Chemical Physics 114 (1987) 55–71
North-Holland, Amsterdam

ELECTRONEGATIVITY AND HARDNESS IN THE CHEMICAL APPROXIMATION

Ludwik KOMOROWSKI

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

Received 20 October 1986

The chemical electronegativity of an atom (Mulliken definition) has been identified with the average value of χ, the electronegativity function given by the rigorous density functional theory. An appropriate definition of hardness is developed, and a scale of hardness for bonded atoms is proposed. The electrodynamical atom model is demonstrated to produce a simple relation between atomic hardness and size. Electronegativity has been calculated for bonded atoms in a variety of molecules and crystals, covalent and ionic, without any specific approximation for the energy function $E(q)$. Expressions for the electronegativity of a molecule have been derived and critically discussed.

1. Introduction

Recent development of the density functional theory has animated and brought again into attention the old chemical idea of electronegativity [1–3]. Given the electron density function $\rho(\boldsymbol{r})$ in a chemical system (atom, molecule) and the energy functional $E(\rho)$, the electronegativity of that system in equilibrium has been identified with its negative chemical potential [1]:

$$\chi = -\mu = -\delta E(\rho)/\delta\rho. \tag{1}$$

By this general and profound definition the very chemical problem of electronegativity has been related to rapidly developing density functional theory. It has been recently indicated that a coherent binding of this definition to traditional electronegativity concepts deserves a detailed and non-trivial analysis which has not yet been attempted [4].

An experimental measure of "the power of atom to attract electrons to themselves" has been searched for by numerous authors over nearly 60 years; all concepts fall into two categories. The first one is exemplified by the spirit of the original Pauling definition [5]: electronegativity shall be a number ascribed to atoms. The most important Mulliken definition enabled extension of this concept to molecules but did not alter its basic foundation. The second approach has been introduced by Iczkowski and Margrave [6] but was earlier suggested also by Pritchard and Sumner [7]: electronegativity has been defined as a derivative of some hypothetical energy function $E(N)$. Equivalence of these two definitions will not be granted, unless a particular form is admitted for $E(N)$, as it was later done by Hinze, Jaffè and Whitehead [8]. To stress the philosophical difference, the electronegativity index exemplified by the Mulliken definition will be hereafter referred to as chemical electronegativity ($\bar{\chi}$), in contrast to the differential electronegativity $\chi = -\mathrm{d}E(N)/\mathrm{d}N$.

Another chemical index independently associated with the density functional theory is hardness. Its novel formulation by Parr and Pearson has been a most natural extension of the differential electronegativity [9]:

$$\eta = \tfrac{1}{2}\left(\partial^2 E/\partial N^2\right)_Z. \tag{2}$$

This notion suffers of the same discomfort as electronegativity itself; the scale of absolute hardness, $\frac{1}{2}(I - \mathrm{EA})$, has been proposed only as an operational definition which does not merge with η unless $E(N)$ is a parabole.

It is worthwhile to notice that the density functional theory, in its branch that touches the elec-

tronegativity problem, has approached the field that for years has been filled up by innumerable works of chemists. From abundance of chemical observations, they have been able to derive ingenious concepts and scales of electronegativity and hardness that have proved their usefullness in predicting and systematizing chemical facts. It can hardly be expected that any rigorous theory at the molecular level can soon be brought, without a loss of purity, to such a state of simplicity that it could be enjoyed by chemists in their practical work. Most typically, the theory approaches a chemical experiment via selective approximations and simplifications based on the bulk of chemical knowledge which then serve as bridges between the rigorous theory and chemical reality. The aim of this work is to propose such a bridging phenomenological concept concerning electronegativity and hardness.

2. The chemical approximation

Following the traditional way of chemical thinking, the atomic energy function will be taken in the form $E(q)$ instead of the more general $E(N, Z)$, where for a given atom $q = Z - N$. The occupation number $N = \int \rho \, d\tau$ is implicitly provided by the density functional theory as shown by Katriel, Parr and Nyden [10]. Consequently, the differential electronegativity of a non-interacting atom is

$$\chi^0 = dE^0/dq. \tag{3}$$

An interacting atom i in a molecular system M can be attributed the differential electronegativity $\chi_{i,M}(q_i)$:

$$\chi_{i,M} = \partial E_M/\partial q_i. \tag{4}$$

The Sanderson principle proved by Donnelly and Parr [2,11] requires that electronegativities of interacting atoms be equal:

$$\chi_{1,M} = \chi_{2,M} = \cdots = \chi_{i,M} = \cdots = \chi_M. \tag{5}$$

This, however, is true if, and only if, the molecule is partitioned into non-interacting fragments [10], and poses a severe limitation on atomic charges that may be employed. In fact, nothing but eq. (5) should be taken as a basis of the population analysis; further discussion will be built on this assumption.

Once the atomic charges q_i are chosen, the energy of the system, E_M, can be arbitrarily decomposed into contributions from atomic cores, $E_i^0(q_i)$, and some binding interaction e_M. Then:

$$\chi_{i,M} = \chi_i^0 + \partial e_M/\partial q_i. \tag{6}$$

χ_i^0 will be hereafter called standard differential electronegativity.

The original Parr and Pearson definition of hardness will be reformulated to introduce the effective charge q:

$$\eta^0 = d\chi^0/dq. \tag{7}$$

(In fact, this definition corresponds strictly to the second-order permittivity in linear perturbation theory and tends to replace eq. (2) in currently published works [12].)

The hardness of an atom in an interacting system may be expressed by the elements of the stiffness matrix [13,14] which are now:

$$\eta_{ii} = \partial\chi_i/\partial q_i = \eta_i^0 + \partial^2 e_M/\partial q_i^2,$$
$$\eta_{ij} = \partial\chi_i/\partial q_j = 0. \tag{8}$$

The diagonal parameter η_{ii} is reminiscent of the standard differential hardness η_i^0; they become equal when e_M contains nothing but the pure electrostatic interactions. Off-diagonal indices η_{ij} vanish identically in two cases: (i) in consequence of the assumed way of partitioning of the system, eq. (5) [10]; (ii) if e_M contains nothing but the coulombic interactions $q_i q_j / r_{ij}$.

The energy function for an atom, $E^0(q)$, remains unknown for non-integral fractional charges q. Hence, any predictions concerning the numerical values for $\chi(q)$ and $\eta(q)$ can hardly be justified. In particular, the frequently used identification $\chi^0(q=0) = \frac{1}{2}(I + \mathrm{EA})$ will be avoided: it results from the assumption that $E^0(q)$ is a parabolic function, which seems to be neither justified nor necessary, though typically employed hitherto, even in most recent theoretical work [15]. The needed relationship between the differential, well defined quantity $\chi(q)$ and the existing scale of electronegativity can be accomplished in a more

general way (cf. ref. [4]). Most naturally, the chemical electronegativity $\bar{\chi}$ of an atom can be considered an average of the function $\chi(q)$ over a suitable region of charge: $\bar{\chi} = \langle \chi(q) \rangle$. Taking the average between $(q-e)$ and $(q+e)$ for an isolated atom or ion we obtain ($e > 0$ stands for the elementary charge):

$$\bar{\chi} = \int_{q-e}^{q+e} \chi^0(q)\, \mathrm{d}q \Big/ \int_{q-e}^{q+e} \mathrm{d}q$$
$$= \left[E^0(q+e) - E^0(q-e)\right]/2e$$
$$= (I + \mathrm{EA})/2e \quad (\mathrm{V}). \tag{9}$$

In consequence, volts remain unique units for chemical electronegativity (SI); ionization energy (I) and electron affinity (EA) are expressed in electronvolt. The integration limits in eq. (9) have been chosen in order to show the equivalence of this definition to the Mulliken electronegativity for atom. However, for various oxidation states and various types of reactions of an atom, another choice may well be shown to be advantageous in describing electronegative character of atom.

The definition (eq. (9)) has remarkable consequences: within an interacting systems, the differential electronegativities of atoms ($\chi_{i,M}$) become equal as required by the Sanderson principle (eq. (5)), but neither the standard (χ_i^0) nor the chemical ($\bar{\chi}_{i,M}$) electronegativities must be equal, though both are in some way related to the charge q. Moreover, eq. (9) provides a basis for extending the definition of the chemical electronegativity to bonded atoms (section 6).

By analogy to eq. (9) the chemical hardness can also be defined accordingly: $\bar{\eta} = \langle \eta(q) \rangle$. To demonstrate the equivalence of $\bar{\eta}$ to the absolute hardness parameter given by Parr and Pearson [9], it is sufficient to impose a constraint for $E^0(q)$, by admitting it as a homogeneous function of charge of the order m. We have: $q\chi^0(q) = mE^0(q)$ and for $q = 0$ it is obtained:

$$\bar{\eta} = \int_{q-e}^{q+e} \eta^0(q)\, \mathrm{d}q \Big/ \int_{q-e}^{q+e} \mathrm{d}q$$
$$= \left[\chi^0(+e) - \chi^0(-e)\right]/2e$$
$$= m(I - \mathrm{EA})/2e^2 \quad (\mathrm{V}/e). \tag{10}$$

Appropriate practical units for $\bar{\eta}$ (as well as for $\eta(q)$) are volt/electron, readily transferable into corresponding SI unit – inverse attofarad – 1 $\mathrm{V}/e = 6.2418\ \mathrm{aF}^{-1}$.

