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Quantumchemical electronegativity and hardness indices for bonded atoms

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An analysis of the electronegativity (χ_A) and hardness (η_A) of a bonded atom (A) is given on the ground of the Hartree–Fock Hamiltonian and based on Mulliken population analysis. Practical expressions for χ_A and η_A are developed within the Koopmans approximation. Electronegativity equalization (EE) has not been pursued, partial EE has been obtained, though. The resulting indices χ_A and η_A describe correctly atoms in simple molecules. The directional effect of the substituent in the benzene ring is properly rationalized and enhanced by means of the electronegativity and hardness of the ring carbons.

1. Introduction

The modern concept of electronegativity has been derived by Parr and co-workers from the density functional theory [1,2].

$$\chi = -\left(\frac{\mathrm{d}E}{\mathrm{d}N}\right)_V . \tag{1}$$

Further work by Parr and Pearson [3] has demonstrated that the chemical hardness, first proposed by Pearson as a qualitative feature of acids and bases [4], also finds its roots in this theory [5]:

$$\eta = \frac{1}{2}\left(\frac{\mathrm{d}^2E}{\mathrm{d}N^2}\right)_V . \tag{2}$$

Despite the spectacular success of the density functional theory in providing support for the experimentally defined electronegativity and hardness, a coherent way for practical indexing of atoms and molecules has not yet been traced. Usefull approximations have recently been developed in order to derive the electronegativity and hardness indices from experimental data [6,7]; the possibility of their quantitative use in estimation of the charge-transfer energy has also been indicated [8]. The widespread interest in electronegativity studies [9] has not yet led to a consensus how much the progressing theory enhances the potential of experimental chemistry. A hint was recently given by Pearson [10,11]; after all, chemical observations were a source of both electronegativity and hardness concepts.

A quantumchemical solution to atomic electronegativities has first been proposed by Iczkowski and Margrave [12], explored by Hinze and Jaffé [13] and further studied recently by Bergman and Hinze [14]. The method was generalized for bonded atoms by Ponec [15]. Numerous studies for bonded atoms were typically based on the electronegativity equalization (EE) principle [16–29].

This work is devoted to the analysis of electronegativity and hardness in the framework of quantumchemical LCAO MO methods based on the self-consistent-field (SCF) Hartree–Fock–Roothaan (HFR) Hamiltonian. The atomic orbitals were chosen as the basis set of wavefunctions. This is the most natural choice in every chemically oriented study owing not only to their wide use in LCAO methods. Atomic orbitals have by now acquired a firm position in describing electronic systems of molecules and atoms by chemists. Orbitals and their hybrids seem to be treated by chemists more as a real property of atoms than as a tool to formally resolve quantum eigenproblems. It is straightforward to require that usefull electronegativity and hardness indices are built on the AO basis.

Exploring AOs in the HFR formalism is not without effect on the electronegativity, since properties of atomic sites become independently defined. It has been shown by Donnely and Parr in their pioneering paper [2] that only a choice of natural orbitals provides an a priori guarantee that the resulting electronegativities of all parts of the system are equal. For AOs, the electronegativity equalization (EE) cannot be taken for granted. Rather, EE is an independent constraint which can be introduced via redistribution of electrons in the population analysis. The problem is nontrivial since every population analysis implicitly involves a formal definition of "an atom in a molecule". Accepting the EE constraint induces a very particular concept of "an atom in a molecule" (see ref. [7] for an introductory discussion) which requires further study before it can be a source of useful atomic charges. Under these circumstances it is natural to give consideration to the Mulliken concept in order to check if electronegativity and hardness parameters derived from inherent HFR (AOs) results and based on Mulliken population analysis possess a meaning for a chemist, despite the inconvenience of possibly losing the electronegativity equalization. A unique conceptual solution to this problem has been presented in this work. Examination of numerical examples is also pursued. From a variety of available HF approaches the widely used CNDO and INDO methods have been selected. The ab initio procedures will produce equivalent results; concentrating on the experimentally tested semiempirical NDO methods leads to results which are easily confronted with experimental features known for molecules.

2. Electronegativity and hardness from the Hartree–Fock–Roothaan Hamiltonian

The eigenvalue problem for the closed shell system is formulated as [30]

$$\mathbf{FC}=\mathbf{SCE} \tag{3}$$

In the matrix representation (3) **F** denotes the matrix of the HFR operator, **S** the overlap matrix, **C** the LCAO-eigenvectors and **E** the orbital energies.

The elements of the energy matrix **F** for the closed shell entity in the atomic orbitals (AO) representation are given by

$$F_{kl}=H_{kl}+\sum_m \sum_n P_{mn}[(kl|mm)-0.5(kn|lm)], \tag{4}$$

or

$$F_{kl}=H_{kl}+G_{kl}, \tag{5}$$

where

$$G_{kl}=\sum_m \sum_n P_{mn} g_{kl,mn} \tag{6}$$

and

$$g_{kl,mn}=(kl|mn)-0.5(kn|lm). \tag{7}$$

The symbols in the above equations correspond to the standard labels commonly used in the literature [30,31].

The electronic energy of the system is given by the expression:

$$E=\sum_k \sum_l P_{kl}(H_{kl}+0.5\,G_{kl}). \tag{8}$$

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

$$\sum_k \sum_l P_{kl} S_{kl}=N. \tag{9}$$

Since the meaning of elements P_{kl} of the bond order matrix is the electron density, derivatives of the energy to P_{kl} will have a meaning of elemental electronegativity at the level of atomic orbitals (but not the orbital electronegativity) [2]:

$$\frac{\partial E}{\partial P_{kl}}=F_{kl}. \tag{10}$$

The elemental hardness can be derived accordingly:

$$\frac{\partial^2 E}{\partial P_{mn}\,\partial P_{kl}}=g_{mn,kl}. \tag{11}$$

Corresponding third and higher energy derivatives are identically zero (eq. (8)): $\partial^n E/\partial P^n=0$, $(n\geqslant 3)$.

The energy of the electronic system is, on the other hand, a function of the number of electrons. Although the real values of this function are limited to integral N, in the HFR method we follow a postulate, first used by Iczkowski and Margrave [12,32,33], and assume $E(N)$ as a continuous and differentiable function. Hence:

$$F_{kl} = \frac{\partial E}{\partial P_{kl}} = \frac{dE}{dN}\frac{\partial N}{\partial P_{kl}} = -\chi_M S_{kl}\,, \tag{12}$$

and

$$g_{mn,kl} = \frac{\partial^2 E}{\partial P_{mn}\partial P_{kl}} = \frac{d^2E}{dN^2}\frac{\partial N}{\partial P_m} S_{kl} = 2\eta_M S_{kl} S_{mn}. \tag{13}$$

χ_M and η_M are the electronegativity and hardness of the whole electronic system. One might expect from eq. (12) that $F_{kl}/S_{kl} = -\chi_M$ for any k, l and, in particular, that diagonal elements F_{kl} in the normalized basis set are all identical: $F_{kk} = F_{ll} = \ldots = -\chi_M$. Elements of the energy matrix calculated in the AO basis set do not meet this requirement; the distribution of the electron density between atomic orbitals is not bound by the requirements of the density functional theory [34]. This limitation, however, does not affect the defining equations (1) and (2). The meaning and value of χ_M and η_M cannot be dependent on the basis. Since in general F_{kl}/S_{kl} and $g_{mn,kl}/S_{kl}S_{mn}$ are not constant for F_{kl} and S_{kl} obtained in the AO basis set, an independent way of determination of χ_M and η_M must be established.

