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The concept of electronegativity. The current state of the problem

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Abstract. A systematic account is given of the current ideas about atomic and group electronegativities and the trends in the development of the concept of electronegativity are analysed. Attention is concentrated on the latest approaches to the definition of electronegativity — the concept of 'orbital' electronegativities and the density functional theory. A procedure is proposed for the determination of 'inductive' electronegativities, which permits a correct theoretical calculation of the electronegativity of a substituent from the electronegativities of individual atoms and the steric structure. It is shown that the approach developed has a series of important advantages — for example, it makes it possible to calculate the group electronegativities of isomeric substituents avoiding the principle of the equalisation of electronegativities. A survey of literature data and generalisation of the method proposed by the authors have made it possible to formulate the concept of electronegativity as an unchanging fundamental immanent characteristic of a chemical element. The bibliography includes 222 references.

I. The electronegativity of atoms

The history of the study of electronegativity (EN) has been described in a series of theoretical, methodological, and retrospective communications.[1–6] The concept and the term 'electronegativity' itself were introduced in 1932 by Pauling, who characterised it as the force with which an atom in a molecule attracts electrons. In Pauling's studies, the electronegativity of atoms was determined on the basis of thermodynamic data from the energies of the single bonds in which they are involved:[7]

$$\Delta E(\mathrm{AB}) = E(\mathrm{AB})_{\mathrm{exp}} - \tfrac{1}{2}[E(\mathrm{AA}) + E(\mathrm{BB})]\,, \qquad (1)$$

where ΔE(AB) is the additional energy of the interaction of the atoms A and B above the additive covalent contribution. Pauling observed that atomic additivity is characteristic of the function $\Delta E^{1/2}$ and that it may serve as a characteristic of the difference between the electronegativities (χ) of the atoms involved in the formation of the bond

$$|\chi_{\mathrm{A}} - \chi_{\mathrm{B}}| = 0.208\Delta E^{1/2}\ (\mathrm{eV}).$$

Having adopted EN for hydrogen as $\chi_{\mathrm{H}} = 2.1$, Pauling calculated the values of χ for a large number of atoms. The data which he obtained served as the basis for the first electronegativity scale. Virtually the same scale may be obtained by using in Eqn (1) the geometrical mean value of the covalent component of the bond energy.[8]

The fruitfulness of Pauling's idea and the practical importance of his scale were convincingly confirmed in studies by various investigators who published the results of thermochemical studies (see, for example, Batsanov's communication [8] and the literature quoted therein).

Later some investigators modified the computational scheme itself, whilst others redetermined the values of EN found by Pauling on the basis of their own experimental data and found new values of χ. As a result, Pauling's scale was significantly expanded and, what is particularly important, the EN for atoms in different valence states were determined. One of the most significant gaps in Pauling's original concept, which postulated a single value of χ for each atom regardless of its hybridisation, was thus abolished. Nevertheless, none of the subsequent studies introduced fundamental changes into Pauling's system of EN and into the method for their determination.

Furthermore, the main cause of the appearance of other approaches to the calculation of χ from physical characteristics of atoms and molecules was believed for a long time to be the impossibility of a thermodynamic description of the values of EN for all the elements in all the their chemical manifestations owing to the lack of the energies of individual bonds.[8]

Pauling's EN scale came to be generally employed and became a kind of reference standard for new methods of calculation of χ, many of the newly created scales being adjusted to Pauling's scale.[9] Furthermore, some of the modern investigators believe that Pauling's original EN scale is not only the most successful but is also adequate [10] and that his method is still one of the fundamental ones for the determination of EN.

Another no less familiar approach to the determination of electro-negativities was developed in 1934 by Mulliken,[11] who determined 'absolute' electronegativities, having expressed them in terms of half the sum of the ionisation energies of a neutral atom:

$$\mathrm{X} \longrightarrow \mathrm{X}^+ + \mathrm{e}^-$$

(first ionisation potential I) and a negative ion

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$$X^- \longrightarrow X + e^-$$

(electron affinity F) in the absence of the overlap of the electron shells of the interacting atoms:

$$\chi_M = \frac{I+F}{2}. \quad (2)$$

Mulliken considered two neutral systems X and Y having identical electronegativities. In this case, the energy changes in the two disproportionation reactions

$$X + Y \longrightarrow X^+ + Y^- \quad \text{and} \quad X + Y \longrightarrow X^- + Y^+$$

should be identical. The energies of the first and second reactions are $I_X - F_Y$ and $I_Y - F_X$, so that, after recalculation for a single valence electron, one obtains Eqn (2) in which EN is expressed in energy units.

Pauling's and Mulliken's scales proved to be linearly related (different workers give different parameters of the corresponding linear regression),[9,12–15] although the dimensions of the EN are in fact not the same. Furthermore, as already mentioned, the EN of atoms on Pauling's scale are regarded as unchanging, whereas the EN on Mulliken's scale should depend on the hybridisation of the atom (like the ionisation potential and the electron affinity). This factor served subsequently as a basis for the creation of scales containing the EN for atoms in different valence states.[8] At the same time, some workers have noted that Mulliken's system does not have a rigorous theoretical basis.[3,9] The use of ionisation potentials and electron affinities makes the Mulliken EN not only easy to obtain but also readily explicable, reflecting the average power of the atom to retain its own valence electron (described by I) and to attract the electron of its partner involved in the bond (described by F).

However, in a series of subsequent studies, only one of the parameters of the Mulliken equation was employed. For example, Vereshchagin[15] assumed that the EN of an atom is expressed directly by its electron affinity F, because EN reflects the 'tendency' of the atom in the molecule to attract electrons. On the other hand, in practice, procedures for the calculation of EN involving the use of the ionisation potential (IP) of the atom came to be most widely used.[16] Thus the employment of average IP for the calculation of EN by the equation

$$\chi = -\frac{I_n}{n} + F,$$

where I_n is the ionisation potential of an n-valent atom and F its electron affinity, made it possible to find the values of χ satisfactorily correlated with the EN found by Pauling.[17]

Martynov and Batsanov[18] put forward the hypothesis that, from the physical standpoint, EN could be usefully determined as the average energy per valence electron and expressed in terms of the arithmetical mean of all the IP of all the valence electrons $\left(\sum_{i=1}^{m} I_i\right) \Big/ m$. Allen[19] identified the average energy of a single valence electron with the weighted mean of the energies of s and p electrons (ε_s and ε_p respectively):

$$\chi_{spec} = \frac{m\varepsilon_s + n\varepsilon_p}{m+n},$$

where χ_{spec} is the 'spectroscopic' EN.

In a later review,[3] he notes that the ionisation potential of a valence electron should in fact be regarded as an objective physical characteristic reflecting the EN of an atom and formulates the equation quoted above as

$$\chi_{spec} = \frac{mI_s + nI_p}{m+n},$$

where I_s and I_p are the IP for s and p electrons respectively.

The employment of the first IP of atoms (in Mulliken's procedure the values of I averaged in a certain way) or of the last IP for the calculation of EN[20,21] leads to results which agree with those obtained by Pauling.[8] This situation can be evidently accounted for by the fact that both the electron affinity and different IP functions and hence EN itself are determined by the same factor — the individual electronic structure of the atom.

This idea constitutes in essence the basis of another widely employed procedure for the determination of EN — χ is found from geometrical relations of the type

$$\chi = aZR^{-n} + b, \quad (3)$$

where a, n, and b are constants, Z is the effective nuclear charge, and R is the covalent atomic radius.

The 'geometrical' EN scale was first put forward by Gordy,[22] who identified EN with the electrostatic potential generated by the effective nuclear charge Z on a covalent sphere with a radius R:

$$\chi = 0.62\frac{Z}{R} + 0.5. \quad (4)$$

The effective nuclear charge Z is the charge of a nucleus partially shielded by electrons:

$$Z = Z^* - \sigma,$$

where Z^* is the formal nuclear charge and σ is the shielding constant.

There are several ways of determining σ, among which Slater's semi-empirical method is the most familiar. According to this method, the electron shells have their own values of σ_i, the sum of which determines the shielding constant of the atoms σ.