The possibility that $E(N)$ may be a sum of homogeneous functions has already been noticed by Parr et al. in their first work on electronegativity [1]; the Thomas–Fermi model has been pointed out as an example. The requirement of homogeneity, less severe than the assumption of parabolic $E^0(q)$ employed by Parr and Pearson, is still sufficient to arrive at the same scale of chemical hardness; more realistic estimations of atomic hardness based on eq. (10) are given elsewhere [16].

3. Electrodynamical analogy

A successful application of the formalism derived from the density functional theory at the level of the chemical approximation gains much of simplicity by building links to the descriptive apparatus already existing in classical electrodynamics, although to apply electrodynamical equations to the chemical potential is reasoning by analogy only. Atoms and ions, either free or bound, have been known to possess a well defined and experimentally accessible electronic polarizability α. The numerical α value for ions is reasonably well related to the ionic radius, $\alpha \approx r^3$ [5,17], inasmuch as experimental values of these radii may be given confidence. Since an atom in an electric field is polarized as if it were a metallic sphere of radius r, it seems not unreasonable to suppose that also its capacity $\sigma = 4\pi\epsilon_0 r$ can be ascribed a physical meaning. Bringing a charge q to a neutral atom will change its potential by q/σ, hence:

$$\chi^0(q) = \frac{q}{4\pi\epsilon_0 r(q)} + c. \tag{11}$$

The constant $c = \chi^0(0)$ is identically zero in classical electrodynamics. We merely note at this point that also $\chi^0(0) = 0$ for the Thomas–Fermi atom, in which the electronegativity of a positive ion is equal to $(Z - N)/R = q/R$, where R is the radius beyond which the density is zero (see ref. [18] for

discussion of this and related models).

Relation (11) is reminiscent of Gordy's definition of electronegativity [19], recalled recently by Pasternak [20] and Politzer et al. [21] with a notable difference: r is now a charge-dependent radius derived from polarizability, not just a covalent radius, and the differential electronegativity $\chi^0(q)$ does not necessarily reproduce numbers from any scale of chemical electronegativity. Under these circumstances we have:

$$\eta^0 = \frac{\mathrm{d}\chi^0}{\mathrm{d}q} = \frac{1 - 4\pi\epsilon_0(q/r)\,\mathrm{d}r/\mathrm{d}q}{4\pi\epsilon_0 r}. \tag{12}$$

For a metallic sphere $\mathrm{d}r/\mathrm{d}q = 0$ and strictly $\eta^0 = (4\pi\epsilon_0 r)^{-1}$. Atoms may behave similarily: atomic hardness has been shown to be proportional to the average of reciprocal atomic radius $\langle r^{-1} \rangle$ [22].

The most adequate name for σ, the analogue of capacity at atomic level would be "softness" (cf. ref. [12]). Relation (12) readily hints to the limitation of phenomenological modelling of an atom as a conductive sphere, though in many chemical instances this analogy might show itself instructive. For a neutral atom ($q = 0$) and for a closed shell ion where a reasonable guess is $\mathrm{d}r/\mathrm{d}q = 0$ equivalence between softness and hardness is granted. Otherwise, softness $\sigma \approx r$ may always be sought via refraction data; the huge body of experimental results is an inexhaustible source of that quantity. Introduction of the softness parameters and their relation to atomic radii allows further discussion in terms of classical electrodynamics. The molecular model is determined by the textbook problem of a system of conductors: charged, weakly interacting conducting spheres, connected by a wire to have their electrostatic potentials equal. Such a model may not be as trivial as it seems to be: it reflects a correct way of dividing the molecule into non-interacting fragments as required by the rigorous Sanderson principle (eq. (5)) [10].

If $\boldsymbol{Q}$ and $\boldsymbol{\chi}$ are vectors of atomic charges and electronegativities, respectively, one may write [23]

$$\boldsymbol{Q} = \boldsymbol{\sigma}\boldsymbol{\chi}, \tag{13}$$

where $\boldsymbol{\sigma}$ replaces the matrix of capacitances. The hardness coefficients are now straightforwardly bound to the elements of $\boldsymbol{\sigma}$ (cf. eq. (12)):

$$\boldsymbol{\eta} = \boldsymbol{\sigma}^{-1}. \tag{14}$$

Real and diagonal $\boldsymbol{\eta}$ and $\boldsymbol{\sigma}$ matrices will be called hardness and softness matrices, respectively. Diagonal elements η_{ii} become approximately $\eta_{ii} = 1/4\pi\epsilon_0 r$ if e_M is purely electrostatic (eq. (8)).

Differential electronegativities of atoms-in-molecules are equal in equilibrium (eq. (5)), thus $\boldsymbol{\chi} = \chi_M \mathbf{1}$. Since softness of a molecule as a whole can also be defined by eq. (11), $Q_M = \sigma_M \chi_M$, and in addition, $Q_M = \Sigma q_i$, thus we conclude:

$$\sigma_M = \mathrm{Tr}\,\boldsymbol{\sigma} = \sum_i^M \sigma_{ii}, \tag{15}$$

or

$$1/\eta_M = \sum_i^M q/\eta_{ii}. \tag{16}$$

The differential softness of a molecule (inverse hardness) is additively composed of the diagonal softness parameters of the component atoms. The relation of this formula to Yang's expression for the chemical hardness of the molecule [24] will be demonstrated in section 7.

4. The energy function

Eq. (12) for the electronegativity of atom has been motivated by an electrodynamical viewpoint. It is interesting to analyze its consequences for the energy function, even though such function will not appear explicitly in this present approach.

The definition of chemical electronegativity ($\bar{\chi}$) and hardness ($\bar{\eta}$), eqs. (9) and (10), has made these quantities completely independent of $E(q)$. Hence, $\bar{\chi}$ and $\bar{\eta}$ values for atoms do not provide any test for the energy function. A test can now be found via eq. (11), which leads to a relation between atomic and ionic radii (r_0, r_+, r_-) and atomic energies (I, EA). Such relation may be, at least in principle, subject to experimental verification.

The review of the energy functions will be limited to standard parameterization: $E(+1) = I$, $E(0) = 0$, $E(-1) = -\mathrm{EA}$. Then one should expect

second and higher ionization energies to be reproduced only crudely. Each function is followed by a specification of its "property" – predicted relation between radii and energies (for c and r refer to eq. (11)).

(a) $c \neq 0$, $r =$ constant: $E(q) = Aq^2 + Bq$. Property: $(4\pi\epsilon_0 r)^{-1} = I - \mathrm{EA}$. The unphysical assumption that the atomic radius does not change upon ionization leads to the familiar parabolic energy function. The above limitation allows transformation of eq. (11) into $\chi^0 = q\eta + c$. Such a function has recently been discussed by Mortier et al. [25] as a first approximation to the $\chi(q)$ function.

(b) $c \neq 0$, $r = (aq + b)^{-1}$: $E = Aq^3 + Bq^2 + Cq$. Properties: $(4\pi\epsilon_0 r_0)^{-1} = I - \mathrm{EA}$, $1/r_0 = \frac{1}{2}(1/r_+ + 1/r_-)$. The $r(q)$ function is exactly the average value $\langle r \rangle$ for the Slater orbital. The properties remain identical if $c = 0$.

(c) $c \neq 0$, $\chi = \chi(0)e^{\gamma q}$. Instead of assuming some function for $r(q)$ we can start from the $\chi(q)$ proposed by Parr and Bartolotti [26], recently discussed by Yang et al. [24]. Combining with eq. (11) gives:

$$E = \frac{\chi(0)}{\gamma}(e^{\gamma q} - 1) = \frac{1}{(4\pi\epsilon_0)}\frac{1}{\gamma}\frac{q}{r(q)}.$$

Properties: $(4\pi\epsilon_0 r_0)^{-1} \approx 0.90\ (I - \mathrm{EA})$, $1/r_0 \approx 0.35\ (1/r_+ + 1/r_-)$. The parameter γ has been taken as in ref. [24], $\gamma \approx 2(I - \mathrm{EA})/(I + \mathrm{EA}) = 1.55 \pm 0.22$.

Although these functions differ significantly in details, they all lead to a similar and reasonable conclusion: the atomic radius (r_0) is inversely proportional to $I - \mathrm{EA}$ and, on the other hand, r_0^{-1} is the average of reciprocal anion and cation radii. Whereas the latter conclusion can merely be judged as reasonable, the former one finds firm support in earlier work. Ray, Samuels and Parr [27] have established a linear relationship for diatomic molecules (the factor $4\pi\epsilon_0$ has been introduced to remain in the SI unit system): $(4\pi\epsilon_0 R_{xx})^{-1} = 0.895(I_x - \mathrm{EA}_x)$. R_{xx} in homonuclear molecules is usually close to the van der Waals radius of the atom, and this experimental correlation corroborates the proposed relation between r_0 and $I - \mathrm{EA}$.