When energy derivatives are considered at the ground state of the given molecule (a closed shell entity), for $N = N_0$ and a constant external potential field V, we have:

$$\chi_M = -\frac{dE}{dN} = -\sum_k \sum_l \frac{\partial E}{\partial P_{kl}}\frac{dP_{kl}}{dN} \tag{14}$$

or (eq. (10))

$$\chi_M = -\sum_k \sum_l F_{kl} a_{kl}\,, \tag{15}$$

where

$$a_{kl} = \frac{dP_{kl}}{dN} \tag{16}$$

The molecular hardness η_M will be expressed accordingly:

$$\eta_M = \frac{1}{2}\frac{d^2E}{dN^2} = \sum_k \sum_l \left(\frac{1}{2}\frac{dF_{kl}}{dN} a_{kl} + F_{kl} b_{kl}\right), \tag{17}$$

where

$$b_{kl} = \frac{1}{2}\frac{d^2P_{kl}}{dN^2}\,. \tag{18}$$

Since

$$\frac{dF_{kl}}{dN} = \sum_m \sum_n \frac{\partial F_{kl}}{\partial P_{mn}}\frac{dP_{mn}}{dN} = \sum_m \sum_n a_{mn} g_{kl,mn}\,, \tag{19}$$

we obtain for the molecular hardness

$$\eta_M = \sum_k \sum_l \sum_m \sum_n \tfrac{1}{2} a_{kl} a_{mn} g_{kl,mn} + \sum_k \sum_l F_{kl} b_{kl}. \tag{20}$$

Two terms of a different origin contribute to the total molecular hardness, η_M. The second term is analogous in its form to the molecular electronegativity, eq. (15). It expresses the effect of attaching an extra electron to (or it losing from) the valence shell of the molecule; it may be called the *valence hardness*:

$$\eta_M^{val} = \sum_k \sum_l F_{kl} b_{kl}\,. \tag{21}$$

This valence hardness is invariant for a given molecule (as is the electronegativity, χ_M) and results for η_M^{val} in different LCAO MO methods must be the same within the accuracy of the method. This is not the case for the first term in eq. (20). This term finds its origin in $dF/dP \neq 0$ and, therefore, it is bound to the form of $F(P)$ dependence implied by the specific Hamiltonian.

3. Electronegativity and hardness of an "atom in a molecule"

The electronegativity of an atom (A) in a molecule (M) is by definition [35]

$$\chi_A \overset{\text{def}}{=} -\left(\frac{\partial E}{\partial N_A}\right)_{N_{B\neq A}}\,. \tag{22}$$

The derivative is subject to the same condition as eq. (14); N_A is the population of the A atom and $N = \sum N_A$ is the total number of electrons in the system. The electronegativity of the molecule can now be decomposed (eq. (14)):

$$\chi_M = -\sum_A \frac{\partial E}{\partial N_A}\frac{dN_A}{dN} = \sum_A \chi_A K_A\,, \tag{23}$$

where the K_A's are Fukui function indices [24–27]. In the AO basis:

$$K_A \overset{\text{def}}{=} \frac{dN_A}{dN} = \sum_{k\in A} \sum_l S_{kl} a_{kl}, \quad \sum_A K_A = 1\,. \tag{24}$$

Rewriting eq. (15) indicating atoms we obtain:

$$\chi_M = -\sum_A \sum_B \sum_{k\in A} \sum_{l\in B} F_{kl} a_{kl} . \tag{25}$$

By combining eqs. (23) and (25) the electronegativity of bonded atom becomes

$$\chi_A = -K_A^{-1} \sum_{k\in A} \sum_l F_{kl} a_{kl} . \tag{26}$$

The relation of χ_A to the orbital electronegativity introduced by Iczkowski and Margrave [12] can be demonstrated. By definition the orbital electronegativity is

$$\chi_k = -\frac{\partial E}{\partial n_k} , \tag{27}$$

where n_k is the population of the orbital, $\sum n_k = N_A$. Eq. (23) can now be rewritten, mutatis mutandis,

$$\chi_M = \sum_A \sum_{k\in A} \chi_k K_k \tag{28}$$

and

$$K_k \overset{\text{def}}{=} \frac{dn_k}{dN} = \sum_l S_{kl} a_{kl} ; \quad \sum_{k\in A} K_k = K_A . \tag{29}$$

Using eq. (15) gives directly χ_k

$$\chi_k = -K_k^{-1} \sum_l F_{kl} a_{kl} . \tag{30}$$

Then, it is straightforward to show

$$\chi_A = K_A^{-1} \sum_{k\in A} \chi_k K_k , \tag{31}$$

which is an analogue of eq. (23). The electronegativity attributed to an atom is a weighted sum of the corresponding orbital electronegativities. It must be stressed again, that the electronegativity equalization principle does hold neither for χ_A nor for χ_k since F_{kl} and S_{kl} obtained for AOs are not bound by the condition $F_{kl}/S_{kl} = -\chi_k = \text{const}$. If they were, then EE would read as $\chi_k = \chi_A = \chi_M$ which is true for the basis of natural orbitals [1].

Decomposition of the molecular hardness into atomic contributions can be, in principle, performed in a similar manner. However, the lack of the EE principle, makes the definition of atomic hardness a sensitive point for further analysis. Most naturally, we can write for a bonded atom

$$\eta_A = \frac{1}{2} \frac{\partial \chi_M}{\partial N_A} , \tag{32}$$

which readily leads to

$$\eta_M = \sum_A \eta_A K_A \tag{33}$$

and

$$\eta_A = K_A^{-1} \sum_{k\in A} \sum_l \left(\tfrac{1}{2} F'_{kl} a_{kl} + F_{kl} b_{kl}\right) , \tag{34}$$

where $F'_{kl} = dF_{kl}/dN$ is given by eq. (19). On the other hand, an additional relation is true (cf. eq. (23)):

$$\eta_A = \frac{1}{2} \frac{\partial \chi_M}{\partial N_A} = \sum_B \eta_{AB} K_B , \tag{35}$$

where

$$\eta_{AB} = \frac{1}{2} \frac{\partial \chi_A}{\partial N_B} = (K_A K_B)^{-1} \sum_{k\in A} \sum_{l\in B} \left(\tfrac{1}{2} F'_{kl} a_{kl} + F_{kl} b_{kl}\right) . \tag{36}$$

Eq. (35) holds if and only if $(\partial N_A/\partial N_B)_{N_0,V} = 0$, which physically means that the source of electrons is external to the molecule, and changing the population of an atom by dN_A does not alter the population of other atoms. Eq. (36) introduces an element of the symmetric atomic hardness matrix $\underset{\sim}{\boldsymbol{\eta}}$. If $\boldsymbol{K}$ stands for a vector of K_A and $\boldsymbol{\eta}$ for the vector of η_A we have simply

$$\eta_M = \boldsymbol{K}\boldsymbol{\eta} = \boldsymbol{K}\underset{\sim}{\boldsymbol{\eta}}\boldsymbol{K}^T . \tag{37}$$

In a general study of electronegativity and the chemical potential Parr and co-workers [34] and Politzer and Weinstein [35] have shown, that the EE rule induces a specific way of partitioning the electrons in the molecule to obtain atoms as non-interacting fragments. In such a case $d\chi_A/dN_B = 0$ and the hardness matrix $\underset{\sim}{\boldsymbol{\eta}}$ would be diagonal. The nondiagonal form of $\underset{\sim}{\boldsymbol{\eta}}$ is one more consequence of abandoning EE in favor of atomic orbitals. In consequence, η_A and not η_{AA} elements deserve the name of atomic hardness.

