_{FD}
NH₃	7.99	7.56	8.13	7.76	8.57	8.58	8.57	8.58	8.07	7.91	6.7
N₂H₄	8.68	8.02	8.91	8.33	9.62	9.64	9.62	9.64	8.8	8.56	6.79
H₂O	9.13	8.54	9.03	9.14	9.67	9.66	9.67	9.66	9.02	8.83	6.34
C₆H₅NH₂	9.47	8.01	10.11	8.39	12.48	12.7	12.49	12.7	10.14	9.48	5.79
C₅H₅N	9.92	8.22	10.69	8.66	13.65	13.93	13.66	13.93	10.72	9.93	5.76
N₂	28.29	15.68	37.54	19.94	593.97	958.9	595.75	962.21	32.52	24.69	7.59
C₄H₆	9.32	7.85	9.97	8.2	12.44	12.68	12.44	12.68	10.04	9.37	5.63
CO	25.58	14.18	29.54	18.68	330.22	649.27	331.83	651.99	30.02	22.7	5.51
CH₃SH	8.38	5.08	8.55	5.13	9.57	9.6	9.57	9.6	8.65	8.27	5.66

Table VII. *Values of the maximum hardness index, in arbitrary units, for the Lewis acids tested in this work, computed upon molecular chemical hardness of Table V by the maximum hardness definition (4).*

Lewis Acids	$Y^{[1]}_{DFE}$	$Y^{[1]}_{GB}$	$Y^{[2]}_{DFE}$	$Y^{[2]}_{GB}$	$Y^{[3]}_{DFE}$	$Y^{[3]}_{GB}$	$Y^{[4]}_{DFE}$	$Y^{[4]}_{GB}$	Y^{S}_{DFE}	Y^{S}_{GB}	Y_{FD}
BCl₃	.999297	.951239	.999308	.952671	.999989	.999996	.999989	.999386	.998707	.998707	.975395
AlCl₃	.998836	.842384	.998905	.838084	.999975	.999993	.999975	.999993	.999374	.998406	.968944
SO₃	.999737	.989313	.999670	.991708	1.	1.	1.	1.	.999706	.999427	.983393
B(CH₃)₃	.991646	.989758	.992164	.990184	.993938	.994105	.993939	.994106	.99245	.991828	.985117
GaH₃	.989219	- .589448	.990076	- .808789	.992899	.992987	.9929	.992988	.991642	.990307	.978937
SO₂	.999702	.983591	.999639	.986276	1.	1.	1.	1.	.999691	.999377	.982195
BH₃	.989805	.987548	.990172	.987818	.992681	.993001	.992682	.993002	.99106	.99033	.984184
GaCl₃	.999137	- .876807	.999282	-1.10858	.999996	.999996	.999996	.999996	.999531	.998699	.968944
CH₂	.992405	.990671	.992977	.991153	.994459	.994566	.99446	.994566	.993031	.992454	.985523

Table VIII. *Values of the maximum hardness index, in arbitrary units, for the Lewis bases tested in this work, computed upon molecular chemical hardness of Table VI by the maximum hardness definition (4).*

Lewis Bases	$Y^{[1]}_{DFE}$	$Y^{[1]}_{GB}$	$Y^{[2]}_{DFE}$	$Y^{[2]}_{GB}$	$Y^{[3]}_{DFE}$	$Y^{[3]}_{GB}$	$Y^{[4]}_{DFE}$	$Y^{[4]}_{GB}$	Y^{S}_{DFE}	Y^{S}_{GB}	Y_{FD}
NH₃	.992173	.991259	.992443	.991703	.993191	.993209	.993191	.993209	.992316	.992011	.988867
N₂H₄	.993371	.992235	.993701	.992791	.9946	.994622	.9946	.994623	.993346	.993172	.989155
H₂O	.993999	.993140	.993865	.994017	.994648	.994645	.994648	.994645	.993855	.993591	.987574
C₆H₅NH₂	.994423	.992212	.995108	.992892	.996792	.9969	.996793	.9969	.995137	.994438	.985067
C₅H₅N	.994919	.992608	.995623	.993333	.997318	.997423	.997319	.997424	.995646	.994926	.984942
N₂	.999375	.997966	.999645	.998742	.999999	.999999	.999999	.999999	.999527	.99918	.991321
C₄H₆	.994238	.991888	.994974	.992558	.996769	.99689	.99677	.996891	.995042	.994301	.984208
CO	.999235	.997514	.999427	.998567	.999995	.999999	.999995	.999999	.999445	.999031	.983505
CH₃SH	.992883	.980639	.993160	.980989	.99454	.994579	.994541	.994579	.993315	.992693	.984367