Another important property of $E(q)$ is featured by the case (b). The corresponding energy functions for $c = 0$ and $c \neq 0$ differ only in $\chi(0)$, this value, however, cannot be verified experimentally. The electrodynamical analogy ($c = 0$) thus can be safely accepted at least as a reference model for a discussion of the atoms.

Table 1
Differential hardness parameters for bonded atoms, calculated from atomic refractions

Atom	Molecule [a]	R_D [b] ($cm^3\ mol^{-1}$)	r [c] (nm)	η_{ii} [d] (V/e)
H	hydrocarbon	1.028 [e]	0.0741	19.4
–C–	hydrocarbon	2.591	0.101	14.3
=C<	hydrocarbon	3.379 [f]	0.110	13.1
≡C–	hydrocarbon	3.579 [g]	0.112	12.9
–N<	ϕNR_2	4.243	0.119	12.1
	ϕNHR	3.650	0.113	12.7
	ϕNH_2	3.144	0.108	13.3
	NR_3	2.744	0.103	14.0
	HNR_2	2.582	0.101	14.3
	H_2NR	2.378	0.0981	14.7
>N	pyridin	2.253 [h]	0.0963	15.0
≡N	RCN	1.880 [i]	0.0907	15.9
>O	R_2O	1.764	0.0888	16.2
	$R(OR)_2$	1.607	0.0860	16.8
=O	R_2CO	1.134 [j]	0.0766	18.8
	$R\phi CO$	1.751	0.0886	16.2
>S	RSH	7.729	0.145	9.94
	R_2S	7.921	0.146	9.87
	ϕSH	8.132	0.148	9.73
	ϕSR	8.54	0.150	9.60
	ϕ_2S	9.05	0.153	9.42
–P<	R_3P	9.01	0.153	9.42
F	RF	0.81	0.0318	45.3
Cl	RCl	5.844	0.132	10.9
Br	RBr	8.741	0.151	9.54
I	RI	13.954	0.177	8.14

[a] R is alkyl, ϕ is phenyl.
[b] Source: ref. [30] (see references therein for earlier papers of the series).
[c] r (nm) $= 0.07347\ R_D^{1/3}$.
[d] $\eta_{ii}\ (F^{-1}) = 1/\sigma_{ii} = 1/4\pi\epsilon_0 r$, $1\ V/e = 6.2418 \times 10^{18}\ F^{-1}$.
[e] Accepted as a general reference.
[f] Includes 1/2 of (=) increment.
[g] Includes 1/2 of (≡) increment.
[h] $R_D(N) = R_D(Py) - 5/6 R_D$ (benzene).
[i] $R_D(N) = R_D(-CN) - R_D(\equiv C-)$.
[j] $R_D(O) = R_D(-CO) - R_D(=C-)$.

5. Hardness and softness of atom-in-molecule

Eqs. (15) and (16) motivate a search for numerical indices η_{ii} (σ_{ii}) which may possibly serve as a measure of hardness of atom-in-molecule. The problem reduces to skillful analysis of radii of bonded atoms. The most natural solution is to explore the abundant refraction data, which has been done tentatively in table 1. The data in table 1 disclose all features qualitatively ascribed to the scale of hardness: (i) the classical sequence of increasing hardness is properly reproduced, P $\approx$ S < N < O; (ii) halogens are ordered in the expected sequence of increasing softness; (iii) the phenomenon of symbiosis may be correctly accounted for [28,29].

The remarkable advantage of the proposed scale is, somewhat roughisly, the same property that was considered a fault of refraction additivity: the hardness of an atom is substantially modified by substituents, what is most clearly exemplified by the nitrogen. Easy access to experimental data of atomic refraction makes the proposed scale a convenient source of hardness for atom-in-molecule, for which Parr and Pearson's absolute hardness cannot be found. However, the hardness parameters in table 1 must not be confused with the scale given by Parr and Pearson for acids and bases [9]. The latter is equivalent to the *chemical* hardness for free atoms and ions (cf. eq. (10)), whereas table 1 contains *differential* hardnesses for bonded atoms in an actual chemical environment. A relation between both scales will be discussed elsewhere [16].

6. Chemical electronegativity of atom-in-molecule

The idea of equalization of atomic electronegativities upon formation of the molecule is as old as the electronegativity itself, in fact it has already served as rationalization of the Mulliken formula [31]. Probably the most widely known and used is now the Sanderson geometric-mean equation [11], which is the simplest and not obviously inferior to others, sometime possessing more justification [27,32]. (Ref. [4] contains discussion of this problem.) The common feature built into all concepts of electronegativity equalization presented so far is their relation to existing scales of chemical electronegativity: $\bar{\chi}$ of a molecule has been tentatively reproduced by some arithmetical functions of chemical electronegativities of atoms, under the assumption, that they become equal as charge flows between that atoms. It has been demonstrated (section 2), that only differential electronegativities are subject to equalization, however, χ values are beyond reach as long as the function $E(q)$ is not specified. Acceptance of the definition of chemical electronegativity $\bar{\chi}$ (eq. (9)) resolves the difficulty but the chemical electronegativity of the molecule $\bar{\chi}_M$ will not be, in general, equal to chemical electronegativities of component atoms, $\bar{\chi}_{i,M}$ [4]. Nevertheless, ascribing numerical values to $\bar{\chi}_{i,M}$ as well as their relation in $\bar{\chi}_M$ may be of primary importance for chemical application.

For atom i bonded in molecule M by some potential $V_{i,M}$ we have (eq. (6)):

$$\chi_{i,M} = \chi_i^0 + V_{i,M}. \tag{17}$$

The chemical electronegativity, according to definition, is:

$$\bar{\chi}_{i,M} = \frac{E_i^0(q_i+e) - E_i^0(q_i-e)}{2e} + \frac{1}{2e}\int_{q_i-e}^{q_i+e} V_{i,M}\,\mathrm{d}q. \tag{18}$$

In a number of molecules chemical intuition prompts to admitting some integral value of charge $n = q/e$ for the atom under consideration, i.e. the bonding of that atom is either covalent ($n = 0$) or ionic ($n \neq 0$). Eq. (18) becomes then:

$$\bar{\chi}_{i,M} = \bar{\chi}_{i,n} + \Delta\bar{\chi}_{i,M}, \tag{19}$$

where

$$\Delta\bar{\chi}_{i,M} = \frac{1}{2e}\int_{e(n-1)}^{e(n+1)} V_{i,M}\,dq. \tag{20}$$

The chemical electronegativity of a bonded atom appears rather realistically as a sum of the chemical electronegativity of a free atom or the respective ion, $\bar{\chi}_{i,n}$, plus some contribution $\Delta\bar{\chi}_{i,M}$ due to the bonding potential.

6.1. Ionic structures

For a purely ionic bond, $\Delta\bar{\chi}_{i,M}$ is simply the local electrostatic potential:

$$\Delta\bar{\chi}_{i,M}^{\text{ionic}} = \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \frac{q_j}{R_{ij}}.$$

Eqs. (19), (20) may be applied strictly to ionic crystals where the meaning of the coulombic potential is free of simplifications if the Madelung lattice potential is used. Table 2 shows the chemical electronegativities $\bar{\chi}_{i,M}$ calculated for ions in a selection of ionic crystals.

The index of chemical electronegativity provides an interesting criterion for the classification of electropositive and electronegative centers at ionic crystals. The cation appears as a prevailing electronegative site on the surface of sodium halides, with Na^+ in corners and edges possessing maximum electronegativity. On the potassium and rubidum fluorides, the (100) surface exhibits a quite uniform electronegativity at cationic and anionic centers. Most surprisingly, the anion, not the cation, seems to be the more electronegative spot on silver chloride and bromide; this would resemble the behaviour of free atoms rather than ions. The chemical electronegativity $\bar{\chi}_{i,M}$ might perhaps be employed as a guide in studying properties of solid surfaces. Adsorption phenomena and heterogenic catalysis are the primary possible targets for such a study.