In analogy to the orbital electronegativity also orbital hardness can be introduced:

$$\eta_k = \frac{1}{2} \frac{\partial \chi_M}{\partial n_k} \quad \text{and} \quad \eta_{kl} = \frac{1}{2} \frac{\partial \chi_k}{\partial n_l} . \tag{38}$$

The following summation rules can be demonstrated:

$$\eta_A = K_A^{-1} \sum_{k \in A} K_k \eta_k \quad \text{and}$$

$$\eta_{AB} = (K_A K_B)^{-1} \sum_{k \in A} \sum_{l \in B} K_k K_l \eta_{kl} . \tag{39}$$

4. Softness

The definition of atomic hardness η_A (eq. (32)) represents a conventional choice and opens the route to atomic hardness parameters from LCAO MO calculation. However, the much needed chemical information – how will the atomic charges change upon ionization of the molecule – is not directly available from η_A. A simple expectation is that this change (ΔN_A) will be large for "soft" atoms; "hard" atoms are those resistant to ionization. Formally, softness σ is the inverse of hardness [3]

$$\sigma_M = \frac{2dN}{d\chi_M} \quad \text{molecular softness} , \tag{40}$$

$$\sigma_A = \frac{2dN_A}{d\chi_M} \quad \text{atomic softness} . \tag{41}$$

If no other processes except ionization are considered, σ_A and σ_M are bound by the simple relation [27]

$$\sigma_A = K_A \sigma_M = K_A / \eta_M . \tag{42}$$

Molecular softness is just the inverse molecular hardness $\sigma_M = 1/\eta_M$. However, since $\chi_M = \chi_M(N_A, N_B, ...)$ a similar relation for atomic softness would not be true. Eqs. (33) and (42) lead directly to

$$\sum \eta_A \sigma_A = 1 \tag{43}$$

and

$$\sigma_M = \sum \sigma_A . \tag{44}$$

The above relationships (which can be readily extended to orbitals) resolve ambiguities concerning additivity of atomic softness discussed by Yang et al. [36]. From eqs. (23), (42), (44) also follows

$$\chi_M = \frac{\sum \chi_A \sigma_A}{\sum \sigma_A} . \tag{45}$$

This relationship has been known since the early work of Parr and co-workers [37]. Recently its derivation for an electrodynamical model of an atom has also been given [7]. Until now it was unclear what kind of electronegativity parameters must be used in eq. (45) and if hardness instead of softness can be used. This work gives a rigorous meaning both to the parameters and to the equation.

5. Estimation of a_{kl} and b_{kl}

The calculation of the energy derivatives of either orbital, atom or the molecule itself will not be complete unless the elementary derivatives a_{kl} (eq. (16)) and b_{kl} (eq. (18)) are attributed numerical values. Unlike the F_{kl}, S_{kl} and $g_{kl,mn}$ integrals, a_{kl} and b_{kl} are not directly produced by an LCAO MO method, in fact they can only be approximated using reasonable criteria. Elementary conditions to be met are (eq. (8)):

$$\sum_k \sum_l S_{kl} a_{kl} = 1 , \tag{46}$$

$$\sum_k \sum_l S_{kl} b_{kl} = 0 . \tag{47}$$

For a closed shell molecule in its ground state, the bond order matrix elements P_{kl} are given by [30,31]

$$P_{kl} = 2 \sum_i^{occ} C_k^i C_l^i . \tag{48}$$

The available data for P_{kl} are necessarily limited to those for a molecule and its ions. The $P_{kl}(N)$ function may then be approximated and differentiated but the accuracy of such a procedure will hardly be satisfying. There is little chance to get a better insight in the $P_{kl}(N)$ function for a nonintegral number of electrons N; the very existence of such a continuous function is subject to a postulate only. This prompts to using an alternative, albeit crude, approximation offered by the Koopmans theorem. According to Koopmans, the effect of ionization of the closed shell electronic system will be limited, approximately, to the HOMO and LUMO orbitals. If the $P_{kl}(N)$ function is expanded into the Taylor series and higher derivatives of P_{kl} are neglected we have:

$$P_{kl}(N)=P_{kl}(N_0)+\left(\frac{\mathrm{d}P_{kl}}{\mathrm{d}N}\right)_{N_0}\Delta N+\frac{1}{2}\left(\frac{\mathrm{d}^2P_{kl}}{\mathrm{d}N^2}\right)_{N_0}(\Delta N)^2. \tag{49}$$

At the level of the Koopmans approximation is obtained

$$P_{kl}(N_0-1)=P_{kl}(N_0)-C_k^{\mathrm{HOMO}}C_l^{\mathrm{HOMO}}, \tag{50}$$

$$P_{kl}(N_0+1)=P_{kl}(N_0)+C_k^{\mathrm{LUMO}}C_l^{\mathrm{LUMO}}. \tag{51}$$

Consequently, then:

$$\bar{a}_{kl}=\left(\frac{\mathrm{d}P_{kl}}{\mathrm{d}N}\right)_{N_0}=\tfrac{1}{2}\,(C_k^{\mathrm{LUMO}}C_l^{\mathrm{LUMO}}+C_k^{\mathrm{HOMO}}C_l^{\mathrm{HOMO}}), \tag{52}$$

$$\bar{b}_{kl}=\frac{1}{2}\left(\frac{\mathrm{d}^2P_{kl}}{\mathrm{d}N^2}\right)_{N_0}=\tfrac{1}{2}\,(C_k^{\mathrm{LUMO}}C_l^{\mathrm{LUMO}}-C_k^{\mathrm{HOMO}}C_l^{\mathrm{HOMO}}). \tag{53}$$

Eq. (49) cannot be claimed as exact function for $P_{kl}(N)$, its role is merely instrumental in providing the $\bar{a}_{kl}$ and $\bar{b}_{kl}$ values. The $\bar{a}_{kl}$ and $\bar{b}_{kl}$ in eqs. (52) and (53) should be considered as an average for a_{kl} and b_{kl} around N_0 rather than as rigorously defined derivatives. This should not be disturbing, considering the approximate character of the $P_{kl}(N)$ function. However, the results obtained by using approximate $\bar{a}_{kl}$ and $\bar{b}_{kl}$ values cannot be claimed to be exact (mathematically) derivatives. From now on, electronegativity and hardness become indices rather than functional derivatives.

The value of such results may be estimated by comparing with expected results for electronegativity and hardness of the molecule (χ_{M} and η_{M}). The Mulliken definition gives:

$$\begin{aligned}\chi_{\mathrm{M}}^{\mathrm{Mulliken}}&=\tfrac{1}{2}(I+A)\\&=\tfrac{1}{2}(\epsilon^{\mathrm{HOMO}}+\epsilon^{\mathrm{LUMO}})\\&=-\sum_k\sum_l F_{kl}(C_k^{\mathrm{HOMO}}C_l^{\mathrm{HOMO}}+C_k^{\mathrm{LUMO}}C_l^{\mathrm{LUMO}})\\&=-\sum_k\sum_l F_{kl}\bar{a}_{kl},\end{aligned} \tag{54}$$

which is identical with eq. (15).