According to Gordy,[22] $\sigma = 1$ for inner electrons and 0.5 for valence electrons. Thus Eqn (4) assumes the form

$$\chi = 0.31\frac{n+1}{R} + 0.5, \quad (5)$$

where n is the number of valence electrons.

The calculation of EN by Gordy's procedure is simple; it is also quite important that this method makes it possible to express electronegativity in terms of fundamental characteristics of the atom — Z and R, demonstrating the 'periodic' character of χ which distinguishes EN, according to the view of many investigators, from other quantitative characteristics of intramolecular interactions.[15] Even within the framework of the same 'geometrical' system, different parameters a and b in Eqn (3) are characteristic of elements belonging to different Periods.

The fact that in Gordy's method the electrostatic potential was first employed to calculate EN must be included among its undoubted advantages. This idea subsequently proved very fruitful.[9]

Allen[19] proposed that the Periodic Table be considered in a three-dimensional form and that the spectroscopic electronegativities of the elements be introduced as the third dimension. In Allen's view, this will make it possible to rationalise the diagonal subdivision of the Periodic Table into metals and nonmetals. With the aid of $\Delta\chi_{spec}$, it is possible to arrange systematically the properties of an extensive range of familiar materials: ionic crystals, covalent compounds, metals, minerals, inorganic and organic polymers, semiconductors, *etc*.

An ideologically similar approach has been used by Sproul,[23,24] who proposed a simple graphical procedure for the determination of the nature of bonds in binary two-component molecules A_nB_m. By plotting the electronegativity difference $\chi_A - \chi_B$ against the average value $\overline{\chi}$ for a wide range of compounds A_nB_m, Sproul observed that the points on the resulting plot form three different regions corresponding to the ionic, metallic, and covalent nature of the bonds between A and B. Regardless of the EN scale employed, the nature of the distribution and separation of the points was reproduced every time.

Strictly speaking, the conclusion that the electronegativities of partner atoms involved in the bond determine the nature of the latter followed from the work of Pauling himself. However, on the basis of empirical data, Sproul showed that the best graphical separation is achieved when Allen's [19] and Nagle's [25] scales are employed. Nagle considered the ratio $(n/\alpha)^{1/3}$, where n is the number of valence electrons and α the polarisability of the isolated atom, as a measure of the polarisability of isolated atoms. Since it is known that $\alpha^{1/3}$ for an isolated atom is proportional to its radius,[26,27] Nagle's EN scale, like that of Gordy, can be assigned to the class of 'geometrical' scales.

There are quite a few approaches to the determination of χ in which the number of valence electrons [28] or directly the number of the Group [14,29] are used.

Returning to the history of the development of 'geometrical' systems, we shall consider the widely familiar study by Pritchard and Skinner,[30] who devised a more rigorous approach to the calculation of the parameter Z in Eqn (4) and obtained, within the framework of Gordy's method, an EN scale which agrees well with Pauling's scale.

Luo and Benson [31] identified EN with the energy of attraction of a valence electron at a distance equal to the covalent radius from the nucleus;

$$\chi_{LB} = \frac{m+n}{R},$$

where m and n are the numbers of s and p electrons respectively and R is the covalent radius. They created a scale of χ_{LB} values, which they called 'covalent potentials'. The Luo – Benson scale is one of the most familiar and frequently employed in the interpretation of experimental EN data.[32] On the basis of the results of the analysis of the frequency distribution of elements with respect to a range of values of χ, Filippov and Gorbunov [33] isolated from the set of known EN data the 'covalent potential' scale and recommended it as the most convenient for practical use.

Neng and Guo [34] proposed another modern EN scale reflecting the properties of the outer valence electrons of isolated atoms. They defined EN as the average nuclear potential of the last valence electron:

$$\chi = \frac{Z^*}{\langle r\rangle_{nl}}.$$

Here $\langle r\rangle_{nl}$ is the average radius, which serves as a specific measure of the distance from the valence electron to the nucleus (the averaging was carried out not only with respect to the orbital radius but also with respect to the possible effects of the nuclear core) and Z^* is the nuclear charge acting on the valence electron separated by the distance $\langle r\rangle_{nl}$ from the nucleus and strictly speaking not identical with Slater's nuclear charge. The EN scale introduced by these investigators [34] for free atoms is correlated with Mulliken's scale.

The relation

$$\chi_A - \chi_B = k(f_{AB} - 0.5),$$

where k is the scaling factor, f_{AB} is the orbital factor determined by the distances from the atoms A and B to the centre of the bond orbital (r_A and r_B respectively), *i.e.*

$$f_{AB} = \frac{r_A}{r_A + r_B}$$

and $f_{AB} - 0.5$ is a measure of the difference between the forces of attraction of electrons by atoms, serves as the basis for the creation of the first nonempirical scale within the framework of the quantum-mechanical FSGO (floating spherical Gaussian orbital) method.[35]

It is noteworthy that the nonempirical FSGO method yields reasonable and reliable values of EN, which are correlated with those on Pauling's scale, but a lot of calculation is then necessary.

The method for the estimation of EN in terms of electron density is very close to the FSGO method:[36] the scale obtained on this basis takes into account the topological properties of the electron distribution density in the molecule. The H – X systems (where X is an atom or group of atoms) with the distances r_H and r_X to the bond critical point (BCP) are considered within the framework of this method. The parameter F_X may serve as an equivalent of the EN of the atom X:

$$F_X = \frac{r_H}{n_X \rho(r_i) r_{HX}},$$

where n_X is the number of valence electrons given up by the atom X to the molecule HX and $\rho(r_i)$ is the electron density at the BCP. If the values of F_X are adjusted to the scale with the boundary values $\chi(Li) = 1.0$ and $\chi(F) = 4.0$, then χ_X can be found from the equation

$$\chi_{\tilde{n}} = 1.938 F_X^{-0.2502}.$$

The values obtained in this way are correlated both with those calculated by Pauling and with the χ_{FSGO}.

We may note that, in systems analogous to H – X the electronegativity of the atom X is expressed in terms of the change in the H – X bond length on ionisation.[37] Marriott *et al.*[38] considered derivatives of HX and showed that the charge density on the hydrogen atom, obtained within the framework of *ab initio* calculations, may be used as a simple measure of the electronegativity of X.

The study of Allred and Rochow [39] initiated the overall direction of the development of the 'geometrical' methods for the calculation of EN. They were the first to represent EN as the force of the interaction of an unshielded atomic nucleus and a valence electron separated by a distance corresponding to the covalent radius R:

$$\chi = 0.36\frac{Z_{ef}}{R^2} + 0.74.$$

The value of Z_{ef} is determined in accordance with Slater's rule. Numerical coefficients adjust χ to Pauling's scale.

Evidently the method for the description of EN as a 'force' corresponds best to its initial definition by Pauling and comparison of the values found by Allred and Rochow with those derived for other systems demonstrated the high quality of their approach.[8,9] The Allred – Rochow EN system is one of the best known and most frequently employed. For example, Allen identifies it, together with Pauling's system, as the best founded and most acceptable at the present time.[3] Employment in the Allred – Rochow equation of experimental values of Z_{ef} obtained from X-ray diffraction data makes it possible to put forward an EN scale [40] which agrees with Pauling's scale.

The 'force' approach to the determination of EN was later developed in many investigations.[8,41,42] Boyd and Markus [43] proposed a theoretical method for the calculation of EN based on a nonempirical electrostatic model, according to which electrostatic forces, which determine χ, act between the effective nuclear charge and electrons at a certain distance r from the nucleus:

$$\chi = cNr^{-2}\left[1 - \int_0^r D(r)dr\right],$$

where c is the normalising coefficient which adjusts the EN to Pauling's scale, N is the atomic number, and $D(r)$ is the radial density function. Application of the Hartree – Fock wave function enabled the authors to obtain electro-negativities which are satisfactorily correlated with the values on empirical scales.[9]

The force acting on an electron (and hence EN) can be determined [42] within the framework of the inverse quadratic dependence on the radius R using the ionisation potential of the valence electron I and the effective principal quantum number n^*:

$$\chi = 0.241\frac{n^*(I/\mathrm{R})^{1/2}}{r^2} + 0.775$$

(R is the Rydberg constant).