6.2. Covalent structures

At another extreme, calculation of the bonding potential within a covalent structure requires a suitable model to mimic bonding interactions. An elegant method of impressive conceptual simplic-

Table 2
Chemical electronegativities of ions in crystal lattices of NaCl type. The Madelung constant $M = 1.7476$ (bulk) is reduced by a factor 0.8914 for (100) wall; 0.8397 for [100] edge; 0.7160 for the corner of a cube closed by (100), (010) and (001) lattice planes. For the source of the data see ref. [51]

Salt	Madelung energy [a] (ev)	Ion	Chemical electronegativity $\bar{\chi}_{i,M}$ (V)						
			bulk	surface (100)	edge [100]	corner	free ionic pair [b]	free ions	neutral atoms
LiF	12.52	Li^+	27.98	29.34	29.99	31.54	33.34	40.5	3.00
		F^-	14.22	12.86	12.21	10.66	8.86	1.70	10.44
NaF	10.90	Na^+	15.30	16.48	17.05	18.40	19.97	26.20	2.89
		F^-	12.60	11.42	10.85	9.50	7.93	1.70	10.44
NaCl	8.95	Na^+	17.25	18.22	18.68	19.80	21.08	26.20	2.89
		Cl^-	10.76	9.79	9.33	8.21	6.93	1.81	8.29
NaBr	8.45	Na^+	17.75	18.67	19.10	20.15	21.37	26.20	2.89
		Br^-	10.13	9.21	8.78	7.73	6.51	1.68	7.60
NaI	7.79	Na^+	18.41	19.26	19.66	20.62	21.74	26.20	2.89
		I^-	9.32	8.47	8.07	7.11	5.99	1.53	6.76
KF	9.43	K^+	8.55	9.58	10.06	11.23	12.59	17.98	2.41
		F^-	11.13	10.10	9.62	8.45	7.09	1.70	10.44
RbF	8.93	Rb^+	6.87	7.84	8.30	9.46	10.69	15.8	2.32
		F^-	10.63	9.66	9.20	8.04	6.81	1.70	10.44
AgCl	9.09	Ag^+	5.52	6.51	6.98	8.10	9.40	14.6	4.45
		Cl^-	10.89	9.90	9.43	8.31	7.01	1.81	8.29
AgBr	8.74	Ag^+	5.86	6.81	7.26	8.34	9.60	14.6	4.45
		Br^-	10.42	9.47	9.02	7.94	6.68	1.68	7.60
KCN	7.75	K^+	10.23	11.08	11.47	12.43	13.55	17.98	2.41
		CN^-	9.66	8.81	8.42	7.46	6.34	1.91	9.01

[a] Madelung energy calculated as 14.40 M/R_{DA} (eV).
[b] Interionic distance same as in crystal lattice.

ity has been elaborated by Parr et al. [33,34]: the simple bond charge model (SBC). According to this model, bonding between two atoms was realized by placing some negative charge $-q$ at the midpoint of two interacting atoms which themselves were attributed charges $+\frac{1}{2}q$ each. The bond charge $|q|$ was related to the equilibrium interatomic distance R_{ij} and to the bond force constant for stretching vibrations, k_{ij}:

$$|q_{ij}| = (4\pi_0)^{1/2}\left(\tfrac{4}{7}R_{ij}k_{ij}\right)^{1/2} \quad \text{(C)}. \tag{21}$$

The bonding electrostatic potential at the site of the ith atom can be viewed as superposition of shares from vicinal bonds $(-2q_{ij}/R_{ij})$ and atoms $(q_{ij}/2R_{ij})$. Since $V_{i,M} = \partial e_M/\partial q_i$ for electrostatic interaction, where e_M is Coulomb energy of the system, eq. (20) is transformed to:

$$\Delta\bar{\chi}^{\text{val}}_{i,M} = \frac{e_M(q_i+e) - e_M(q_i-e)}{2e}. \tag{22}$$

Further analysis is conditional to admitting a reasonable model for electrostatic interactions in molecular ions formed by adding $(q_i - \text{e})$ or subtracting $(q_i + e)$ an electron to the ith atom in the molecule. To warrant a consonance with the SBC model it has been assumed: (i) the extra charge attributed to ith atom $(\pm e)$ is distributed over all vicinal bonds, proportionally to their formal bond orders β_{ij}, (ii) within each particular bond, the extra-charge is added in equal parts to the atomic charge and to bond charges $-q_{ij}$, (iii) interactions within bonds vicinal to ith atom are considered independently. The valency contribution to the chemical electronegativity of ith atom becomes:

$$\Delta\bar{\chi}^{\text{val}}_{i,M} = \frac{1}{4}\frac{1}{v_i}\sum_{j\neq i}\beta_{ij}\frac{|q_{ij}|}{4\pi\epsilon_0 R_{ij}}$$
$$= \frac{1.7916}{v_i}\sum_{j\neq i}\beta_{ij}\left(R_{ij}k_{ij}\right)^{1/2} \quad \text{(V)} \tag{23}$$

(R_{ij} in Å, k_{ij} in N cm^{-1} = mdyne Å^{-1}). $v_i = \sum_{j\neq i}\beta_{ij}$ stands for the formal valency of ith atom. The factor 1/4 in eq. (23) reflects this particular model of charge distribution and must be considered arbitrary. Table 3 contains a collection of relevant results for the carbon atom. $\Delta\bar{\chi}^{\text{val}}_{i,M}$ show remarkable dependence on hybridizaton factor, with no need to specify the exact valence state of atom. the role of vicinal atoms seems to be of marginal importance for carbon.

Chemical electronegativities for bonded carbon atoms are substantially higher than Mulliken–Jaffè valence state electronegativities, χ_v, also indicated in table 3. Nevertheless, the coincidence of χ_v and $\bar{\chi}_{i,M}$ is quite impressive as for that simplified approach.

A conceptual relation between electronegativity and the force constants for bonds adjacent to the atom has long been known. It was first quantified by Gordy [36], whose widely used formula was based on a purely statistical argument. Here, the valence state contribution to the chemical electronegativity of bonded atoms is conveniently found from R_{ij} and k_{ij} data for a real molecule, what may show itself advantageous even with respect to calculating χ_v by means of the quantum chemical procedure.

$\Delta\bar{\chi}^{\text{val}}_{i,M}$ calculated by eq. (23) for atoms other than carbon is significantly affected by substituents, as illustrated in table 4. Though the chemical electronegativities $\bar{\chi}_{i,M}$ are in a few cases considerably higher than the corresponding valence state electronegativities χ_v (Si, B), they are in satisfactory agreement for most elements shown in table 4. Moreover, variation of the chemical electronegativities due to substituents meets quite precisely the chemical expectations. Bonding to halogens increases $\bar{\chi}_{i,M}$ of an atom in the correct order: fluorine gives maximum effect. Bonding to hydrogen rises the chemical electronegativity of O by 5.09 V, N by 4.82 V, C by 4.48 V, B by 3.84 V; such a sequence reflects the expected polarity of X–H bonds. A similar order is discovered for hydrogen bonded to third-row elements, where $\Delta\bar{\chi}^{\text{val}}_{i,M}$ for S, P and Si in hydrides are: 4.26, 3.84 and 3.70 V, respectively.

The meaning and usefulness of the $\bar{\chi}_{i,M}$ index is further demonstrated by the data in tables 5 and 6 for halogens and hydrogen. The chemical electronegativity of bonded atoms shows a remarkable flexibility as compared to the valence state electronegativity, with values for $\bar{\chi}_{i,M}$ still covering the range close to χ_v.

Table 3
Chemical electronegativity of bonded carbon atom (eqs. (19) and (20))

Molecule (atom)	Bond	Force constant k_{ij} [a] (N cm^{-1})	Bond length R_{ij} (nm)	$10^4(R_{ij}k_{ij})^{1/2}$ (N$^{1/2}$)	$\Delta\bar{\chi}_{i,M}^{val}$ (V)	$\bar{\chi}_{i,M}$ [b] (V)	Ref. for R_{ij}, k_{ij}
C (sp^3)						$\chi_v = 7.98$ V [c]	
$\underline{C}H_4$	C–H	5.8	0.108	2.50	4.48	10.74	[35]
$\underline{C}H_3CH_3$	C–H	5.3	0.111	2.42			
	C–C	4.6	0.154	2.66	4.44	10.70	[35]
$\underline{C}H_3CCH$	C–H	4.9	0.107	2.29			
	C–C	5.3	0.146	2.75	4.30	10.56	[35]
$\underline{C}H_3F$	C–H	5.4	0.11	2.44			
	C–F	5.8	0.139	2.84	4.55	10.81	[35]
$\underline{C}H_3Cl$	C–Cl	3.64	0.177	2.54	4.37	10.63	[36] [d]
$\underline{C}H_3Br$	C–Br	3.13	0.191	2.44	4.35	10.61	[36] [d]
$\underline{C}H_3NH_2$	C–N	4.86	0.147	2.62	4.41	10.67	[36] [d]
$\underline{C}H_3OH$	C–O	5.00	0.143	2.67	4.42	10.68	[36] [d]
$\underline{C}H_3CN$	C–C	5.3	0.149	2.81	4.50	10.76	[36] [d]
$\underline{C}H_3NC$	C–N	5.45	0.143	2.79	4.48	10.84	[36] [d]
C (sp^2)						$\chi_v = 8.79$ V [c]	
$\underline{C}H_2CH_2$	C–H	6.2	0.106	2.56			
	C=C	10.9	0.134	3.82	5.71	11.97	[35]
$\underline{C}_6H_6$	C–H	5.1	0.108	2.35			
	C⋯C	7.7	0.139	3.27	5.45	11.71	[35]
$H_2\underline{C}O$	C–H	5.2	0.109	2.38			
	C=O	13.0	0.121	3.97	5.68	11.94	[35]
$H\underline{C}OOH$	C–O	5.4	0.142	2.77			
	C=O	11.8	0.124	3.82	5.73	11.99	[36] [d]
C (sp)						$\chi_v = 10.39$ V [c]	
$H\underline{C}CH$	C–H	6.3	0.106	2.58			
	C≡C	16.3	0.120	4.42	7.09	13.37	[35]
$CH_3\underline{C}CH$	C–C	5.3	0.146	2.78			
	C≡C	15.9	0.121	4.39	7.13	13.39	[35]
$CH_3C\underline{C}H$	C–H	6.0	0.106	2.52	7.02	13.28	[35]
$H\underline{C}N$	C–H	6.2	0.107	2.58			
	C≡N	18.8	0.115	4.65	7.40	13.66	[35]
$Cl\underline{C}N$	Cl–C	5.2	0.167	2.95			
	C≡N	16.7	0.115	4.38	7.22	13.48	[36]
$Br\underline{C}N$	Br–C	4.2	0.179	2.74			
	C≡N	16.9	0.117	4.45	7.20	13.46	[36]
$CH_3\underline{C}N$	C–C	5.3	0.149	2.81			
	C≡N	17.5	0.117	4.52	7.33	13.59	[36]