Parr and Pearson's definition of hardness [3] at the level of the Koopmans approximation leads to

$$\begin{aligned}\eta_M^{\mathrm{val}}&=\tfrac{1}{2}(I-A)\\&=-\tfrac{1}{2}(\epsilon^{\mathrm{HOMO}}-\epsilon^{\mathrm{LUMO}})\\&=\tfrac{1}{2}\sum_k\sum_l F_{kl}(C_k^{\mathrm{LUMO}}C_l^{\mathrm{LUMO}}-C_K^{\mathrm{HOMO}}C_l^{\mathrm{HOMO}})\\&=\sum_k\sum_l F_{kl}\bar{b}_{kl},\end{aligned} \tag{55}$$

which is identical to eq. (21).

6. χ_{A} and η_{A} in the framework of the NDO approximation

The expressions for atomic electronegativity and hardness allow direct calculation of χ_{A} and η_{A} (or η_{AB}) by any LCAO MO method. It is interesting to demonstrate the decomposition of these quantities into various terms in order to gain more understanding how χ_{A} and η_{A} indices can be compared to other measures of electronegativity and hardness. Analysis based on the CNDO approximation [31] is particulary attractive.

6.1. Electronegativity

The definition (eq. (26)) yields:

$$\chi_{\mathrm{A}}=\chi_{\mathrm{A}}^0(q_{\mathrm{A}})+V_{\mathrm{A}}^{\mathrm{ion}}+V_{\mathrm{A}}^{\mathrm{cov}}. \tag{56}$$

Terms have been separated following natural criteria:

$$V_{\mathrm{A}}^{\mathrm{cov}}=-K_{\mathrm{A}}^{-1}\sum_{k\in\mathrm{A}}\sum_{l\neq k}F_{kl}\bar{a}_{kl}. \tag{57}$$

This term may be labeled the covalent potential, in order to be distinguished from $V_{\mathrm{A}}^{\mathrm{ion}}$ which contains off-diagonal, charge depending contributions

$$V_{\mathrm{A}}^{\mathrm{ion}}=\sum_{\mathrm{B}\neq\mathrm{A}}q_{\mathrm{B}}\gamma_{\mathrm{AB}}. \tag{58}$$

Diagonal terms were separated in χ_{A}^0

$$\chi_{\mathrm{A}}^0=\mu_{\mathrm{A}}+\tfrac{1}{2}\gamma_{\mathrm{AA}}K_{\mathrm{A}}^{-1}\sum_{k\in\mathrm{A}}P_k\bar{a}_{kk}+(q_{\mathrm{A}}-\tfrac{1}{2})\gamma_{\mathrm{AA}}, \tag{59}$$

where the charge independent part μ_{A} is:

$$\mu_{\mathrm{A}}=\tfrac{1}{2}K_{\mathrm{A}}^{-1}\sum_{k\in\mathrm{A}}(I_k+A_k)\bar{a}_{kk}. \tag{60}$$

In eqs. (58–60), q, γ, I and A denote the atomic charge, Coulomb integral, ionization energy and electron affinity, respectively.

The expression for χ_A contains directly not only the selfterm (χ_A^0) usually focused on in electronegativity studies, but also the effect of the bonding potential.

6.2 Hardness

η_A in the defining equation (eq. (34)) can be divided into the valence and HF contributions in very much the same way as η_M (cf. eq. (20)). The valence hardness η^{val} can be decomposed into a set of terms directly related to χ_A

$$\eta_M^{val} = \eta_A^0 + \eta_A^{ion} + \eta_A^{cov}, \tag{61}$$

where

$$\eta_A^0 = -\tfrac{1}{2}K_A^{-1}\sum_{k\in A}(I_k + A_k)\bar{b}_{kk} - \gamma_{AA}(q_A - \tfrac{1}{2})K_A^{-1}\sum_{k\in A}\bar{b}_{kk} - \tfrac{1}{2}\gamma_{AA}K_A^{-1}\sum_{k\in A}P_{kk}\bar{b}_{kk}, \tag{62}$$

$$\eta_A^{ion} = -V_A^{ion}K_A^{-1}\sum_{k\in A}\bar{b}_{kk}, \tag{63}$$

$$\eta_A^{cov} = K_A^{-1}\sum_{k\in A}\sum_{l\neq k}F_{kl}\bar{b}_{kl}. \tag{64}$$

Decomposition of the interatomic η_{AB}^{val} hardness ($A \neq B$) is also simple under CNDO approximation:

$$\eta_{AB}^{val} = (K_A K_B)^{-1}\sum_{k\in A}\sum_{l\in B}(H_{kl}^{core} - 0.5P_{kl}\gamma_{AB})\bar{b}_{kl}. \tag{65}$$

The HF contributions to the hardness can be expressed in analogous fashion.

7. Results and discussion

The conceptual result of this work as presented in the preceeding sections has been tested numerically for many molecules by means of the simple semiempirical, all-valence, recently modified INDO method [38–40].

7.1. Inherent electronegativity and hardness

Standard electronegativities χ_A^0 for bonded atoms and their dependence on the atomic charge (q_A) are among the most easily appreciated results of the calculation. Clearly, the linear (statistical) dependence $\chi_A^0(q_A)$ has been established; figs. 1 and 2 serve as examples. This is by no means unexpected, as such a linear function has been a key assumption for some time. Here, however, it comes about as a relation between the independently calculated q_A and χ_A^0 unrestricted by the EE principle. This relationship is a source of two important parameters: $\bar{\chi}_A$, the standard average electronegativity (intercept) and $\bar{\eta}_A$, the standard average hardness (slope).

$$\chi_A(q_A) = \bar{\chi}_A + q_A\bar{\eta}_A. \tag{66}$$

$\bar{\chi}_A$ and $\bar{\eta}_A$ appear to describe inherent properties of an atom manifested through its bonding to a variety of species. Such a point of view has been first pro-

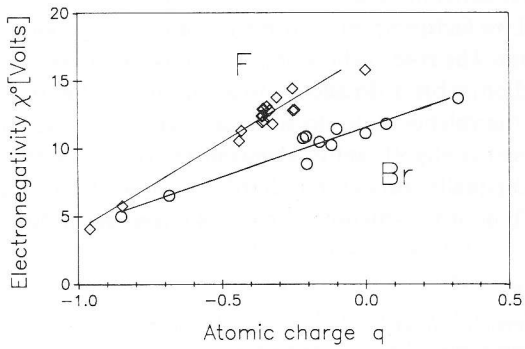

Fig. 1. Standard electronegativity of bonded fluorine and bromine as a function of the actual atomic charge.

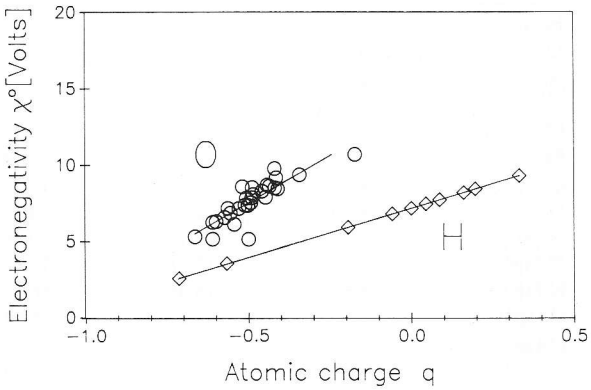

Fig. 2. Standard electronegativity of bonded oxygen and hydrogen as a function of the actual atomic charge.

posed by Huheey [41], who used the equation $\chi=\chi_v+bq$ for the valence state electronegativities of a free atom. Results of this work are compared to Huheey's in table 1. There is a crucial difference between the two sets of data: one is for a free atom in a chosen valence state, the other is for a bonded atom whose valence state is indirectly taken into account.