Sanderson's 'geometrical' system,[44–54] based on the inverse cubic law, relates the EN of an atom to its volume electron density (ED), which is determined by the atomic number N and the covalent radius R:

$$\mathrm{ED} = \frac{3N}{4\pi R^3}\,.$$

Sanderson suggests that a dimensionless quantity, which he called the 'stability ratio' (SR), be used as a measure of ED. It is obtained by dividing the ED for the atom by the ED for the inert gas in the given Period (the value of R for the latter is interpolated). The stability ratios thus obtained, characterising according to Batsanov [8] not isolated atoms (as postulated by Sanderson himself) but atoms in molecules, form an intrinsic electronegativity scale (SR), which can be adjusted to Pauling's scale by means of the following equation:[8,9]

$$\chi = (0.21\mathrm{SR} + 0.77)^2\,.$$

The values of SR are correlated satisfactorily with experimental data.[9]

More than 20 different 'geometrical' EN systems are known.[55] It is assumed that the increase in the accuracy of such systems is associated with the increase in the power exponent n in Eqn (3). However, Batsanov [8] has noted that the accuracy increases also with increase in the constant term b. The increase is caused by the parallel increase in the difference between the dimensionalities of the thermochemical and geometrical EN.

In order to reduce this difference to a minimum, Batsanov proposed a new geometrical EN system. Having adopted as a basis the Cottrell–Sutton formula

$$\chi = 0.5\left(\frac{Z}{R}\right)^{1/2} + 0.2$$

(one of the earliest geometrical systems), he put forward the following relation whereby the maximum approach of the values of χ to Pauling's scale is achieved:

$$\chi = \alpha\left(\frac{Z^*}{R}\right)^{1/2},$$

where α is a correction factor:

$$\alpha = \frac{1 + 0.1n}{1 + 0.01(n^*)^3}\,,$$

n being the number of the Group of the element in the Periodic System.

By modifying this equation, it is possible to calculate the EN of atoms in the crystalline state, which is necessary for the interpretation of the nature of the bonds in binary and complex compounds.

As noted above, several tens of EN scales, based on different properties of atoms and molecules, which are not always identical, are known. As a rule each scale is satisfactorily correlated with several other EN scales. This apparently reflects the identity of their nature despite the fact that the values of EN proposed by different workers may differ both in dimensionality and in the methodology of their determination and even in the physical significance attributed to them.

We may note that the criteria of the validity of a particular approach to the determination of EN are lacking, which is perhaps the principal problem as regards the concept of EN. For this reason, investigators test the correctness of any new EN system by comparing it with the scales already available. The necessary correspondence can be achieved with by no means all the scales and investigators have to be satisfied as a rule by a more or less acceptable reproduction of a proportion of them.

Indeed the question arises which physical (or chemical) characteristic or property should be regarded as the most adequate expression of χ, how should EN be measured, and what is its dimensionality. In order to answer these questions, it is essential to understand what EN actually is. Paradoxically, despite the more than adequate, from the scientific point of view, age of the concept of EN, controversy as to 'what is electronegativity' has not been resolved even now. The majority of investigators tend to adopt Pauling's original treatment: 'EN is the force with which an atom in a molecule attracts electrons'. However, the current content of this concept is much wider. Since EN is undoubtedly an individual atomic characteristic, the question naturally arises what individual property of the atom determines its power to attract electrons in the molecule. Finally, is this property additive and to what extent? Evidently the property must be characteristic of an individual free atom (the majority of approaches are based precisely on this idea), but at the same time it can remain unchanged or vary in proportion to the initial value on formation of bonds. It has to be said that an exact unambiguous answer has not been obtained to the majority of these questions to this day.

II. The electronegativity of groups

The development of the concept of EN has inevitably led to the appearance of the idea of the EN of a group (substituent).

In 1951, Sanderson put forward the postulate according to which the EN of a molecule is equal to the EN of any atom in it and proposed a method for the averaging of the EN on the basis of their geometrical mean.[9] Sanderson's total equalisation principle initiated the overall direction of the development of the concept of EN and made it possible to calculate the EN of groups and substituents from the atomic χ.

If EN is a characteristic not only of an atom but also of a group, the question of the quantitative determination of the group EN is legitimate. According to Pauling's classical definition, the latter is the force with which the group attracts valence electrons in the molecule.

The EN of groups of atoms were first calculated by Pritchard and Skinner [30] in a study of the thermochemical characteristics of disproportionation reactions of mercury derivatives.

Finemann [56] later modified Pauling's classical method for the determination of the EN of hydrocarbon radicals:

$$\Delta E = E(\mathrm{AR}) - \tfrac{1}{2}[E(\mathrm{AA}) + E(\mathrm{RR})]\,,$$

where A is an atom and R a radical. The quantity $\chi_{\mathrm{Me}} = \chi_{\mathrm{C}}$ was adopted as the standard.

Subsequently this thermodynamic approach was developed and partially applied in practice. The results of the analysis of the thermodynamic parameters of various reactions and experimental bond energy data have been described in detail in a monograph.[8]

When Pauling's method is employed, account is frequently taken of the results of other physicochemical studies. Thus the following equation has been employed:[57,58]

$$D(\mathrm{AB}) = [D(\mathrm{AA})D(\mathrm{BB})]^{1/2} + k|\chi_{\mathrm{A}} - \chi_{\mathrm{B}}|^2\,.$$

Here the force constant k is optimised on the basis of the values of χ_{B} obtained from the parameters of NMR spectra. Examples of a similar use of hydrolysis [59] and basicity constants, oxidation potentials, *etc.*[15] are known.

1. Determination of electronegativity from correlations with physical properties

The concept of EN is directly related to ideas concerning bond energies. The energy of chemical bonds determines in its turn many physical characteristics of compounds, for example spectroscopic characteristics. Thus the numerous correlations between EN and various spectroscopic parameters, frequently employed in finding new values of χ, have a physical justification.

It has been noted [8,15] that it is most useful to employ bond force constants, which are determined solely by the energies of the interactions between atoms. Such a relation was first established by Gordy,[60] who expressed the force constant k as a function proportional to the product of the EN of the atoms involved in the bond. Furthermore, the force constant k_{AB} of the A–B bond can be expressed, as in Pauling's method, in terms for the corresponding values for homogeneous bonds, k_{AA} and k_{BB}, and the difference between the EN of the atoms A and B:[61]

$$k_{AB} = (k_{AA}k_{BB})^{1/2} + (\chi_A - \chi_B)^2 .$$

However, since the force constants are difficult to obtain, correlations between EN and the vibrational frequencies of atoms have come to be most widely employed.

As early as 1954, Bell *et al.*[62] found a linear relation between the vibrational frequency of the P=O bond in the compounds ABCP(O) and the sum of the EN of the groups A, B and C. Subsequently this approach was extended [63] to the carbonyl derivatives ABC=O.[64,65]

Relations between the vibrational frequency of a functional group and not only the EN of the substituents but also the EN of the atom attached to the group are widely known. Thus it has been shown [66] that there is a linear relation for the compounds $CH_2=CHX$ between the frequencies of the out-of-plane deformation vibrations of the CH_2 groups and the Pauling EN of the atoms X. A similar dependence on the EN of a halogen atom is characteristic of the ν(H–Hal) stretching vibrations.

Subsequently similar relations were discovered not only for the compounds HR [67,68] but also for the methyl derivatives CH_3X.[69] Correlations between the EN and the vibrational frequency of the OH,[70] CN, CH, *etc.*[15] groups have also been obtained. It has been shown [71] that the vibrational frequencies of the $-CH_2-$ fragment in the molecules $A-CH_2-B$ are directly related to the sum of the electronegativities of A and B. On the other hand, a dependence of ν on χ^2 has been found for these systems.[72] Similar relations have been noted also in a series of other investigations (see, for example, a monograph [15] and the literature quoted therein). Relations between ν and $\chi^{1/2}$ have been established for the vibrational frequencies of the C–Si bonds in silane derivatives.[73] Vereshchagin [15] has noted that the correlations between the parameters of vibrational spectra and EN can be extended to compounds of any complexity.