To facilitate a discussion respecting the prototype picture of Figure 1, the results of Tables VII and VIII are represented in Figures 2-4 for the Lewis acids and bases of Tables II and III, respectively.
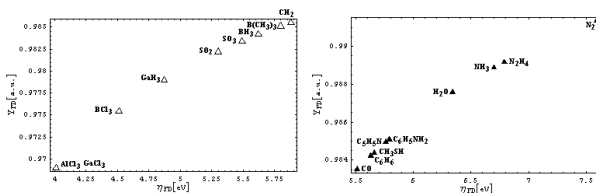
Figure 2. *Graphical correlation between the values of the molecular chemical hardness η of equation (17) and the maximum hardness index Y of equation (4) by using the Tables V-VIII for the Lewis acids and bases of Tables II and III, in the case of experimental finite-difference (FD) based definition of atomic chemical hardnesses of Table IV, in left and right pictures, respectively.*

In Figure 2 only the finite-difference based results are depicted. They are grounded on the atomic chemical hardness (26) with the experimental atomic IP and EA [41]. Despite this "experimentally" assumed picture the predicted chemical hardness ordering looks like:

$$\text{FD: (A8, } \mathbf{A2})<(\text{A9, } \mathbf{A5})<(\text{A4, } \mathbf{A7}, \text{A3, A6, A1}) , \quad (28a)$$

$$\text{FD: (}\mathbf{B2}, \mathbf{B3}, \mathbf{B1}, \text{B5, B6})<(\text{B7, B9, B8})< \text{B4} , \quad (28b)$$

providing the *soft<borderline<hard* classifications of acids and bases of Tables II and III, respectively.

The FD chain relationships (28) confirm that the Pearson classification is only partly fulfilled: by marking in bold the cases when the actual analysis fits with Pearson one, clearly appears that in the case of acids, in each Pearson classes (soft, borderline, and hard) only one acid from the computed set is recovered; for bases, only those classified as soft are here recovered as such although in an enlarged set. Therefore, the percentage of actual/Pearson approaches goes to 33% for both acids and bases considered apart of some internal ordering relativity.

On the other hand, the actual endeavor gives insight also into the type of chemical bonding: in accordance with the acid-base bonding characterization (11) all considered FD

computed molecules are of hard-hard acid-base interaction type, although with different resulting maximum hardness values.
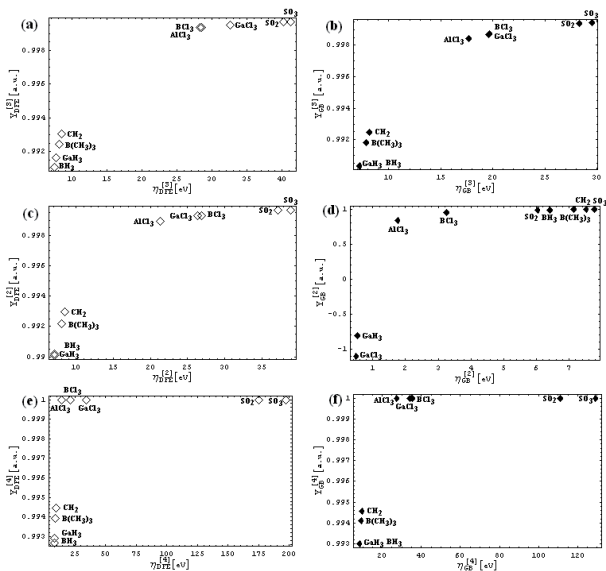
Figure 3. *Graphical correlation between the values of the chemical molecular hardness η of equation (17) and the maximum hardness index Y of equation (4) for the Lewis acids of Table II employing the softness-, the second- and the fourth- order density functional electronegativity –DFE and Ghosh-Biswas-GB based atomic radii values of chemical hardness of Tables V-VIII: the draws (a), (c), and (e) –for DFE, and (b), (d), and (f) – for GB computation frames, respectively.*

In Figure 3, all other ways for chemical hardness computation are collected for the acids of Table II. However, since the DFE/GB[1] with DFE/GB[2] – in one hand and DFE/GB[3] with DFE/GB[4] – in other hand were found to give similar qualitative results, only the most complex pictures were chosen for representation, namely the DFE/GB[2] and DFE/GB[4] ones with the draws in Figure 3: (c), (e) – for DFE, and (d) and (f) – for GB methods, respectively.

As before, the bond and bonding issues are addressed: the soft-to-hard classification for chemical bond nature and the soft-hard types of chemical bonding.