Both the inherent electronegativity ($\bar{\chi}_A$) and the hardness ($\bar{\eta}_A$) for bonded atoms differ significantly from those for free atoms. This is clear for univalent atoms, where details concerning the choice of the valence state do not obscure the picture. Atoms are considerably softer when bonded; still fluorine is hardest, lithium and sodium are softest. Bonded hydrogen appears to be slightly softer than iodine, while free hydrogen is harder than chlorine. The electronegativity of bonded halogens is remarkably higher than that of the corresponding free atoms. The latter effect has been anticipated in earlier work [7].

Two factors seem to affect $\bar{\chi}_A$ and $\bar{\eta}_A$ for a bonded atom. The role of the valence state is clearly seen for carbon, table 1. In accord to a common belief based on the valence state electronegativities of free atoms, C(sp) is slightly more electronegative than C(sp^2) and equally, moderately hard. Surprisingly, the sp^2 carbon in five-member rings is somewhat harder. A bonded C(sp^3) appears the most electronegative of all and also the hardest. Also N(sp^3) is more electronegative than N(sp). The collection of molecules for oxygen was insufficient to distinguish between valence states while keeping the charge interval broad enough.

The second factor affecting $\bar{\chi}_A$ and $\bar{\eta}_A$ is the chemical environment. When considered separately, CF_3 carbon ($\bar{\eta}=38.04$ V/*el*) is harder than CH_3 carbon ($\bar{\eta}=17.91$ V/*el*), the latter being more electronegative. Both CF_3 and CH_3 seem to become much softer when bonded to an aromatic ring ($\bar{\eta}=8.8$ V/*el*). The phenomenon itself has been known experimentally as *symbiosis* [42]: hard F makes C harder than soft H can, a soft phenyl ring makes the vicinal carbon equally soft. This symbiotic behavior occurs obviously beyond the charge dependence of $\bar{\chi}_A(q_A)$; its refinement is crucial before a reliable general list of $\bar{\chi}_A$ and $\bar{\eta}_A$ can be completed. The data for C(sp^3) in table 1 are average for all types of bonded carbon.

7.2. Ionic potential

The straightforward meaning of the term V^{ion} in eq. (56) hints to its correlation with the known field effect of the substituent. A substituted phenyl ring has

Table 1
Inherent electronegativity and hardness for atoms

Atom	Free atom [a]		Bonded atom [b]				
	χ_v [V]	b [V/el.]	$\bar{\chi}$ [V]	$\bar{\eta}$ [V/el.]	R [c]	n [d]	Δq [e]
H	7.17	12.85	7.18	6.40	0.999	10	1.047
Li	3.10	4.57	2.07	3.00	0.994	6	0.848
Na	2.80	4.67	1.18	3.23	0.998	6	0.870
F	12.18	17.36	16.87	12.80	0.970	21	0.961
Cl	9.38	11.30	12.73	8.15	0.949	20	1.117
Br	8.40	9.40	11.58	7.27	0.962	12	1.175
I	8.10	9.15	10.22	6.88	0.998	7	1.211
O	9.65 [f]	15.27 [f]	13.15	11.21	0.900	29	0.665
N (all)	7.39 [f]	13.10 [f]	10.06	8.99	0.933	53	1.615
N (sp^3)	11.54	14.78	11.61	9.68	0.864	12	0.605
N (sp)	15.68	16.46	10.58	12.32	0.772	15	0.606
C (sp^3)	7.98	13.27	9.21	8.41	0.829	41	1.765
C (sp^2)	8.79	13.67	6.09	7.57	0.990	66	1.388
C (sp^2) [g]	8.79	13.67	6.34	8.37	0.996	41	0.796
C (sp)	10.39	14.08	6.74	7.55	0.906	28	1.255

[a] Ref. [39]. [b] This work. [c] Correlation coefficient. [d] Number of points. [e] Charge interval. [f] p valence state. [g] Five-member rings.

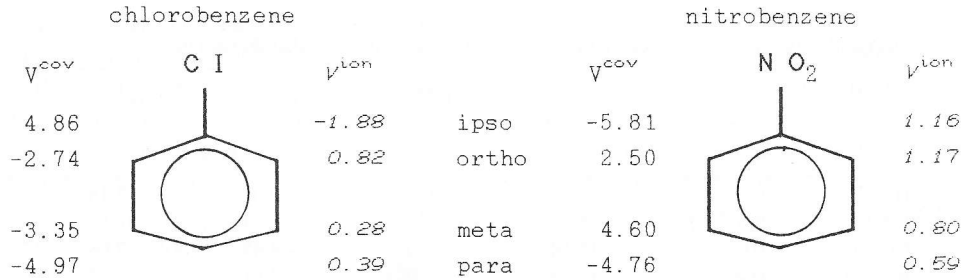

Fig. 3. Ionic and covalent potentials at the ring carbons in chlorobenzene and nitrobenzene.

been selected as a test. The ionic potential decreases with increased distance from a substituent (fig. 3). The *para*-carbon being a probe, a linear relationship between the field substituent constant by Swain and Lupton [43] and the ionic potential has been established (fig. 4):

$$V^{\text{ion}} = 0.442\, F + 0.061, \quad (\text{corr. coeff. } R = 0.897)\,,$$

or

$$F \approx 2.26\, V^{\text{ion}}\,.$$

A similar relation holds for the Taft inductive index σ_I [44]:

$$V^{\text{ion}} = 7.09\, \sigma_I + 0.052, \quad (\text{corr. coef. } R = 0.891)\,,$$

or

$$\sigma_I \approx 1.41\, V^{\text{ion}}\,.$$

The *meta*-carbon ionic potential follows a similar pattern. For small, partially ionic molecules, the ionic

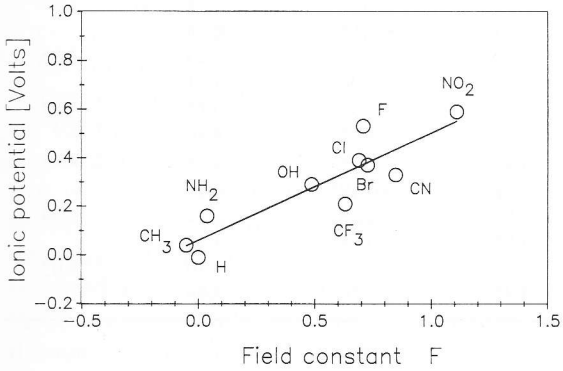

Fig. 4. Ionic potential at the *para*-carbon atom in substituted benzenes, as a function of the field constant F by Swain and Lupton (ref. [43]).

potentials show truly electrostatic behavior, table 2.