A large number of studies have been devoted to relations between the EN of atoms and groups and NMR spectroscopic data. Spin–spin coupling constants, particularly for olefinic derivatives, are used to calculate the unknown values of χ.[74,75] Numerous linear relations between EN and vicinal constants have been discovered.[15] The chemical shifts of protons have also been considered as characteristics of EN. For example, an expression relating the difference between the proton shifts of methylene and methyl groups to the EN of the substituent X has been established:[76]

$$\chi = 1.71 + 0.02315[\delta(CH_3) - \delta(CH_2)] .$$

Inamoto and coworkers [77,78] have shown that the chemical shifts in the ^{13}C NMR spectra of certain aliphatic (EtX) and aromatic (PhX) derivatives reflect the influence of the EN of the corresponding substituent X. In order to account for experimental NMR data, a new 'inductive' parameter of the substituents has been proposed. It is calculated by a formula similar to Gordy's equation [Eqn (4)]:

$$i = \frac{Z_{ef} + 1}{n_{ef}} .$$

The relations describing the influence of the EN of the substituent on the shielding of the nuclei continue to be used widely even to this day in ^{1}H,[79] ^{13}C,[80–82] ^{19}F,[83,84] ^{13}P,[85] ^{119}Sn,[15,86] *etc.* spectroscopy.

Correlations between EN and the shifts of the absorption maxima of compounds in UV spectra, ^{35}Cl NQR spectroscopic frequencies, and other physicochemical parameters are known.

2. Theoretical approaches to the quantitative estimation of group electronegativities

The experimental methods described above have undoubtedly played and continue to play an important role in the quantitative estimation of Group EN. At the same time, it is evident and reasonable that procedures for the calculation of EN of groups using the EN of their substituent atoms are theoretically of greatest interest among all the diverse approaches to the solution of this problem.

The majority of studies in this field may be assigned to two principal aspects. The first identifies the donor–acceptor properties of the substituent with the nature of its central atom (CA). Thus the problem of the determination of the group EN (χ_g) reduces to finding a value of the EN at the first (central) atom of the group modified depending on the environment:

$$\chi_g = \chi(CA) + \delta\chi(CA) .$$

Thus, in Gordy's method,[22] on passing from the calculation of the EN of atoms to that of the EN of groups the number of valence electrons n in Eqn (5) is replaced by the effective quantity n^*, reflecting the 'electron atmosphere' of the first atom. The latter is calculated from the EN of the first atom and a series of independent parameters introduced by various investigators in a fairly arbitrary fashion.[87,88] The corresponding equation has the form

$$\chi = a\frac{n^* + 1}{R} + b$$

A similar 'geometrical' approach to the determination of the EN of the central atom as a measure of the EN of the group is used in the Luo–Benson method of 'covalent potentials' (U_X):[31,88–92]

$$U_X = \frac{n_X}{R_X}$$

where n_X is the number of valence electrons of the central atom and R_X is its covalent radius.

The fundamental difference between this method and others consists in the fact that the covalent radius of the central atom (R_X) is considered as the variable. Since this experimental physical quantity characterises the size of the atom in the 'covalent' molecule, *i.e.* the atom in the energetically optimal valence state and not the free state, one can postulate that the calculated values of R_X are reliable. This hypothesis has been confirmed by the satisfactory correlation between U_X and the results of other workers.[91–93]

The contribution of the environment of the central atom to the overall EN of the group is calculated within the framework of certain approaches on the basis of a kind of similarity of the additive scheme, which admittedly does not have a rigorous physical and mathematical justification. Thus the following equation has been proposed for the calculation of the EN of the group AX_m:[94]

$$\chi(AX_m) = \chi(A) + \frac{m}{6}[\chi(X) - \chi(A)] .$$

If the substituents at A were different, similar relations were employed. For example, the EN of the group $CX^1X^2X^3$ (Refs 64, 65) was calculated by the equation

$$\chi(CX^1X^2X^3) = 0.5\chi(C)\sum \frac{\chi^2(X)}{12\chi(H)}.$$

The other aspect, developed in Sanderson's studies,[44–54] is based on the principle of the equalisation of electronegativities which he postulated. In this approach the group EN is considered as a function of the averaging of the EN of all the atoms constituting the substituent. Apart from the geometrical-mean function, proposed by Sanderson himself,[95,96] the arithmetical-mean [8,15] harmonic-mean,[97] *etc*.[98] functions were examined.

All the theoretical methods specified above for the determination of the group EN are linked by the idea that the EN of a free atom changes when the latter forms a covalent bond. Thus an internal electronegativity, equalised *in situ*, is attributed to the 'bound' atom. It can be determined also by its environment, among other factors. The *in situ* EN of atoms determine in their turn the donor–acceptor properties of the group itself.

A logical development of the entire EN theory consisted in the fact that an intrinsic and unique value of EN was assigned to each atom, as had been done in the original study by Pauling, after which the EN of the atom in different valence states were introduced, and finally there arose the concept of the *in situ* EN of the bound atom, which depends on its environment, *i.e*. on the state of the atom in the molecule.

Consequently any attempt to designate the relation between the 'free' EN and the EN *in situ* involves the principal problem in chemistry — what is an atom in a molecule? In practice the consideration of the EN of chemical groups and the atoms in them makes it necessary to take into account the distribution of electron density.

III. The concept of 'orbital' electronegativities and the equalisation principle

As noted above, Mulliken's definition of EN [11] postulates the dependence of EN on the valence state of the atom, which made it possible to abandon the idea of the existence of a unique EN for each atom regardless of its hybridisation. The need to take into account the orbital in which the valence electron is located then arises.

While studying this problem Hinze and Jaffe [99–101] introduced the concept of the 'orbital' EN and developed a semi-empirical method for the calculation of the ionisation potential (I_V) and the electron affinity (F_V) for any valence state v. This made it possible to find the EN by Mulliken's method taking into account the corresponding valence states of the atoms:

$$\chi_M = \frac{I_v + F_v}{2}. \qquad (6)$$

The calculated values proved to be linearly related to those determined by Pauling's method.

It is noteworthy that quantum-mechanical calculations are used to evaluate the orbital EN for pure *s*, *p* and *d* states. In order to obtain the EN of an atom, they are added together in conformity with the degree of hybridisation of the atom:[15]

$$\chi = n_s\chi_s + n_p\chi_p + n_d\chi_d + \ldots$$

The orbital EN (χ_l) may be expressed [102] also in terms of the radius of the valence shell and the quantum number *l*:

$$\chi_l = \frac{l}{R}.$$

If χ_1, χ_2, and χ_3 are the EN of the *s*, *p*, and *d* orbitals respectively, then the atomic EN is expressed as follows:

$$\chi_a = 0.43\sum^{2}\chi_l + 0.24.$$

It has also been suggested that the orbital EN be calculated by Mulliken's method with the aid of the modified Eqn (6):[103–107]

$$a = \frac{I_v + F_v}{2} = \frac{I_0 + P_0 + P^+ + P^-}{2},$$

where I_0 and P_0 are respectively the ionisation potential of the free atom and the energy of the transition of the free atom to the given valence state and P^+ and P^- are the energies of the promotion of the cation and anion formed from the atom in the valence state v.

Special mention should be made of the study of Iczkowski and Margrave,[108] which to a large extent determined the subsequent development of the ideas about the orbital EN. In 1961, these workers first represented the energy of an isolated atom (E) as a function of the filling of the electron shell:

$$E(\delta) = E_o + a\delta + b\delta^2 + c\delta^3 + d\delta^4, \qquad (7)$$

where E_o is the energy of the ionised core, δ is the partial charge of the atom, and *a*, *b*, *c*, and *d* are empirical coefficients, which depend on the nature of the atom and its valence state.