[a] 1 N cm^{-1} = 1 mdyne Å^{-1}. [b] $\bar{\chi}_{i,M} = \bar{\chi}_{i,0} + \Delta\bar{\chi}_{i,M}^{val}$; for carbon atom $\bar{\chi}_{i,0} = (I + EA)/2e = 6.26$ V.
[c] Mulliken–Jaffè valence state electronegativity [28].
[d] For the C–H bond the standard values were assumed: $k_{ij} = 5.3$, $R_{ij} = 1.1$, $(R_{ij}k_{ij})^{1/2} = 2.41$.

6.3. *Non-ionic crystals*

A practical equation for the chemical electronegativity of bonded atom, eqs. (20), (23), hints to the new possibility of calculating the chemical electronegativity of an atom within a crystalline lattice other than ionic. The force constant k_{ij} in eq. (23) may be replaced by the Debye frequency ν_D (cm^{-1}) $= (1307/2\pi)(k_{ij}/\mu)^{1/2}$ [39]. Introducing the Debye temperature $\Theta_D = h\nu_D/k_B$ we obtain $k_{ij}^{1/2} = 3.342 \times 10^{-3}\Theta_D\mu^{1/2}$. Finally, the lattice contribution to the chemical electronegativ-

Table 4
Chemical electronegativity of bonded atoms: $\bar{\chi}_{i,M} = \bar{\chi}_{i,0} + \Delta\bar{\chi}^{\mathrm{val}}_{i,M}$. R_{ij} and k_{ij} from ref. [36] except where indicated

Molecule (atom)	Bond	Force constant k_{ij} (N cm^{-1})	Bond length R_{ij} (nm)	$\Delta\bar{\chi}^{\mathrm{val}}_{i,M}$ (V)	$\bar{\chi}_{i,M}$ (V)	χ_v [a] (V)
N	–	–	–	0	7.23 [b]	11.54 (sp^3)
$\underline{N}H_3$	N–H	7.1 [c]	0.102 [c]	4.82	12.05	
$\underline{N}F_3$	N–F	6.3 [c]	0.137 [c]	5.26	12.49	
$\underline{N}(CH_3)_3$	N–C	3.97	0.147	4.33	11.56	
P	–	–	–	0	5.61 [b]	8.90 (sp^3)
$\underline{P}H_3$	P–H	3.33	0.145	3.94	9.55	
$\underline{P}F_3$	P–F	4.59	0.152	4.73	10.34	
$\underline{P}Cl_3$	P–Cl	2.00	0.212	3.69	9.30	
$\underline{P}Br_3$	P–Br	1.63	0.223	3.42	9.02	
$\underline{P}(CH_3)_3$	P–C	2.14	0.187	3.58	9.19	
As	–	–	–	0	5.29 [b]	8.30 (sp^3)
$\underline{As}H_3$	As–H	2.81	0.156	3.75	9.04	
$\underline{As}F_3$	As–F	3.92	0.172	4.65	9.94	
$\underline{As}Cl_3$	As–Cl	2.03	0.216	3.75	9.04	
$\underline{As}(CH_3)_3$	As–C	2.44	0.198	3.94	9.23	
Si	–	–	–	0	4.77 [b]	7.30 (sp^3)
$\underline{Si}H_4$	Si–H	2.95	0.145	3.70	8.48	
$\underline{Si}F_4$	Si–F	7.16	0.154	5.95	10.72	
$\underline{Si}Cl_4$	Si–Cl	3.75	0.202	4.93	9.70	
$\underline{Si}Br_4$	Si–Br	2.92	0.219	4.53	9.30	
$\underline{Si}(CH_3)_4$	Si–C	3.31	0.193	4.53	9.30	
B	–	–	–	0	4.29 [b]	6.33 (sp^2)
$\underline{B}_2H_6$	B–H	3.9	0.118	3.84	8.13	
$\underline{B}F_3$	B–F	8.83 [d]	0.129 [d]	6.05	10.34	
$\underline{B}Cl_3$	B–Cl	4.63 [d]	0.174 [d]	5.08	9.38	
$\underline{B}Br_3$	B–Br	3.66 [d]	0.187 [d]	4.69	8.98	
O	–	–	–	0	7.54 [b]	15.25 (sp^3)
$H_2\underline{O}$	O–H	8.4 [c]	0.096 [c]	5.09	12.64	
S	–	–	–	0	6.21 [b]	10.73 (sp^3)
$H_2\underline{S}$	S–H	4.25	0.133	4.26	10.47	

[a] Mulliken–Jaffè valence state electronegativity [28].
[b] $\bar{\chi}_{i,0} = (I + \mathrm{EA})/2e$. [c] Ref. [35]. [d] Ref. [37].

ity, $\bar{\chi}_{i,s}$, of an atom in a solid, for a cubic lattice of an element is:

$$\Delta\bar{\chi}^{\mathrm{cryst}}_{i,s} = 1.339 \times 10^{-2}\Theta_{\mathrm{D}}(RM)^{1/2} \quad (\mathrm{V}), \qquad (24)$$

where R (nm) is the nearest-neighbour interatomic distance and M the atomic weight. The chemical electronegativity for a number of metals has been presented in table 7.

Eq. (24) is readily extended to anisotropic lattices by appropriately averaging the product $\Theta_{\mathrm{D}}(RM)^{1/2}$, as shown for carbon in table 7. The lattice contribution $\Delta\bar{\chi}^{\mathrm{cryst}}_{i,s}$ can also be calculated for the surface states of an atom. Since an atom at the surface uses only a fraction of its formal coordination number, $\Delta\bar{\chi}^{\mathrm{cryst}}_{i,s}$ will be reduced according to the ratio β_{ij}/v_i in eq. (23). Hence, e.g.,

$$\bar{\chi}^{\mathrm{bulk}}_{i,s} = \bar{\chi}_{i,0} + \Delta\bar{\chi}^{\mathrm{cryst}}_{i,s},$$

$$\bar{\chi}^{\mathrm{plane}}_{i,s} = \bar{\chi}_{i,0} + \tfrac{1}{2}\Delta\bar{\chi}^{\mathrm{cryst}}_{i,s}, \quad \text{etc.}$$

It is clear, that the whole spectrum of chemical electronegativity between $\bar{\chi}_{i,0}$ and $\bar{\chi}_{i,s}$ may be ascribed to atoms at various surface locations.

Additions of the $\Delta\bar{\chi}^{\mathrm{cryst}}_{i,s}$ contribution shifts the chemical electronegativity index of an atom to remarkably high values, table 7, comparable to electronegativities of ions in ionic crystals. It is

Table 5
Molecular contribution to chemical electronegativity of atoms $\Delta\bar{\chi}^{\mathrm{val}}_{i,M}$ in diatomic molecules. R_{ij} and k_{ij} from ref. [42] except where indicated

Molecule	Force constants k_{ij} (N cm^{-1})	Bond length (nm)	$\Delta\bar{\chi}^{\mathrm{val}}_{i,M}$ (V)
H_2	5.7 [a)]	0.0742 [a)]	3.68
F_2	3.60 [a)]	0.1435 [a)]	4.07
Cl_2	3.225	0.19881	4.54
Br_2	2.475	0.33809	4.26
I_2	1.720	0.2666	3.84
HF	9.6 [a)]	0.0917 [a)]	5.32
HCl	5.161	0.12756	4.60
HBr	4.114	0.14145	4.32
HI	3.138	0.16090	4.02
IF	3.600	0.1908	4.69
ICl	2.386	0.23209	4.22
IBr	2.071	0.2485	4.06
BrF	4.089	0.1756	4.80
BrCl	2.80	0.2138	4.38
ClF	4.484	0.1628	4.84

[a)] Ref. [43].

interesting to note that the chemical electronegativity of a metal is increased by interaction with the lattice whereas in ionic lattices the electronegativity of a cation is lowered by the lattice potential. The physical meaning of the electronegativity index for solids will be examined in section 8.