7.3 Covalent potential

This parameter resulting from eq. (59) seems to be equally interesting as it is complex. Rigorously, it expresses a change in the bond covalent energy when the number of electrons on one atom is affected. One can hardly think of a chemical situation that would correspond to such a pure effect. Yet the meaning of V^{cov} in small molecules gives little doubt (table 2). In hydrogen halides the covalent potentials show remarkable difference between hydrogen and halogen atoms. The role of H in the overall covalent energy is considerably more important (by V^{cov} in table 2). One is led to presume that engaging H in HX in an interaction with another species, as e.g. H_2O, will lower the covalent energy, thus leading to the ionization of HX, much more so than if the halogen atom were affected. This very reasonable guess provides a hint toward the understanding of V^{cov}. Another hint comes from analyzing covalent potentials on carbons in substituted benzenes (fig. 3).

There is a dramatic difference in V^{cov} between ϕ_{Cl} and ϕ_{NO_2}, the ionic potentials being understood and regular. The V^{cov} indices for the *meta*-, *ortho*- and *ipso*-positions not only differ by 5–10 V (ϕ_{Cl} versus ϕ_{NO_2}) but also have opposite signs. Known the chemical behavior of halobenzenes and nitrobenzene in electrophilic substitution, the authors were tempted to seek a correlation between V^{cov} and the σ_m Taft constant as a measure of the resonance effect [44]. While the trends are similar, no reasonable correlation could be established. This may have its explanation in the complexity of both σ_m and V^{cov}. The inductive constant σ_I comes from an analysis of the inductive effect in pure form, by choosing an appro-

Table 2
Electronegativity of atoms bonded in diatomic molecules; ionic and covalent potential are also shown (in V)

Molecule	Atom	Charge transfer q	χ_A^0	V^{ion}	V^{cov}	χ_A	χ_M
H_2	H	0.0	7.18	0.0	0.0	7.18	7.18
F_2	F	0.0	15.80	0.0	−5.54	10.26	10.26
Cl_2	Cl	0.0	12.14	0.0	−4.47	7.68	7.68
Br_2	Br	0.0	11.13	0.0	−3.61	7.53	7.53
I_2	I	0.0	10.02	0.0	−2.83	7.19	7.19
HF	H	0.333	9.32	−3.45	−8.86	−3.00	6.88
	F		12.83	3.45	−4.48	11.81	
HCl	H	0.197	8.45	−1.60	−7.78	−0.93	6.15
	Cl		10.99	1.60	−3.41	9.18	
HBr	H	0.161	8.21	−1.28	−7.41	−0.48	6.03
	Br		10.48	1.28	−3.08	8.69	
HI	H	0.087	7.74	−0.63	−6.65	0.46	6.03
	I		9.97	0.63	−2.50	8.11	
ClF	Cl	0.247	14.18	−1.88	−3.13	9.17	8.19
	F		12.85	1.88	−9.62	5.10	
BrF	Br	0.323	13.71	−2.40	−2.46	8.84	7.99
	F		11.80	2.40	−9.53	4.67	
IF	I	0.441	13.33	−3.00	−1.72	8.61	8.04
	F		10.55	3.00	−8.25	5.31	
BrCl	Br	0.072	11.82	−0.46	−3.36	8.00	7.61
	Cl		11.37	0.46	−4.76	7.07	
ICl	I	0.194	11.51	−1.15	−2.50	7.86	7.53
	Cl		10.48	1.15	−4.70	6.93	
IBr	I	0.119	10.86	−0.68	−2.64	7.55	7.45
	Br		10.25	0.68	−3.61	7.32	
LiH	Li	0.562	3.74	−2.71	1.37	2.40	4.80
	H		3.57	2.71	2.14	8.42	
LiF	Li	0.848	4.78	−4.64	−0.19	−0.05	5.15
	F		5.79	4.64	−0.17	10.26	
LiCl	Li	0.702	4.16	−3.46	−0.20	0.50	5.39
	Cl		6.85	3.46	−0.15	10.16	
LiBr	Li	0.685	4.09	−3.43	−0.20	0.45	5.20
	Br		6.54	3.43	−0.15	9.83	
LiI	Li	0.604	3.76	−2.95	−0.23	0.58	4.86
	I		6.18	2.95	−0.15	8.98	
NaH	Na	0.714	3.38	−3.04	0.79	1.13	3.55
	H		2.60	3.04	1.08	6.71	
NaF	Na	0.961	4.37	−4.47	−0.07	−0.18	4.17
	F		4.10	4.47	−0.07	8.50	
NaCl	Na	0.870	4.01	−3.83	−0.22	−0.05	4.47
	Cl		5.21	3.83	−0.19	8.85	
NaBr	Na	0.852	3.94	−3.83	−0.23	−0.12	4.34
	Br		5.01	3.83	−0.18	8.66	
NaI	Na	0.790	3.70	−3.53	−0.27	−0.10	4.03
	I		4.66	3.53	−0.20	7.99	

priate set of saturated molecules. The σ_m or R resonance constant by Swain and Lupton [43] originate as a mere difference of the overall Hammett constant and the separately established σ_I. Since the Hammett substituent constant σ is a relative measure (versus benzoic acid), it seemed more appropriate to chose

the difference $\delta_C = (\chi_C - \chi_{benzene}) - V_C^{ion}$ as a relative measure of the resonance effect in substituted benzenes. δ_C still contains the covalent potential on C, but also an effect of change in χ^0 upon substitution of benzene. A correlation was observed with the resonance constant R of Swain and Lupton:

$$\delta_{meta} = 7.15R, \quad (\text{corr. coeff. } R = 0.792) .$$

This rather encouraging result indicates that indeed V^{cov} may describe in pure form what is known as the resonance effect, but this is obscured in experimental data by other effects hidden in the Hammett constant.

7.4. Electronegativity of bonded atoms

For a chemist, each atom possesses some mysterious power to attract electrons for which Pauling provided a qualitative measure. By thinking so, chemists describe an atom as such, thus referring to its inherent property. This philosophy is readily extended to ions and, in a way, to molecules, since electronegativity is experimentally accessible for these entities [45]. This is not so with bonded atoms. Do they also possess the individual power to attract electrons? Sanderson's philosophy of electronegativity equalization precludes even a discussion of that question. There is, however, a simple chemical argument indicating differences between bonded atoms: the difference between bonded carbon and nitrogen cannot be reduced to the difference of their charges. A bonded atom may be attributed its specific power which is stimulated by three factors:

(i) some inherent original property,
(ii) the actual state of an atom (its charge),
(iii) the interaction with neighbours (potential).

The electronegativities (χ) given by eq. (22) and eq. (56) provide a measure to all three effects. The standard electronegativity (eq. (59)) contains but the first two effects. Results for diatomic molecules are shown in table 2. The first conclusion is that the standard electronegativities of bonded A and B atoms are balanced, if not equalized in AB, a natural effect of the charge transfer. Electronegativities χ, in turn, show dramatical differences between A and B atoms. Electronegativities χ_A and χ_B reveal an electropositive and electronegative end of the AB molecule, sometimes in a quite unexpected fashion: halogen is more electronegative than hydrogen in HX, while hydrogen, not cation, electronegativity is dominant in hydrides. In alkali halides the halogen is more electronegative due to the strong potential from the cation. The electronegativity of the AB molecule is always somewhere in the middle between χ_A and χ_B.

Verification of these results is hardly possible. Qualitatively they do not contradict chemical knowledge: the electronegative and electropositive end of the molecule is properly assigned. Striking is a prediction: in H_2O $\chi_O = 8.20$ V and $\chi_H = -3.00$ V. Thus association of water with hydrogen halides is correctly expected as X–H...OH_2 or H–X...HOH. In each case, bonded hydrogen should act as electron donor (transmitter!), due to its lower electronegativity.