According to the authors themselves, it is sufficient to restrict Eqn (7) to second-order terms (at least for *s* and *p* elements):

$$E(\delta) = E_o + a\delta + b\delta^2. \qquad (8)$$

If it is assumed that $E_o = 0$, $E(1) = I$, and $E(2) = I + F$, then the values of *a* and *b* expressed in Mulliken terms are obtained:

$$a = \frac{3I - F}{2}, \quad b = \frac{F - I}{2}.$$

Iczkowski and Margrave regarded $E(\delta)$ as a continuous and differentiable function of δ and identified the EN of an isolated atom with the first derivative of the energy with respect to the occupation number of the valence orbitals:

$$\chi = \frac{dE}{d\delta}. \qquad (9)$$

In this representation, the EN of an atom may be expressed as a linear function of δ:

$$\chi(\delta) = a + 2b\delta. \qquad (10)$$

It was subsequently proposed that a more rigorous three-term equation be employed:[109]

$$\chi(\delta) = a + b\delta + c\delta^2$$

with empirical coefficients differing markedly from those in Eqn (10) (here the contribution of the quadratic terms is relatively small). Nevertheless the linear Eqn (10) has in fact come to be most widely used and has become best known. On substituting into it the parameters *a* and *b* expressed in the Mulliken form, it is possible to obtain the following expressions for the EN of a cation, a neutral atom, and an anion respectively:

$$\chi(0) = \frac{3I - F}{2}, \quad \chi(1) = \frac{I + F}{2}, \quad \chi(2) = \frac{3F - I}{2}.$$

On the one hand, the identity of the equation for the EN of a neutral atom $\chi(1)$ with the Mulliken expression served, according to Iczkowski and Margrave, as confirmation of the correctness of their approach. On the other hand, Mullay [9] noted that such results yielded an additional theoretical justification of Mulliken's scale itself, which may possibly make it the best among all others.

It is noteworthy that Iczkowski and Margrave were not the first to relate the *in situ* EN of an atom to its partial charge δ. As early as 1951, Sanderson [95] suggested, on the basis of the principle of the total equalisation of electron density, a simple scheme for the calculation of δ. Here the *in situ* χ was calculated as the geometrical mean.

Nevertheless, it was in fact Eqns (9) and (10) that became the 'starting' point for the further development of the theory and methods for the calculation of EN.

Hinze *et al.*[110] developed ideas concerning orbital EN and identified the donor–acceptor properties of an isolated atom with the EN of its valence orbital. Having adopted as a basis the definition of lczkowski and Margrave, who expressed the EN of an isolated atom in terms of the potential acting on the valence orbital [Eqn (9)], the authors suggested that similar relations be used for the orbital EN (χ_{a_j}):

$$\chi_{a_j} = \frac{\partial E_a}{\partial n_j}, \tag{11}$$

where E_a is the energy of the atomic orbital j and n_j is its population.

Next, having postulated that the function $E_a(n)$ is continuous and differentiable and having restricted it to the quadratic dependence on n, they obtained a linear equation relating the EN of the orbital to its population:

$$\chi_{a_j} = a_a + 2b_a n_{a_j}. \tag{12}$$

This equation is analogous to Eqn (10). According to the data of Whitehead *et al.*,[111] the parameters a_a and b_a may be expressed, as in Eqn (10), in terms of the ionisation potential and the electron affinity, but in this case not of the atom but of the corresponding orbital j. Furthermore, Whitehead showed that the parameters a_a and b_a can be determined by using the parameters of the population of all the valence orbitals of the atom other than j.

As mentioned above, Eqns (10) and (11) identify the EN (the EN of an isolated atom and the orbital EN) with the potential, which possesses *a priori* the equalisation property. This factor reasonably led the creators of the theory of orbital EN to the idea of their equalisation. In conformity with Meek's hypothesis,[105] the orbital EN of the atoms A and B are equalised on formation of the bond A–B:

$$\frac{\partial E_A}{\partial n_A} = \frac{\partial E_B}{\partial n_B},$$

hence the functions of the charges on each of these atoms also become equal:

$$a_A + 2b_A n_{A_j} = a_B + 2b_B n_{B_j}.$$

Thus, bearing in mind that two electrons participate in the formation of the bond, *i.e.* $n_{A_j} + n_{B_j} = 2$, the equation obtained can be used to establish the charge distribution. On the basis of the foregoing, an iterative method for the calculation of the EN of haloalkyl groups has been developed;[110] with its aid, it has been possible to calculate certain group χ.

Subsequently Huheey [112,113] proposed a simple scheme for the determination of the EN of groups based on the Iczkowski–Margrave Eqn (10), but in this instance operating with the values of a_A and b_a taken from the studies of Hinze, Whitehead, and Jaffe. On the basis of Sanderson's study, Huheey postulated the equality of the EN of the group and its constituent atoms. Thus the following expression was obtained for the substituent AB_n:

$$\chi_{AB_n} = \chi_A = \chi_{B_1} = ... = \chi_{B_n} = a_A + 2b_A\delta_A = a_B + 2b_B\delta_{B_1} = ... = a_B + 2b_B\delta_{B_n}.$$

Having solved these equations, it is possible to obtain, as in the method of Hinze, Whitehead, and Jaffe, the charges and the group EN. The solutions can then be found for a neutral group, a cation, and an anion (subject to the condition that $\delta_g = \Sigma\delta = 0, +1$, and -1 respectively). Having applied his approach, Huheey calculated the EN of almost 100 substituents and, what is no less important, analysed the significance of the coefficients in the equation relating the EN of a group (atom) to the charge and identified a_A with the intrinsic value of the EN of the atom and b_A with the sensitivity of the EN to a change in the charge.

A similar approach, based on the hypothesis of the equality of a_A and b_A, *i.e.* $\chi_a = a_a + b_a\delta_a = a_a(1 + \delta_a)$, and the principle of the total equalisation of the EN, made it possible to obtain the following expression for the group EN:[9]

$$\chi = (N + \delta_g)/\sum_1^N \frac{n_i}{\chi_{a_i}}, \tag{13}$$

where $N = \Sigma n_i$ is the total number of atoms, n_i is the number of atoms in the group, and χ_i is the EN of the ith atom on Pauling's scale before the formation of the molecule.

Subsequently Mullay [114] established another relation between the coefficients a_a and b_a, namely $b_a = 1.5a_a$, and expressed the *in situ* orbital EN in the following manner:

$$\chi_{a_j} = a_a(1 + 1.5\sum\sigma_a). \tag{14}$$

The EN of a chemical group AB is then determined as the EN of its central atom on which an effective charge $d_j \ll 0$ is accumulated at the expense of the orbital j, ensuring a bond between the central atom and the rest of the molecule. Subject to the condition of the conservation of electroneutrality ($\delta_{A_j} + \delta_{B_j} = 0$) and the equalisation of the orbital EN ($\chi_A = \chi_B$), it is possible to obtain an expression for the calculation of group EN analogous to Eqn (13):[3]

$$\chi_g = \frac{N + 1.5\sigma_g}{\sum_1^N n_i/\chi_i}.$$

The group EN obtained within the framework of this method, which takes into account the hybridisation of the valence orbital and the effective charge on the group, have reasonable values.

Subsequently this approach was improved: a term taking into account the interatomic electronic repulsion of the valence orbitals was added to Eqn (14):[115,116]

$$\chi_{a_j} = a_{a_j}(1 + 0.5\sum\delta_{a_i} + 1.5\sum\delta_{a_i}).$$

Thus the concept of orbital EN became the basis of the modern concept of EN, with the aid of which not only have the new easy methods for the calculation of EN been created but its physical nature has been to a large extent elucidated. Certain principal postulates of this concept of EN have been subjected to serious criticism at various times;[3] the very legitimacy of identifying the EN solely with orbitals has been questioned;[9] in some investigations, it has been shown that the idea of using orbitals in discussing EN is not always necessary.[117] The arbitrary nature of the assumption of the continuity and differentiability of the relation between the energy of the system (atom, molecule) and the number representing the filling of the orbitals by valence electrons [the function $E(q)$], the assumption constituting the basis of the theory of orbital EN, has also been noted.[6] This hypothesis is strictly speaking invalid for an isolated atom: in this case, the values of the argument q can only be discrete.