Table 6
Chemical electronegativity of atoms in diatomic molecules, calculated using data from table 5. $\bar{\chi}_{i,M} = \bar{\chi}_{i,0} + \Delta\bar{\chi}^{\mathrm{val}}_{i,M}$

Partner atom	Chemical electronegativity $\bar{\chi}_{i,M}$ (V)				
	H	F	Cl	Br	I
H	10.85	15.76	12.89	11.92	10.78
F	12.49	14.51	13.13	12.40	11.45
Cl	11.77	15.28	12.83	11.98	10.98
Br	11.49	15.24	12.67	11.86	10.82
I	10.78	15.13	12.51	11.66	10.60
$\bar{\chi}_{i,0}$ [a)]	7.17	10.44	8.29	7.60	6.76
χ_v [b)]	7.17	12.18	9.38	8.40	8.10

[a)] $\bar{\chi}_{i,0} = (I + \mathrm{EA})/2e$.
[b)] Mulliken–Jaffè valence state electronegativities [28].

7. Chemical electronegativity of a molecule

Preliminary analysis of this problem is possible in the framework of the chemical approximation. It will be shown that even a zeroeth-order approximation within this approach leads to physically correct conclusions.

The chemical electronegativity of a molecule can be found directly from the definition, eq. (9):

$$\bar{\chi}_M = (E_{M^+} - E_{M^-})/2e. \tag{25}$$

Subscripts "+" and "−" refer to molecular ions M bearing the charge $+e$ and $-e$, respectively. The total energy E_M may now be decomposed into atomic cores E_i^0 and binding interaction e_M (cf. ef. (6)):

$$E_M = \sum E_i^0 + e_M. \tag{26}$$

In a crude approximation, e_M could be represented as a sum of coulombic terms $\frac{1}{2}\sum q_i V_i$ and a remainder – the covalent energy. Then we further assume, rather arbitrarily, that the covalent contribution does not alter significantly upon ionization. Hence:

$$\bar{\chi}_M = \frac{1}{2e}\sum\left(E_{i+}^0 - E_{i-}^0\right) + \frac{1}{4e}\sum\left(q_{i+}V_{i+} - q_{i-}V_{i-}\right). \tag{27}$$

Two extreme situations will be distinguished in order to transform this equation into useful expressions:

(i) The molecule possess donor and acceptor centers, atom D and A, respectively, which entirely contribute to ionization of the molecule, leaving other atoms unaffected. If atomic charges on atoms other than D and A are negligible, the interaction term in eq. (27) would vanish and a familiar equation is obtained:

$$\bar{\chi}_M = (I_{\mathrm{D}} + \mathrm{EA}_{\mathrm{A}})/2e. \tag{28}$$

Eq. (28) can be rather safely applied to diatomic, ionic molecules.

(ii) When no donor and/or acceptor center can be pointed out in a polyatomic molecule we as-

Table 7
Solid state chemical electronegativities of metals (eq. (24)). Closest packing lattices A1, A2, A3 have been selected

Metal	Debye temperature Θ_D [a] (K)	Interatomic distance R [b] (nm)	$\Delta\bar{\chi}_{i,s}^{cryst}$ [c] (V)	$\bar{\chi}_{i,0}$ (V)	$\bar{\chi}_{i,s}$ (V)
Li	335 [d]	0.3039	6.51	3.00	9.51
Na	156 [d]	0.3716	6.10	2.85	8.95
K	91.1 [d]	0.4544	5.14	2.41	7.55
Rb	55.5 [d]	0.495	4.83	2.34	7.17
Cs	39.5 [d]	0.5324	4.45	2.18	6.63
Cu	343 [d]	0.2556	18.51	4.48	22.99
Ag	226.2 [d]	0.2889	16.91	4.44	21.35
Au	162.4 [d]	0.2884	16.39	5.77	22.16
Be	1000	0.2226	18.96	4.66	23.62
Mg	290	0.3197	10.82	3.82	14.64
Ca	230	0.3947	12.25	3.06	15.31
Sr	170	0.4303	13.98	2.85	16.83
Zn	250	0.2665	13.97	4.70	18.67
Cd	172	0.2979	13.33	4.50	17.83
Al	390	0.2864	14.52	3.21	17.73
Pb	88	0.3500	10.03	4.28	14.31
Ta	245	0.2860	23.60	4.25	27.85
Nb	275 [d]	0.2858	18.97	3.88	22.85
Cr	485	0.2498	23.40	3.76	27.16
Mo	380	0.2725	26.01	3.92	29.93
W	310	0.2741	29.47	4.30	33.77
Fe	420	0.2482	20.94	4.03	24.97
Co	385	0.2506	19.81	4.26	24.07
Ni	375	0.2492	19.21	4.44	23.65
Ir	285	0.2714	27.56	5.39	32.95
Pd	275	0.2751	19.92	4.48	24.40
Pt	225	0.2775	22.17	5.57	27.74
non-metal					
C [e]	1800	0.154	32.76	6.26	39.02
C [f]	950	0.336 }	33.91	6.26	40.17
C [g]	2100	0.142 }			

[a] Ref. [38] except where indicated. [b] Ref. [5, p. 410]. [c] $\bar{\chi}_{i,0} = (I + \mathrm{EA})/2e$. [d] Ref. [40].
[e] Diamond, ref. [52]. [f] Graphite (⊥), ref. [52]. [g] Graphite (||), ref. [52].

sume that each atom takes part in the ionization by q_{i+} and and q_{i-}. This may be true in aromatic or other conjugated systems where also the atomic charges of individual atoms are small, $q_{i,M} \approx 0$. The electrodynamical analogy suggests a guide relation for that situation:

$$\Delta q_i = (\eta_M/\eta_{ii})\Delta Q_M. \tag{29}$$

Hence: $q_{i+} = e\eta_M/\eta_{ii}$ and $q_{i-} = e\eta_M/\eta_{ii}$.

Under these circumstances we also have $\Delta V_{i+} = -\Delta V_{i-}$ and the second term in eq. (27) becomes simply

$$\sum_i (\eta_M/\eta_{ii})V_i.$$

The first term in eq. (27) can also be transformed using the traditional relation $E_{i+}^0 - E_{i-}^0 = \bar{\chi}_{i,0}(\Delta q_{i+} - \Delta q_{i-})$ which will be strictly valid only for $\Delta q_i/e = 1$. Eq. (27) becomes now:

$$\bar{\chi}_M = \sum_i (\eta_M/\eta_{ii})(\bar{\chi}_{i,0} + V_{i,M}) = \sum_i (\eta_M/\eta_{ii})\bar{\chi}_{i,M}, \tag{30}$$

where $V_{i,M}$ is effective electrostatic potential at the ith atom due to the atomic charges on other atoms (cf. section 6.1). Summation needs not go over all atoms, but only sufficiently soft atoms must be considered. If the atomic charges $q_{i,M}$ are small enough, $V_{i,M} \approx 0$ and eq. (30) reduces to:

$$\bar{\chi}_M = \sum_i (\eta_M/\eta_{ii})\bar{\chi}_{i,0}. \tag{31}$$

The form and meaning of this latter equation will readily be recognized when it is applied to the diatomic molecule AB. Eqs. (31) and (16) yield:

$$\bar{\chi}_{AB} = (\bar{\chi}_{A,0}\eta_B + \bar{\chi}_{B,0}\eta_A)/(\eta_A + \eta_B) \tag{32}$$

or, equivalently, the softness parameters may be introduced:

$$\bar{\chi}_{AB} = (\bar{\chi}_{A,0}\sigma_A + \bar{\chi}_{B,0}\sigma_B)/(\sigma_A + \sigma_B). \tag{33}$$

$\bar{\chi}_{A,0}$ and $\bar{\chi}_{B,0}$ are chemical electronegativities of free atoms.

Both equations derived for $\bar{\chi}_{AB}$ have already been proposed in the past. Eq. (28) has been recently discussed by Perdew et al. [32] and by Nalewajski [44], who also arrived at eq. (32) in the quantum-chemical treatment of the problem. Eqs. (32) and (33) find some earlier precursors, too. Ray, Samuels and Parr [27] have derived two equations similar to eq. (33); one stemmed from the SBC model, another was based on the simple charge transfer model for electronegativity equalization using the parabolic $E(N)$ function. Instead of the softness parameters, these authors have introduced the covalent radius, and, alternatively, the $2/(I - \mathrm{EA})$ value for an atom. The equivalence of these quantities to atomic softness (inverse hardness) has now become evident. The authors also derived appropriate formulae (analogues of eq. (33)) for the ABC- and AB_m-type molecules; they all find unification in the general equation (31).