Mapping the electronegativity χ_C on ring carbons in monosubstituted benzenes reveals dramatic differences in electronegativity (table 3). The site preferred for electrophilic attack is the most electronegative one; still the electrophile (e.g. Cl_2 in table 2) acts as an acceptor being even more electronegative itself. The stimulating effect of the substituent on reactivity (I^+, I^-) is hardly seen, except, maybe in overall electronegativity of the molecule, which is lower than in benzene for I^+ substituents and higher for I^-.

Electronegativity predicts the addition of HX to a double bond in CH_3–HC=CH_2 in accord to the Markovnikov rule: $\chi_{CH_2} = 5.75$ V, $\chi_{CH} = 5.35$ V; the more electronegative halogen is directed to the relatively electropositive center CH while hydrogen goes to CH_2.

Table 3
Electronegativity of ring carbons in monosubstituted benzenes (in V). The electronegativity of the molecule (χ_M) is also given

Molecule	C-*orto*	C-*meta*	C-*para*	χ_M
ϕ_{CH_3}	3.45	2.76	11.12	5.81
ϕ_{Br}	3.32	2.17	11.27	5.97
ϕ_{Cl}	3.59	2.52	11.38	6.03
ϕ_F	3.96	2.91	11.48	6.09
ϕ_{OH}	3.68	2.55	11.20	5.82
ϕ_{NH_2}	3.43	1.27	10.32	5.30
ϕ_{CHO}	5.21	6.36	6.58	6.59
ϕ_{COOH}	5.97	6.06	6.22	6.42
ϕ_{CN}	5.60	6.77	6.23	6.27
ϕ_{NO_2}	9.53	11.58	2.05	7.19
benzene	5.86	5.86	5.86	5.86

7.5. Softness

Softness of a free atom, $(I-A)^{-1}$ has been shown to be directly related to its radius [46], a similar property was observed for diatomic homonuclear molecules: $(I-A)^{-1}=0.9\ (4\pi\epsilon_0 R_{xx})$ [37]. The proportional relation between atomic radii and softness was also demonstrated for the electrodynamical model of an atom [7], $\sigma=8\pi\epsilon_0 R$. Atomic radii calculated from this latter formula for atoms in diatomic molecules (see data in table 4) are typically 20–30% smaller than chemical covalent radii. For larger molecules, the geometrical meaning of the softness σ is lost entirely; unreasonable halogen radii are obtained in halobenzenes: $R_F=0.04$ Å, $R_{Cl}=0.145$ Å, $R_{Br}=0.230$ Å.

A hint how to ease this discomfort comes from the work of Yang et al. [36]. These authors argued that molecular softness is an average rather than a sum of the free atom softnesses, $\sigma_M=N^{-1}\sum\sigma'_A$. Hence, $\sigma'_A=N\sigma_A$, (eq. (44)), where N is the number of atoms in the molecule. This novel softness σ' gives more realistic radii for halogen in the aforementioned example of halobenzenes: $R_F=0.48$ Å, $R_{Cl}=1.74$ Å, $R_{Br}=2.76$ Å. Such radii are not invariant, though, and vary considerably between molecules: R_F is 0.96 Å in HF and 0.63 Å in ClF. Thus σ' can hardly be identified as a universal parameter of an atom, as proposed by Yang. Except for free atoms and in homonuclear molecules, the softnesses, σ', are not bound to be the reciprocal of the chemical hardness. Eq. (43) holds as $\sum\eta_A\sigma'_A=N$, but the electrodynamical relation $\eta_A\sigma'_A=1$ is not obeyed. Although the Yang softnesses σ' do not have the correct meaning of derivatives as σ's do, they may be used safely in the important eq. (45), where the factor N would cancel. Thus, using atomic radii $R\approx\sigma'$ in this equation is also justified. However the softness could not be replaced by a reciprocal atomic hardness η_A^{-1}.

The longstanding belief that softness is equivalent to the inverse hardness has been motivated by the properties of free atoms and molecules. A review of table 4 discloses that this is rarely true for bonded atoms; such is the case of an anion in a considerable number of ionic molecules. The physical meaning of σ and η is not identical according to their definitions employed in this work (eqs. (32) and (41)). In σ ionization of the molecule is implied, while in η a change in atomic charge of one particular atom is assumed. It is yet to be seen, which one provides the more practical description of a bonded atom.

7.6. Hardness

The meaning of atomic hardness is not as easily rationalized as the electronegativity alone. Sample data for diatomic molecules and substituted benzenes are given in table 4 and table 5, respectively. Obviously, the two bonded atoms in an AB molecule possess very different hardness properties, typically $\eta_A<\eta_M<\eta_B$, with higher hardness accompanying high electronegativity, table 2. Bonded atoms may show hardnesses very different from that in their free state, e.g. (all data in Volts/electron): $\eta_{Cl}=4.70$, $\eta_{Cl/HCl}=9.70$, $\eta_{Cl/ICl}=3.33$. Although η_A depends on how the atom is bonded, no direct relation to the atomic charge was determined. In some instances η_A is quite surprizing: 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 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 the halide anion is very hard. This would not be true for a free anion, hence the interaction (mainly electrostatic) with the partner must be responsible for the effect. The inverse softness, sometimes unreasonably high for the set of atoms in table 4, does not show this effect of exchanging hardness.

The usefullness of the hardness parameter for a chemist can hardly be seen from the data in table 4; diatomic molecules are rarely partners in acid–base interactions, where hardness has a proven role to play. But still, looking at hydrogen halides, the more electronegative and hard halogen is less likely to be a reactive end of the HX molecule than the soft hydrogen of very low electronegativity. In general, hardness should probably be used in conjunction with electronegativity only, to make a judgement on reactivity. This is the case in substituted benzenes, where the most electronegative site is also the hardest, and this may explain why it is preferred by an (hard) electrophile as Cl_2 (HSAB rule).

Table 4
Hardness and softness of atoms in diatomic molecules (in V/el.)

Molecule (M)	Atom (A)	σ_A^{-1}	η_A^{val}	η_M^{val}	η_{AB}^{val}
H_2	H	24.49	13.24	13.24	24.49
F_2	F	13.88	6.94	6.94	9.11
Cl_2	Cl	10.10	5.05	5.05	6.86
Br_2	Br	9.15	4.58	4.58	5.77
I_2	I	8.06	4.03	4.03	4.57
HF	H	29.60	3.00	9.87	13.29
	F	14.80	13.31		
HCl	H	23.69	0.93	7.08	11.11
	Cl	10.10	9.71		
HBr	H	22.42	0.48	6.50	10.44
	Br	9.16	8.97		
HI	H	20.47	−0.46	5.57	9.13
	I	7.65	7.82		
ClF	Cl	7.28	6.98	5.52	10.88
	F	22.81	0.95		
BrF	Br	6.34	6.40	5.04	10.58
	F	24.78	−0.21		
IF	I	5.39	5.49	4.46	8.80
	F	25.76	−0.47		
BrCl	Br	8.17	5.39	4.78	6.42
	Cl	11.48	3.90		
ICl	I	7.77	4.95	4.37	5.74
	Cl	12.35	3.33		
IBr	I	7.37	4.40	4.22	5.04
	Br	9.89	3.50		
LiH	Li	6.25	0.71	3.76	3.87
	H	9.46	8.38		
LiF	Li	10.69	0.25	5.30	0.78
	F	10.52	10.27		
LiCl	Li	10.21	−0.18	5.04	0.96
	Cl	9.97	10.14		
LiBr	Li	9.96	−0.12	4.91	0.98
	Br	9.69	9.81		
LiI	Li	9.16	−0.18	4.49	1.20
	I	8.80	8.95		
NaH	Na	5.70	0.58	3.24	2.10
	H	7.46	6.70		
NaF	Na	8.85	0.31	4.41	0.40
	F	8.81	8.50		
NaCl	Na	9.77	0.15	4.57	0.60
	Cl	9.01	8.85		
NaBr	Na	9.18	0.24	4.52	0.64
	Br	8.80	8.66		
NaI	Na	8.62	0.28	4.22	0.80
	I	8.28	8.00		