Slater [118] emphasised that in the fundamental equations of the X_α SCF method there are no limitations associated with the requirement that q is integral because atomic and electronic systems obey Fermi statistics, a characteristic feature of which is fractional energy level occupation numbers. At the same time, he justified the expansion of the function $E(q)$ in the series

$$E(q) = E(0) + \left(\frac{\partial E}{\partial q}\right)q + \frac{1}{2!} - \left(\frac{\partial^2 E}{\partial q^2}\right)q^2 + \frac{1}{3!} - \left(\frac{\partial^3 E}{\partial q^3}\right)q^3 + ... \tag{15}$$

Eqn (15) is analogous to the empirical Iczkowski–Margrave Eqn (7). Comparison demonstrates the correspondence between the coefficients a and b in the Iczkowski–Margrave equation and the first and second derivatives of the energy with respect to the occupation number in the Slater formula.

Klopman [119–121] also showed that it is possible to expand the energy in a series analogous to the series in Eqn (7). Within the

framework of the theory of atomic spectra, he expressed the energy of a free atom by the equation

$$E_a = \sum_i B_a^l + \frac{1}{2}\sum_{ij} A_a^+ \delta_{ij} + \frac{1}{2}\sum_{ij} A_a^- (1 - \delta_{ij}) , \quad (16)$$

where B_a^l is the energy of the ith electron in the atomic spin-orbital in the electron shell with the quantum number l, A_a^+ and A_a^- are the energies of the interaction of electrons with identical and opposite spins respectively, and δ_{ij} is the Kronecker parameter.

If the electrons are in the same orbital, $A_a^+ = A_a^- = A_a$ and Eqn (16) assumes the form

$$E_{a_j} = n_{a_j} B_a^l + \frac{1}{2} n_{a_j}(n_{a_j} - 1) A_a . \quad (17)$$

Having put $a_a = B_a^l - A_a/2$ and $2b_a = A_a/2$, we obtain from Eqn (17) an expression for EN:

$$\chi_{a_i} = \frac{\partial E_{a_j}}{\partial n_{a_j}} = B_a^l - \frac{A_a}{2} + \frac{A_a}{2} n_{a_j} ,$$

which corresponds fully to the Hinze – Jaffe formula (12).

Later Mullay [114] showed that the relation between the Klopman parameters B_a^l and A_a is linear. This enabled him to express the orbital EN by employing only one of the parameters:

$$\chi_{a_j} = A_a(0.5 + 0.15 N s_j) .$$

Here N is the number of valence electrons and s_j is the fraction of the s character of the orbital j.

From this expression, the author obtained a formula whereby a series of values of EN on Pauling's scale were determined:

$$\chi_{a_j}^0 = 1.67 \frac{G_j Z_{ef}^2}{n_{ef}^2} + 041 ,$$

where G_j is a function which depends linearly on the p character of the orbital j and Z_{ef} and n_{ef} are the effective nuclear charge and the effective principal Slater quantum number.

Furthermore, it should be noted that Klopman confirmed within the framework of his approach the validity of the equalisation principle for orbital EN, having described them not only in atomic but also in molecular terms:[122]

$$\frac{\partial E_m}{\partial n_j^i} = \frac{\partial E_m}{\partial n_k^i} ,$$

where E_m is the energy of the molecule, n_j^i the electron density of the orbital j corresponding to the ith electron, and n_k^i the electron density of the orbital k corresponding to the ith electron. Thus Klopman concluded that all the orbitals in the molecule are equipotential and actually proposed the term 'molecular orbital EN'.

The total equalisation principle, which became an indissoluble component of the concept of orbital EN, has been subjected to a many-sided criticism.[3, 9, 15] One of its main deficiencies is the impossibility of a differentiated determination of the EN of isomeric groups, although their donor – acceptor properties should undoubtedly differ. Some investigators have noted that the equalisation principle, possessing undoubted simplicity, does not reflect a series of fundamental chemical ideas, for example the resonance electrostatic effects.[15, 112, 1113, 123, 124] There exists also the view that, under conditions where the electron density is displaced, the total equalisation principle does not work at all because the electrostatic potential arising under these conditions inhibits further displacement of electron density and at best one can only speak of a partial equalisation of the EN.

Thus Pritchard [123] suggested that the real difference between the electronegativities of bound atoms, taking into account the overlap of the orbitals, reaches $\sim 10\%$ of the initial difference $\Delta\chi$. Quantum corrections for this overlap were subsequently introduced,[15] which permitted an additive calculation of the electron distribution in a series of fluoromethane derivatives.

Whilst modifying this method for the determination of EN, Huheey [125] proposed 80% equalisation of electron density and introduced a corresponding coefficient of 0.8 into the calculation.

The method involving the incomplete equalisation of the EN has also been developed in other investigations [126, 127] based on the electrostatic model postulating the expansion of the energy in a power series. The authors multiplied the atomic charges (obtained by minimising the total energy) by an arbitrary constant, which takes into account the potential arising when electrons are displaced and also the influence of remote atoms. The iterative procedure for the calculation of EN was performed until constant values of the latter called the 'residual' EN were obtained. A rigorous determination of such EN became possible only subject to the removal of the condition involving the restriction of the dependence of E on q to the quadratic term.[128]

Thus the concept of orbital EN undoubtedly promotes the development and understanding of the problem of EN as a whole, permitting the theoretical justification and the binding into a single whole of many general ideas and postulates (for examples, Mulliken's definition of EN, Sanderson's principle of the equalisation of EN, the dependence of EN on the valence state of the atom, the dependence of the energy of the atom on the charge, *etc*.). At the same time, one cannot fail to mention also a whole series of important problems remaining open to discussion, such as the possibility of the continuous expansion of E in terms of q for an isolated atom, the legitimacy of the total equalisation of EN and the specific equalisation algorithm (geometrical mean, arithmetical mean, *etc*.), the physical significance of the *in situ* EN of an atom in a molecule, and certain others, which have not so far received an adequately rigorous justification.

Many of these problems have been solved within the framework of the density functional theory (DFT), which has recently appeared and has undergone an extremely dynamic development. It permitted the current interpretation of many facts which have been insufficiently rigorously justified and treated.

IV. Electronegativity and the density functional theory

Any property characterising the state of a molecule is a function of parameters the values of which manifest the individuality of the given compound. The density functional theory considers a molecule as a set of nuclei and electrons. The parameters employed are the number of electrons N and the energy of the interaction of the nuclear core with the ith electron $\upsilon(r)$ at any point in the molecular system (its nuclear potential):[129]

$$\upsilon(r) = \sum_n \frac{Z_n}{r_{n_i}} ,$$

where n is the index of the nucleus, Z_n is the nuclear charge, and r_{n_i} is the distance from the nucleus n to the ith electron.

If N = const, the energy of the system is determined as the functional $E[N,\upsilon(r)]$, and the task of describing the interaction between the nuclei and electrons consists in finding an analytical expression for the energy E as a function of the independent parameters N and $\upsilon(r)$.

The function of the distribution of electron density of the ground state $\rho(r)$, simultaneously determining N and $\upsilon(r)$ and hence containing all the information about the system itself and its energy, is introduced within the framework of the DFT in accordance with the Hohenberg and Kohn theorems:[129]

$$E(N,\upsilon) = E(\rho) = \int \rho(r)\upsilon(r)\mathrm{d}r + F(\rho) .$$

By applying the variational principle to the functional $E_{el}[\rho(r)]$ (E_{el} is the electronic energy of the system), it is possible to obtain

the Euler equation, which is analogous to the Schrodinger equation:

$$\upsilon(r) + \frac{\partial \mathrm{F}(r)}{\partial \rho(r)} = \mu\,,$$

where $F(r)$ is the sum of the electron kinetic energy and the electron repulsion energy, $\rho(r)$ is the electron density functional, and μ is the Lagrange multiplier, called the electron chemical potential, which has the same value throughout the entire system and is determined as the partial derivative of the energy E with respect to the number of electrons N at a constant external potential υ:

$$\mu = \left(\frac{\partial E(r)}{\partial \rho(r)}\right)_{\upsilon(r)} = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(r)}\,.$$

Thus $\mu[N\upsilon(r)]$ is a global characteristic, which, together with the energy, is a fundamental property of the ground state of the system.