Yang et al. [24] have recently derived an equation identical in form to eq. (31), but without making distinction between the chemical and differential electronegativity and hardness. These authors have argued, basing on empirical argument, that molecular softness should be expressed by the average of softness of component atoms, or

$$\frac{1}{I - \mathrm{EA}} = \frac{1}{M}\sum_i^M \frac{1}{I_i - \mathrm{EA}_i}. \tag{34}$$

The present discussion based on the electrodynamical model readily explains the source of apparent contradiction of this equation with eq. (16). Analysis of the energy function (section 4) has demonstrated that $\eta^0(0) = (4\pi\epsilon r_0)^{-1} \approx I - \mathrm{EA}$ for reasonable energy functions. Hence, Yang's result should be written as

$$\frac{1}{\eta_M} = \frac{1}{M}\sum_i^M \frac{1}{\eta_i^0(0)}, \tag{35}$$

where $\eta_i^0(0)$ are hardness of free, isolated atoms, whereas eq. (16) contains differential hardness of bonded atoms, η_{ii}. Since $\eta_i^0(0) \neq \eta_{ii}$ for real molecules (section 2), eqs. (16) and (34) express different properties, both being rather crude approximations. Eq. (16) is advantageous in approaching the physics of interatomic interactions, eq. (34) is a rule of thumb for a rough estimation of $I - \mathrm{EA}$ for a molecule.

The derivation of eqs. (28) and (31) enables a critical view on their possible applications. Eq. (28) might describe rather accurately the chemical electronegativity of a purely ionic molecule. Eq. (31) obviously overestimates the covalent character of a molecule. It may well be expected that eqs. (28) and (31) trace rational limits for the

Table 8
Chemical electronegativities of diatomic molecules (in volt)

Molecule	$\bar{\chi}_{AB}$ [a)]	$(I_D + EA_A)/2e$ [b)]	$(\bar{\chi}_{A,0}\bar{\chi}_{B,0})^{1/2}$
HF	8.15	8.49	8.79
HCl	7.89	8.60	7.73
HBr	7.46	8.47	7.38
HI	6.88	8.32	6.96
IF	7.32	6.92	8.58
ICl	7.41	7.04	7.53
IBr	7.15	6.90	7.18
BrF	8.09	7.62	9.00
BrCl	7.92	7.73	7.95
ClF	8.71	8.20	9.36

a) Eq. (32) for $\bar{\chi}_{i,0}$ see table 6; η_{ii} from table 1.
b) I and EA from ref. [28].

chemical electronegativity of a molecule. Results for a few diatomic molecules are shown in table 8. The difference between $\bar{\chi}_M$ (eq. (31)) and $(I_D + EA_A)/2e$ decreases when the A–B bond becomes more covalent; it vanishes for a homonuclear molecule. Comparison with a commonly used landmark, $(\tilde{\chi}_{A,0}\bar{\chi}_{B,0})^{1/2}$, indicates that despite all results being rather close (cf. ref. [4]), it must not be expected that any simplified, phenomenological approach can ever reproduce a real $(I + EA)/2e$ value for a molecule.

8. Chemical electronegativity and Fermi energy

The formal correspondence between the Mulliken definition of electronegativity and the Fermi energy for an intrinsic semiconductor has stimulated a number of comparative studies [45–49]. The familiar energy diagram, fig. 1, provides a direct motivation toward such identification. Indeed:

$$\begin{aligned} E_F &= \tfrac{1}{2}(E_{CB} - E_{VB}) \\ &= \tfrac{1}{2}[(E_0 - E_{CB}) - (E_{VB} - E_0)] \\ &= \tfrac{1}{2}(EA_s + I_s) = e\bar{\chi}_s. \end{aligned} \tag{36}$$

Subscript "s" refer to the solid state data. Experimental verification of eq. (36) can be obtained by means of simple relationships: $E_F = \Phi - \frac{1}{2}E_g$ for a semiconductor and $E_F = \Phi$ for a metal. Corresponding correlations have been reported in the literature.

Gordy and Orville-Thomas [45] were the first to note a linear relationship between the workfunction Φ and the Pauling electronegativity for metals. Nethercot [46] has also explored Pauling electronegativities as well as Sanderson geometric-mean formula, and was able to reproduce accurately the workfunction for a number of binary DA systems (I–VII, II–VI, III–V). Poole et al. [47] have applied Nethercot's method to DA_2 systems using the Sanderson scale of electronegativity. Chen et al. [48] obtained a reasonable linear correlation between $\Phi - \frac{1}{2}E_g$ and $(M_D M_A)^{1/2}$, where M are Mulliken electronegativities that also included promotion energies. Alonso and Girifalco [49] have found that correlation of Φ with pure Mulliken electronegativity for metals is less satisfactory than with electronegativities from the Pauling scale. Though undoubtly impressive, the above results seem somewhat fortuitous; they exhibit a common lack of conceptual purity in correlating Φ and $\bar{\chi}$. First, the fundamental question has been escaped: why should the solid state workfunction be reproduced by the electronegativity of a free atom (or molecule)? Secondly, the authors seem to have taken too much liberty in choosing the electronegativity scale, It is well known that the Pauling scale of electronegativity is only formally related to measured physical observables (dissociation energies). Actual numbers on the scale are a result of extensive polishing, according to chemical expectations. Eq. (36) requires that only pure Mulliken $\frac{1}{2}(I + EA)$ values be used in correlations. Also, the Sanderson geometric-mean formula, though widely accepted, has not yet found (rather surprisingly) a firm theoretical foundation [26]. This present chemical approximation neatly removes the above disadvantages.

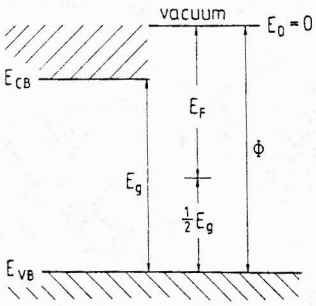

Fig. 1. Energy diagram for an intrinsic semiconductor.

The chemical electronegativity of bulk solid, χ_s, may be found from eq. (30), which should be valid since $q_i = 0$ for atoms or molecules in a crystal. Since electronegativities $(\bar{\chi}_{i,0})$ and effective potentials $(V_{i,s})$ of all individual atoms (molecules) in crystal are identical, we have:

$$\bar{\chi}_s = (\bar{\chi}_{i,0} + V_{i,s})\eta_s \sum_i 1/\eta_{ii}. \tag{37}$$

This expression can be much simplified for atomic and molecular lattices where $V_{i,s} \approx 0$ and eq. (16)

strictly holds:

$$1/\eta_s = \sum_i 1/\eta_{ii}. \tag{38}$$

Hence:

$$\bar{\chi}_s = \bar{\chi}_{i,0} \tag{39}$$

which is just a relation missing so far: chemical electronegativity of bulk solid is proved to be equal to the chemical electronegativity of a non-interacting individual atom. Since summation in eq. (38) goes in fact to infinity, an additional conclusion is born: differential hardness of a bulk solid, η_s, must be zero for atomic and molecular lattices. This result obtained on the ground of the electrodynamical analogy finds support in earlier work by Parr and Pearson who proposed $\bar{\eta} = 0$ for the chemical hardness of metals [9]. Application of eq. (37) to a set of binary crystals of semiconductors provides an interesting verification of the electrodynamical equation (38). Since $V_{i,s} \neq 0$ for ionic lattices, eq. (37) can be written as $\bar{\chi}_s = a\bar{\chi}_M + b$, where $\bar{\chi}_M$ is given by eq. (28). Fig. 2 represents a plot of the idealized calculated photoelectric threshold $\Phi_{calc} = \frac{1}{2}(I_0 + EA_A) + \frac{1}{2}E_g$ versus the experimental value Φ_{exp}. Satisfactory linear correlation around the line of unit slope indicates that $a \approx 1$, thus eq. (38) is corroborated.

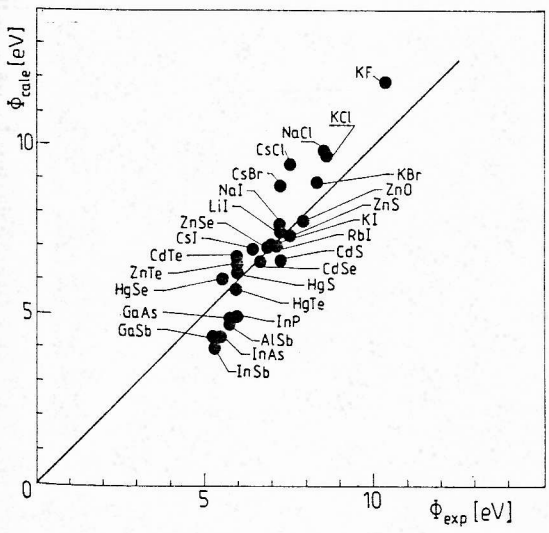

Fig. 2. Calculated and experimental work functions for binary semiconductors DA. Φ_{exp} and E_g are the same as in refs. [46,48].

9. Summary

In principle, pure chemical knowledge and experience allows a reasonable estimation of the electronegative character of atoms, yet translation of that knowledge into some numerical indexing has been a target of innumerable works. It is rather astonishing to see that development of quantum-chemical methods and their widespread use by chemists has not appeased a desire of some more simple and still meaningful description of chemical properties of bonded atoms. An interesting feature of the present chemical approximation is the remarkable capacity to unify the existing concepts of electronegativity and hardness.