7.7. *Interatomic hardness* η_{AB}

Only the valence part η_{AB}^{val} was subject to analysis, the results are collected in last column of table 4 and in table 6. The parameter has an easy interpretation (eq. (43)), it describes the sensitivity of the B atom to the changes at the A site. However, the numbers in table 4 show that this connectivity between B and A

Table 5
Valence hardness of the ring carbon in monosubstituted benzenes (in V/el.)

Molecule	C-*orto*	C-*meta*	C-*para*	η_M
ϕ_{CH_3}	2.96	2.23	11.10	5.46
ϕ_{Br}	2.31	1.02	11.28	5.30
ϕ_{Cl}	2.60	1.38	11.38	5.35
ϕ_F	2.98	1.79	11.48	5.38
ϕ_{OH}	3.06	1.84	11.20	5.36
ϕ_{NH_2}	3.04	0.76	10.32	5.02
ϕ_{CHO}	3.44	4.90	5.18	5.18
ϕ_{COOH}	4.33	6.32	4.11	5.26
ϕ_{CN}	4.40	5.85	5.16	5.20
ϕ_{NO_2}	8.32	11.29	−2.05	5.14
benzene	5.54	5.54	5.54	5.54

described by η_{AB}^{val} is mainly covalent. The stronger the covalent bond, the higher is the index, reaching 13.29 V/el in HF and approaching zero in the very ionic NaF.

The index shows considerable flexibility: it does distinguish relations between the ring carbons in substituted benzenes, and enhances the effect of substitution. It translates to numbers what has been deduced from the valence structures of the benzene ring: the *meta*-carbon is the least sensitive to the substitution, (table 6).

Table 6
Intercarbon valence hardness η_{AB}^{val} (eqs. (43) and (68)) in monosubstituted benzenes between the *ipso*-carbon (substituted) and three other ring carbons: *orto*–, *meta*– and *para*– to the substituent

Molecule	η_{AB}^{val} [V/el.]		
	C-*orto*	C-*meta*	C-*para*
ϕ_{CH_3}	15.46	−0.78	4.42
ϕ_{Br}	18.86	−0.79	6.71
ϕ_{Cl}	17.66	−0.78	5.58
ϕ_F	16.77	−0.82	4.61
ϕ_{OH}	16.58	−0.84	4.71
ϕ_{NH_2}	22.72	−0.89	7.62
ϕ_{CO}	25.66	1.14	3.32
ϕ_{COOH}	21.78	1.30	3.51
ϕ_{CN}	29.67	−0.11	2.56
ϕ_{NO_2}	23.04	0.60	9.36
benzene	19.32	0.00	2.86

8. Conclusion

Electronegativity and hardness indices, although unrestricted by the EE principle, demonstrate the expected properties, of which the linear dependence on the atomic charge is most appealing. In a number of molecules an effect of partial electronegativity equalization is observed.

The results for the hardness have the same formal structure of hardness matrix as introduced by Nalewajski and co-workers [25,27]. The present work has for the first time demonstrated the combination rules between hardness matrix elements, atomic hardness indices and total molecular hardness.

Every potential use electronegativity and hardness parameters must be preceeded by a reflection: what it means if atom A in a pair AB is the more electronegativity one. At least three possible parameters for bonded atoms emerge from this study, all corresponding to some common chemical viewpoint. Inherent electronegativity, $\bar{\chi}^0$, describes a general property of an atom, corrected for the particular bonding (valence) state. Standard electronegativity, χ^0, gives the power to attract electrons by a bare atom with some actual charge q. The authors believe that the third index, the actual electronegativity χ, provides the most comprehensive description of an atom, by introducting three effects in one: inherent power of the atom, atomic charge and molecular bonding potential. Application of that index (and the actual hardness η as well) is limited to the instances when the molecule interacts as such, without breaking or dissociation. These are the conditions when the first contact between molecules occurs and the active complex is formed. It is not yet clear, how much help these indices might offer in describing real chemical interactions. Their use can only be qualitative so far. Quantitative use of electronegativity and hardness has not yet been developed. With the electronegativity and hardness of bonded atoms available by the Hartree–Fock method, the need to quantify the interaction in terms of χ and η is even more pressing. A formalism, if created, will probably not provide any precise bonding energies or heats of reactions. The wide use of Pauling's original idea of electronegativity as an index provides a clue, though, how important it is for a chemist to predict even the trends, and not necessary precise experimental data. This may be

important where other methods can hardly compete, e.g.: adsorption on solid surfaces, the acid–base chemistry, solvation of big molecules, interaction between atoms bonded to distant ends of the same molecule (proteins), complementary pairing of DNA bases, and possibly even transport phenomena at the membranes. The indexing of bonded atoms offered by this work contains a potential, needed for semi-quantitative chemical predictions in these situations.

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Appendix

Calculation of the derivatives in INDO (for matrix elements of the HFR operator see ref. [31])

$$\left(\frac{\mathrm{d}F_{kl}}{\mathrm{d}N}\right)_{N_0} = \sum_m \sum_n a_{mn}[(kl|mn) - 0.5\,(kn|lm)]\,.$$

$$\left(\frac{\mathrm{d}F_{kl}^{\mathrm{AB}}}{\mathrm{d}N}\right)_{N_0} = -0.5\,a_{kl}^{\mathrm{AB}}\gamma_{\mathrm{AB}}\,.$$

$$\left(\frac{\mathrm{d}F_{kk}^{\mathrm{AA}}}{\mathrm{d}N}\right)_{N_0} = \sum_{m\in\mathrm{A}} a_{mm}^{\mathrm{AA}}[(k_\mathrm{A}k_\mathrm{A}|m_\mathrm{A}m_\mathrm{A})$$

$$-0.5\,(k_\mathrm{A}m_\mathrm{A}|k_\mathrm{A}m_\mathrm{A})] + \sum_{\substack{m\in\mathrm{B}\\ \mathrm{B}\neq\mathrm{A}}} a_{mm}^{\mathrm{BB}}\gamma_{\mathrm{AB}}\,.$$

$$\left(\frac{\mathrm{d}F_{kl}^{\mathrm{AA}}}{\mathrm{d}N}\right)_{N_0} = 0.5\,a_{kl}^{\mathrm{AA}}[3(k_\mathrm{A}l_\mathrm{A}|k_\mathrm{A}l_\mathrm{A}) - (k_\mathrm{A}k_\mathrm{A}|l_\mathrm{A}l_\mathrm{A})]\,.$$

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