Concerning the first issue, several ordering combinations are obtained:

$$DFE^S: (\mathbf{A3}, A5, A6, \mathbf{A1}) < (A8, A9) < (A2, A4, \mathbf{A7}), \qquad (29a)$$

$$GB^S: (A5, \mathbf{A3}, A6, \mathbf{A1}) < (A8, A2, A9) < (A4, \mathbf{A7}), \qquad (29b)$$

$$DFE^{[2]}: (A5, \mathbf{A3}, A6, \mathbf{A1}) < (A8, A2, A9) < (A4, \mathbf{A7}), \qquad (29c)$$

$$GB^{[2]}: (\mathbf{A2}, A5) < (A8, A9) < (A4, A3, A6, A1, \mathbf{A7}), \qquad (29d)$$

$$DFE^{[4]}: (\mathbf{A3}, A5, A6, \mathbf{A1}) < (A8, A9, A2) < (A4, \mathbf{A7}), \qquad (29e)$$

$$GB^{[4]}: (A5, \mathbf{A3}, A6) < (A1, A8, A2) < (\mathbf{A9}, A4, \mathbf{A7}). \qquad (29f)$$

The results are complex and deserve a close inspection. At a glance, one observes the drastically discrepancy of the actual orderings vs. the Pearson scheme of Table II. However, as before, the fit with Pearson classification does not exceed 33% of cases – and this by assuming the comparison between classes while neglecting the exact relative orderings. Moreover, the actual maximum hardness approach offers the perspective of hard and soft classification of Lewis acids, beyond the simple assessment of global chemical hardness values. That is the case, for instance, of the $DFE^{[4]}$ and $GB^{[4]}$ frames of computations when, at almost equal values among the hardness values of different species, the soft and borderline classification was decided by the graphical splitting in Y groups providing that as bigger it is as more stable bond is associated.

Actually, the graph $Y(\eta)$ furnishes the global soft-to-hard classification respecting the displacements of the Y values within "islands" on its (interpolated or virtual) curve of the type of that represented in Figure 1. Nevertheless, the inner quantum chemical bonding is described as hard-hard type in all cases excepting the $GB^{[2]}$ approach which also allows soft-hard (or hard-soft) $GaCl_3$ and GaH_3 species. However, such exception may suggest that both Ghosh-Biswas atomic scale and the second (consequently, also the first) DFE computation frames in Table I may be considered as inappropriate for the present characterization of bond and bonding nature of Lewis acids.

The last remark is nothing else than the confirmation of the fact that a more complex way of atomic radii involvement in chemical hardness definition, in the sense of atomic potential and of chemical action influences, may lead to better results. Following this line, we may conclude the analysis of Lewis acids of Table II with the recommendation of the grouping (29e) as the best soft-to-hard ordering; this is also the most complex computational approach with the most higher frequency of ordering appearance among the compared models. Moreover, the hard-hard acid-base interaction stands as the dominant mechanism of chemical bonding.

In the same manner, the investigation of Figure 4 provides the chemical hardness orderings of Lewis bases of Table III along the computational scheme implemented:

$$DF^S: (B9, \mathbf{B1}, B8, B7)<(B3, \mathbf{B6}, \mathbf{B5})<(B2, B4), \qquad (30a)$$

$$GB^S: (B9, \mathbf{B1}, B8, B7)<(B3, \mathbf{B6}, \mathbf{B5})<(B2, B4), \qquad (30b)$$

$$DFE^{[2]}: (B9, \mathbf{B1}, B8, B7)<(B3, \mathbf{B6}, \mathbf{B5})<(B2, B4), \qquad (30c)$$

$$GB^{[2]}: (\mathbf{B1})<(B9, B3, B8, \mathbf{B5}, \mathbf{B6}, \mathbf{B7})<(B2, B4), \qquad (30d)$$

$$DFE^{[4]}: (B9, \mathbf{B1}, B8, B7)<(B3, \mathbf{B6}, \mathbf{B5})<(B2, B4), \qquad (30e)$$

$$GB^{[4]}: (B9, \mathbf{B1}, B8, B7)<(B3, \mathbf{B6}, \mathbf{B5})<(B2, B4). \qquad (30f)$$