The development of the ideas of both the DFT and of the entire modern concept of EN has to a large extent been determined by the studies of Parr and Pearson and coworkers.[130–136]

Parr and coworkers[131] made the fundamentally important assumption that the negative chemical potential and the EN are identical:

$$\chi = -\mu = \left(\frac{\partial E}{\partial N}\right)_{\upsilon}\,. \tag{18}$$

Subsequently Parr and Pearson[132] determined the second derivative of the energy with respect to the number of electrons as the absolute hardness (η)

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right), \tag{19}$$

reflecting the 'resistance' of the chemical potential μ (or the electronegativity χ) to a change in the number of electrons:

$$\eta = \frac{1}{2}\left(\frac{\partial \chi}{\partial N}\right) = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right). \tag{20}$$

Correspondingly the softness of the system is defined as the reciprocal of the hardness:

$$S = \frac{1}{2\eta}\,. \tag{21}$$

Having postulated a quadratic dependence of the energy of the system on the number of electrons (in the absence of overlap of the valence orbitals), the electronegativity of the atom χ^0 and its hardness η^0 can be expressed in terms of the ionisation potential I and the electron affinity F:

$$\chi^0 = \frac{I+F}{2}, \quad \eta^0 = \frac{I-F}{2}. \tag{22}$$

Thus the definition of EN within the framework of the DFT agrees with Mulliken's ideas about the 'absolute' EN, while the parameter η, defined by Eqn (20), is[32] the 'absolute' hardness.

1. The principle of hard and soft acids and bases

The concepts of chemical hardness and softness were first introduced in the study of the properties of Lewis acids (electron acceptors) and bases (electron donors). Pearson[133–135] divided them into soft (readily polarisable) and hard (poorly polarisable). He also formulated the principle of 'hard and soft acids and bases' (HSAB), according to which hard acids combine preferentially into complexes (react) with hard bases, whilst soft acids combine similarly with soft bases.[133, 134] This principle has been widely applied in various branches of chemistry, but a quantitative characteristic of the 'hardness' of acids and bases was lacking for a long time.[6] The definition of hardness η within a framework of the DFT readily elucidates the physical significance of this parameter. According to the Klopman theorem, the ionisation potential I and the electron affinity F can be expressed in terms of the energy of frontier orbitals: the highest occupied (HOMO) and the lowest unoccupied (LUMO):[134, 136, 137]

$$-E_{\mathrm{HOMO}} = I, \quad -E_{\mathrm{LUMO}} = F\,.$$

Thus the hardness of the system is determined by half the difference between the energy levels:

$$\eta = \frac{E_{\mathrm{HBMO}} - E_{WZMO}}{2}\,. \tag{23}$$

Clearly a 'hard' molecule should have a large energy gap between the LUMO and the HOMO, while a 'soft' molecule should have a small gap, which in fact explains the difference between their polarisabilities.

Another important postulate put forward by Pearson[138] is the principle of maximum hardness, according to which the system tends to acquire the maximum hardness. This principle, like the HSAB principle, was initially based on experimental relations and only then received a mathematical justification within the framework of DFT.[136–140] According to Eqn (22), the quantity η increases with increase in ionisation potential and with decrease in electron affinity. Thus the system endeavours not to give up its electrons and not to accept extraneous ones, *i.e.* to remain stable.

Pearson's principle of maximum hardness combines a whole series of familiar empirical relations, rules, and concepts: the octet principle postulated by Lewis and Langmuir, the 18 electron rule. Hückel's $(4n + 2)$ aromaticity rule for organic systems, and the Wade–Mingos $(2n + 2)$ rule for inorganic systems, as well as the concept of the maximum thermodynamic stability of the molecule in the case where all its bonding orbitals are fully occupied whilst the antibonding orbitals are unoccupied.[137] The view that chemical hardness is a quantitative characteristic of the stability of electronic systems and can be used instead of the overall energy has been generally established in the literature.[141–151]

Together with the chemical potential (EN) and hardness, yet another parameter, playing an important role in the modern studies of reactivity and selectivity, namely the Fukui function $\mathrm{f}(r)$, defined by Parr and Yang[152] (see also Refs 148–153),

$$\mathrm{f}(r) = \left(\frac{\partial \mu}{\partial \upsilon(r)}\right)_N = \left(\frac{\partial \rho(r)}{\partial N}\right)_{\upsilon(r)},$$

has been introduced within the framework of the DFT.

Yang *et al.*[154] established that a high local reactivity corresponds to a large Fukui function at a point r in the molecule. This means that $\mathrm{f}(r)$ is an important reactivity index. The Fukui function is an intramolecular characteristic which can be used to determine intramolecular reactivity indices, in particular the local hardness and the local softness $s(r)$. The latter is defined as follows:

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{\upsilon(r)} = \left(\frac{\partial \rho(r)}{\partial N}\right)_{\upsilon(r)}\left(\frac{\partial N}{\partial \mu}\right)_{\upsilon(r)} = \mathrm{f}(r)S\,,$$

where S is the global softness [see Eqn.(21)], which can be calculated in terms of the local softness $s(r)$ values:

$$S = \int s(r)\mathrm{d}r\,.$$

Evidently the local characteristics of the molecule should determine the selectivity of the reactions involving it.[155–158] Thus in the interaction with a hard reagent, a 'locally hard' atom should serve as the preferred reaction centre, whilst in a reaction with a soft reagent a, 'locally soft' atom should be used for this purpose.

Thus the DFT yields a satisfactory qualitative justification of Pearson's HSAB principle and leads to the possibility of a quantitative estimation of the corresponding parameters.

2. The density functional theory and the electronegativity equalisation principle

The density functional theory justifies not only the continuity of the expansion of the energy E in a power series in terms of the charge q but also confirms the validity of the total equalisation of the EN, which follows from the variational principles for the electron density of the ground state.[159, 160] Furthermore, the DFT identifies EN with the chemical potential μ, which is characterised, by definition, by the equalisation property, like any other potential.

The mathematical formalism of the principle of the total equalisation of EN, based on the ideas of the DFT, has become the basis for the creation of a wide variety of approaches, which makes it possible to calculate the partial charges on atoms,[161–167] to model the chemical bond,[6, 168–170] to interpret the reactivities of various compounds,[164, 171–176] *etc*. We shall examine the approaches concerning the mathematical interpretation of the principle of the equalisation of EN and the method for the determination of the EN of atoms and groups based on it.

Thus using the mathematical procedures of the DFT, Parr and Bartollotti [177] justified not only the principle of the total equalisation of EN proposed by Sanderson but also his method of averaging EN on the basis of the geometrical mean.

In describing a bound atom, the authors examined its valence state as the ground state perturbed by the environment and proposed the following scheme for the formation of a molecule.