The voluminous meaning of the word electronegativity may lead to ambiguities: what kind of action of a bonded atom is being compared when its electronegative character is considered? "A power to attract electrons to itself" can be demonstrated in several ways, very clearly seen in the example of a $D^{\delta+}A^{\delta-}$ molecule. Which one of two bonded atoms is said to be more electronegative?

(i) A, since it has attracted electrons from its partner and bears more negative charge.

(ii) D, since it would accumulate more electrons when extra charge $q < 0$ is added to the molecule.

(iii) Electronegativities of $D^{\delta+}$ and $A^{\delta-}$ are equal.

Probably none of these answers would be unanonimously accepted by chemists. This present work has built in a fourth answer to this question, by defining the chemical electronegativity in the same way for free and bonded atoms. Let a bonded atom get in contact with a source of electrons external to the molecule: more electronegative atom will attract more electrons without changing either the bonding state of its partner or its charge.

Both partners in the $D^{\delta+}A^{\delta-}$ pair have been attributed different indices of chemical electronegativity which reflect an otherwise obvious fact that atoms retain their chemical identity despite

being bonded. The index $\bar{\chi}_{i,M}$ for bonded atoms extends smoothly the meaning of chemical electronegativity for a free atom. It shows an interesting advantage over the valence state electronegativity of a free atom. The latter is calculated for a hypothetical valence state of a free atom, whereas $\bar{\chi}_{i,M}$ is easily found for an atom in a given chemical environment.

The chemical electronegativity of the molecule as a whole seems to have less meaning than it might have been expected, observing the efforts toward finding a unified formula for $\bar{\chi}_M$. Its use (as a measure of a power to attract electrons) seems to be limited to π interactions between molecules, and to formation of CT complexes. Though the field is of primary importance from the physicochemical point of view, it has rarely been discussed in terms of electronegativity. Since reproducing the molecular energies, ionization energy and electron affinity, remains beyond the reach of electronegativity-based speculation, $\bar{\chi}_M$ is to be considered merely as a guide index, with rather feeble relation to any real properties of the molecule. This also concerns the famous Sanderson geometric-mean formula which has never been proved to reproduce real $\frac{1}{2}(I + \mathrm{EA})$ values for molecules (neither was it ever claimed to do so). Sanderson's formula seems to owe its fame and frequent use to its usefulness in calculating the atomic charges via the electronegativity equalization procedure. The present approach has entirely circumvented the problem of atomic charges, thus also the need for the geometric-mean formula has not appeared.

Another common use of $\bar{\chi}_M$ has been the estimation of the group electronegativities for substituents or ligands [50]. Introduction of the chemical electronegativity index $\bar{\chi}_{i,M}$ for bonded atoms has offered another solution. Instead of using rather unreliable formulae for $\bar{\chi}_M$ one can characterize the group by the $\bar{\chi}_{i,M}$ index for the central atom.

The chemical approximation has enabled calculation of electronegativity indices for atoms in crystals, which may be of primary importance, as $\bar{\chi}_{i,s}$ contains readily available a priori information on atoms in solid. Its usefulness in studying adsorption phenomena is to be examined.

Acknowledgement

This work was sponsored in part under contract CPBP 03.08. The author is gratefully indebted to the referee for his suggestions.

References

[1] R.G. Parr, R.A. Donnelly, M. Levy and W. Palke, J. Chem. Phys. 68 (1978) 3801.
[2] R.A. Donnelly and R.G. Parr, J. Chem. Phys. 69 (1978) 443.
[3] R.G. Parr, in: Electron distribution and the chemical bond, eds. P. Coppens and M.B. Hall (Plenum Press, New York, 1982).
[4] L. Komorowski, Chem. Phys. Letters 103 (1983) 201.
[5] L. Pauling, The nature of the chemical bond (Cornell Univ. Press, Ithaca, 1960).
[6] R.P. Iczkowski and J.L. Margrave, J. Am. Chem. Soc. 83 (1961) 3547.
[7] H.O. Pritchard and F.H. Summer, Proc. Roy, Soc. A 235 (1956) 136.
[8] J. Hinze, M.A. Whitehead and H.H. Jaffè, J. Am. Chem. Soc. 85 (1962) 148.
[9] R.G. Parr and R.G. Pearson, J. Am. Chem. Soc. 105 (1983) 7512.
[10] J. Katriel, R.G. Parr and M.R. Nyden, J. Chem. Phys. 74 (1981) 2397.
[11] R.T. Sanderson, Chemical periodicity (Reinhold, New York, 1960).
[12] W. Yang and R.G. Parr, Proc. Natl. Acad. Sci. US 82 (1985) 6723.
[13] R.F. Nalewajski, J. Am. Chem. Soc. 106 (1984) 944.
[14] R.F. Nalewajski and M. Koniński, J. Phys. Chem. 88 (1984) 6234.
[15] J. Robles and L.J. Bartolotti, J. Am. Chem. Soc. 106 (1984) 3723.
[16] L. Komorowski, Chem. Phys. Letters 134 (1987) 536.
[17] J.N. Wilson and R.M. Curtis, J. Phys. Chem. 74 (1970) 187.
[18] P. Politzer, J. Chem. Phys. 80 (1984) 380.
[19] W. Gordy, Phys. Rev. 69 (1946) 604.
[20] A. Pasternak, Chem. Phys. 26 (1977) 101.
[21] P. Politzer, R.G. Parr and D.R. Murphy, J. Chem. Phys. 79 (1983) 3859.
[22] J.L. Gasques and E. Ortiz, J. Chem. Phys. 81 (1984) 2741.
[23] J.D. Jackson, Classical electrodynamics (Wiley, New York, 1975).
[24] W. Yang, Ch. Lee and S.K. Ghosh, J. Phys. Chem. 89 (1985) 5412.
[25] W.J. Mortier, K. van Genechten and J. Gasteiger, J. Am. Chem. Soc. 107 (1985) 829.
[26] R.G. Parr and L.J. Bartolotti, J. Am. Chem. Soc. 104 (1982) 3801.

[27] N.K. Ray, L. Samuels and R.G. Parr, J. Chem. Phys. 70 (1979) 3680.
[28] J.E. Huheey, Inorganic chemistry: principles of structure and reactivity (Harper and Row, New York, 1983).
[29] T.L. Ho, Chem. Rev. 75 (1975) 1.
[30] A.I. Vogel, J. Chem. Soc. (1948) 1833.
[31] R.S. Mulliken, J. Chem. Phys. 2 (1934) 782.
[32] J.P. Perdew, R.G. Parr, M. Levy and J.L. Balduz Jr., Phys. Rev. Letters 49 (1982) 1691.
[33] R.G. Parr and R.F. Borkman, J. Chem. Phys. 49 (1968) 1055.
[34] R.F. Borkman, G. Simons and R.G. Parr, J. Chem. Phys. 50 (1969) 58.
[35] M.D. Newton, W.A. Lathan, W.J. Hehre and J.A. Pople, J. Chem. Phys. 52 (1970) 4064.
[36] W. Gordy, J. Chem. Phys. 14 (1946) 305.
[37] N.N. Greenwood, in: Pergamon texts in inorganic chemistry, Vol. 8. The chemistry of boron (Pergamon Press, Oxford, 1975).
[38] F. Seitz, The modern theory of solids (McGraw-Hill, New York, 1940).
[39] N.L. Alpert, W. Kaiser and H.A. Szymański, IR theory and practice of infrared spectroscopy (Plenum Press, New York, 1970).
[40] C. Kittel, Introduction to solid state physics (Wiley, New York, 1966).
[41] S. Trascatti, J. Chem. Soc. Faraday I 68 (1972) 229.
[42] A.J. Downs and C.J. Adams, in: Pergamon texts in inorganic chemistry, Vol. 7. The chemistry of chlorine, bromine, iodine and astatine (Pergamon Press, Oxford, 1975).
[43] J.A. Pople and D.L. Beveridge, Approximate molecular orbital theory (McGraw-Hill Book, New York, 1970).
[44] R.F. Nalewajski, J. Phys. Chem. 89 (1985) 2831.
[45] W. Gordy and W.J. Orville-Thomas, J. Chem. Phys. 24 (1956) 439.
[46] A.H. Nethercot Jr., Phys. Rev. Letters 33 (1974) 1088.
[47] R.T. Poole, D.R. Williams, J.D. Riley, J.G. Jenkin, J. Liesegang and R.C.G. Letkey, Chem. Phys. Letters 36 (1975) 401.
[48] E.C.M. Chen, W.E. Wentworth and J.A. Ayala, J. Chem. Phys. 67 (1977) 2642.
[49] J.A. Alonso and L.A. Girifalco, Phys. Rev. B 19 (1979) 3889.
[50] S.G. Bratsch, J. Chem. Educ. 62 (1985) 101.
[51] L. Komorowski, Chem. Phys. 76 (1983) 31.
[52] Gmelin Handbuch der Anorganischen Chemie, 8 Auflage "Carbon, Pt.B" (1968).