Although the ordering chemical hardness percentage respecting Pearson classification of Table III records no sensible modification, few notable differences now appeared: there is quite an inversion between the Pearson recommended hard bases B7-B9 which are now classified as soft, while the previous soft and borderline bases B2 and B4 are here situated as hard in almost all ordering schemes (30a)-(30f).
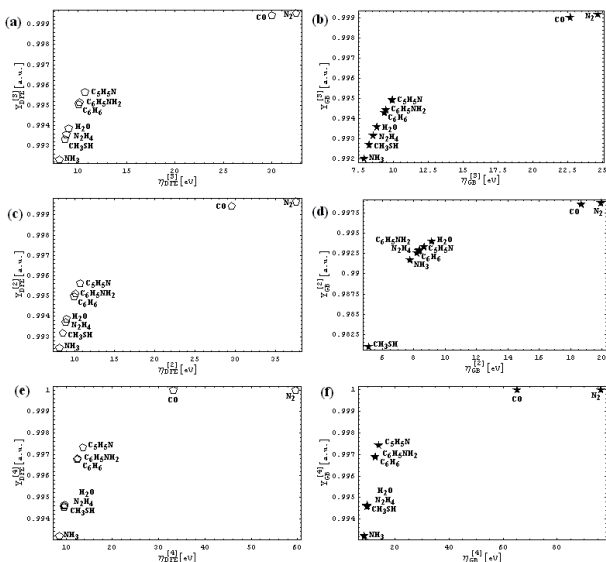
Figure 4. *Graphical correlation between the values of the molecular chemical hardness η of equation (17) and the maximum hardness index Y of equation (4) for the Lewis bases of Table III employing the softness-, the second and the fourth order density functional electronegativity -DFE and Ghosh-Biswas-GB based atomic radii values of chemical hardness of Tables V-VIII: the draws (a), (c), and (e) –for DFE, and (b), (d), and (f) – for GB computation frames, respectively.*

This strongly suggests that the Pearson classification of the chemical compounds against their enthalpy of formation is rather relative to chemical reaction considered and not to inner structural atoms-in-molecule information.

The second observation is that unlike the acids, the actual bases ordering looks quite similar, excepting the already criticized GB[2] scheme, for all employed finite difference, Ghosh-Biswas and density functional electronegativity recipes. Therefore, the present suggested soft-to-hard Lewis bases classification is that recommended by (30e) hierarchy – rooting on the most complex conceptual-computational containing algorithm.

From the bonding perspective, all discussed bases originate in hard-hard acid-base interactions in accordance with the introduced maximum hardness criteria (11).

Future studies on different molecular, atomic and ionic compounds are in progress, in view to further clarify the role of the maximum hardness index in elucidation of quantum nature of the chemical bond bonding as driven by inner electronic structures.

5. Conclusions

There is an accepted reality that the actual quantum chemistry needs specific conceptual and analytic tools to distinguish among subtle faces of the chemical bond and bonding nature. Such matter had traveled across the chemistry's history and appears more intriguing since the advent of quantum theory and structure computation. In this context, the aim to rationalize the chemical reactivity on the specific principles and postulates stands as a fundamental epistemological necessity; this is the position from where the actual study is unfolded.

Here, the hard and soft acids and bases and maximum hardness principles are assumed as fundamental principles of reactivity that, apart of their recognized mathematical justifications [18, 30], need no perpetual experimental or computational validation which should pay tribute to ad hoc assumptions or approximations.

Instead, the HSAB and MH principles should guide the chemical analysis through their related reactivity indices. Since the chemical hardness stands as a structural index another reactivity index – the maximum hardness index Y - was advanced in order to combine the both hardness principles with a consistent prediction of the hard-soft combined character of the chemical bonding and of the associated soft-to-hard ordering. This way, the chemical stability is assessed by means of maximum chemical hardness values with values from $-\infty$ to

maximum 1 reflecting the soft-hard (hard-soft) anti-bonding to soft-soft and hard-hard acid-base bonding hierarchies.

The advantage of the present methodology relies on linking the structural parameter hardness (η) with its maximum measure (Y) without benchmarking on certain reaction and on the associate enthalpy or energy for classification output.

However, the ordering is still dependent of the way of computation but the cutting role can be assessed to atoms-in-molecule most complex applied scheme of computation. Alternatively, a workable soft-to-hard ordering of Lewis acids and bases should be realized by counting of the statistical appearance frequency over systematically related schemes of computation. Nevertheless, a statistical based approach seems to be the key in building a sort of universal *soft<borderline<hard* classification of Lewis acids and bases.

An illustration of this concept was exposed for a selected series of molecular Lewis acids and bases using a breath way of analytical atoms-in-molecule implementation, from IP and EA finite difference up to density functional electronegativity based methods. Their soft-to-hard classification was facilitated by identifying the compounds grouped in "islands" on the Y(η) graphs. The fit with the Pearson's scheme of classification was about 33%, albeit with hard and soft recorded inversions for certain bases.

The present approach leaves open room for future assessment of the quantum chemical bond and bonding in isolate and reactive states through chemical indices derived from the assumed fundamental electronegativity and chemical hardness unified principles [29].

Acknowledgements

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