The initial hypothetical molecule AB, consisting of an atom A with the parameters μ_A^0, ρ_A^0, N_A^0, and υ_A^0 and an atom B with the parameters μ_B^0, ρ_B^0, N_B^0, and υ_B^0, possesses intrinsic values of μ_{AB}, δ_{AB}, $N_{AB} = N_A + N_B$, and $\upsilon_{AB} = \upsilon_A^0 + \upsilon_B^0$. Before charge transfer, the atoms A and B are in the valence states A* and B* characterised by the parameters μ_A^* and μ_B^*, ρ_A^* and ρ_B^*, N_A^0 and N_B^0, and υ_A^* respectively. After charge transfer, the atoms A and B are in states to which the parameters μ_A, ρ_A, N_A and μ_B, ρ_B, N_B correspond. Under these conditions, one can write for the molecule (in accordance with the total equalisation principle)

$$\mu_{AB} = \mu_A + \mu_B,$$

$$\rho_{AB} = \rho_A + \rho_B,$$

$$N_{AB} = N_A + N_B = N_A^0 + N_B^0.$$

Thus $\Delta N_A - N_A^0 = N_B - N_B^0$, which is proportional to $\mu_A^* - \mu_B^* = \mu_A^0 - \mu_B^0$ corresponds to the charge transfer. Under these conditions, the equalised EN is determined as the geometrical mean of the EN of the neutral atoms before charge transfer:

$$\mu_{AB}^2 = \mu_A^2 = \mu_B^2 = \mu_A^* \mu_B^* \simeq \mu_A^0 \mu_B^0 .$$

Bearing in mind that the chemical potential μ is identified with EN, we obtain for the molecule AB

$$\chi_{AB} = (\chi_A \chi_B)^{1/2} .$$

At the same time, according to the definitions of the chemical potential (EN) and the absolute hardness within the framework of the DFT [Eqns (18)–(20)], one can formulate the following expression for the *in situ* EN:

$$\chi = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(r)} = \chi^0 + 2\eta^0 \Delta N , \qquad (24)$$

where χ^0 is the intrinsic orbital EN of the atom, η^0 is its absolute hardness, and ΔN is the number of electrons participating in the charge transfer. Thus it is easy to show that the charge transfer along the bond AB is determined by the values of EN and of the hardness of the atoms A and B:

$$\Delta N = \frac{\chi_A^0 - \chi_B^0}{2(\eta_A^0 + \eta_B^0)} . \qquad (25)$$

Eqns (24) and (25) were first obtained already by Huheey and Watts,[178, 179] who used instead of the hardness η the charge capacity parameter $k = 1/2\eta$, characterising the power of the atom to delocalise the partial charge, *i.e*. the 'softness'.

The stabilisation energy corresponding to the given charge transfer can be expressed in terms of the same parameters:[132]

$$\Delta E = \frac{(\chi_A^0 - \chi_B^0)^2}{4(\eta_A^0 + \eta_B^0)} . \qquad (26)$$

Like Pauling's original formula, Eqn (26) demonstrates the proportionality of the polar component of the energy to the square of the difference between the EN of the partner atoms involved in the bond.

Komorowski *et al*.[180] identified ΔE with the power of the atoms A and B to effect charge transfer [they introduced the CTA (charge-transfer affinity) parameters] and emphasised that the polarity of the bond is determined not only by the EN of the atoms A and B but also by their hardnesses and it is not permissible to neglect them, as had been done in Eqn (26). Furthermore, whilst considering the pair interactions of the substituents with the reference reaction centre, the authors found an interesting linear relation between the inductive constants (σ_F) of the substituents and the corresponding CTA parameters. On the one hand, this makes the latter adequate characteristics of the groups and, on the other, it demonstrates the impossibility of a direct (disregarding the hardness) comparison of the inductive constants σ and the electronegativities χ. In their description of the *in situ* polarity of the bond AB, Allen and coworkers [3, 181, 182] neglected the hardnesses of A and B and introduced the bond polarity index BPI, directly related to the difference between the EN. Komorowski and coworkers [180, 183] find in the BPI a contradiction both with Pauling's original concept and with its DFT-based justification.

On passing from a simple diatomic molecule AB to a system comprising/atoms Yang *et al*.[184] obtained the following expression for the averaging of atomic EN taking into account the electroneutrality principle ($\sum \Delta N_i = 0$) and the total EN equalisation condition ($\chi_i = \chi$):[10]

$$\chi = \sum_1^L \frac{\chi_i^0}{\eta_i^0} \Big/ \sum_1^L \frac{1}{\eta_i^0} . \qquad (27)$$

This equation may be formulated also using the values of the softness of atoms:[176]

$$\chi = \frac{\sum \chi_i^0 s_i}{\sum s_i} . \qquad (28)$$

Similar relations of type (27) and (28) have been obtained independently by different workers in the study of equalised EN based on the DFT-justified approaches.[185–188] At the same time, in describing the EN of bound atoms, many investigators indicate the need to take into account their interaction and to introduce the corresponding corrections.

Mortier and coworkers [161–163, 173] proposed a scheme for the equalisation of the *in situ* EN taking into account the influence of the charge on the neighbouring atom q_B on the electronegativity χ_A:

$$\chi_A = \chi_A^0 + \Delta\chi_A + 2(\eta_A^0 + \Delta\eta_A) + \sum \frac{q_B}{r_{AB}} .$$

The last term (the Madelung potential) includes the interatomic distance parameter r_{AB}, which takes into account the influence of the geometrical parameters of the molecule on the equalisation of the EN of its constituent atoms.

The interaction of the atomic charges is taken into account within the framework of the Rappe–Goddard model [16] by

introducing into Eqn (18) an additional parameter containing the Coulombic integral J_{AB}, which describes the potential between A and B:

$$\chi_A = \chi_A^0 + 2\eta_A^0 + \sum J_{AB} q_B \, .$$

A similar additional term has also been used by Wells.[12]

As already mentioned, Eqn (25) makes it possible to calculate the charge transfer in the bond. Such a calculation is frequently used to determine the ionicity parameters, but the values thus obtained are lower by approximately a factor of two compared with the traditional estimates by Pauling's method.[6] This is associated with the failure to take into account the interaction between the atoms. Urusov[6] therefore proposed an approach, called the 'model of interacting spheres' according to which the electron density of the molecule is regarded as a superposition of the electron densities of atoms with the effective charges $q+$ and $q-$. This approximation makes it possible to some extent to take into account the repulsion between the electrons of different atoms and their attraction to the 'foreign' nucleus. Within the framework of this method, an expression has been obtained for the ionicity parameter:

$$\Delta N = \frac{\chi_A^0 - \chi_B^0}{\eta_A^0 + \eta_B^0} \, .$$

It yields values twice as high as those found by Eqn (25). Furthermore, in Urusov's view,[6] the EN equalisation principle can be applied more accurately and correctly in the model of interacting spheres than in the DFT.

Special mention should be made of a study [183] the authors of which developed a quantum-chemical method for expressing the *in situ* EN and the hardness without the direct employment of the EN equalisation principle. They assumed that the EN of a molecule χ_m can be divided into the additive contributions of its constituent atoms χ_a:

$$\chi_m = -\frac{dE_m}{dN} = -\sum \frac{dE_m}{dN_a} \frac{dN_a}{dN} = \sum \chi_a K_a \, , \qquad (29)$$

where $\chi_a = -(dE_m/dN)$ is the EN of the bound atom and $K_a = dN_a/dN$ is the index of the Fukui function.[189]

On passing to group EN, one can write [180]

$$K_g = -\frac{dN_g}{dN} = \sum \frac{dN_a}{dN} = \sum K_a \, ;$$

since $\sum N_a = N$, it follows that

$$\chi_g = \frac{\sum \chi_a K_a}{\sum K_a} \, . \qquad (30)$$

Evidently this expression is virtually identical with Eqns (27) and (28) based on the EN equalisation principle; the Fukui index K_a is related to the softness s_i in Eqn (28) by the expression $s = K_a/\eta_m$,[183] where η_m is the hardness of the molecule. Furthermore, the authors showed that the *in situ* χ_a can be replaced in Eqn (30) by χ_a^0 — the EN of free atoms (groups):

$$\chi_g^0 = \frac{\sum \chi_a^0 K_a}{\sum K_a} \, .$$

Evidently on passing to a molecule, *i.e.* for $\sum K_a = 1$, the expression obtained reproduces formula (29).

As noted by Komorowski *et al.*[180] themselves, the approach presented presupposes any level of additivity — the EN of the molecule can be divided not only into the contributions of atoms but also into those of groups or even into 'mixed' contributions:

$$\chi_m = \sum \chi_a K_a + \sum \chi_g K_g \, .$$

An orbital additive level of representation of formula (29) is also possible.

We may note that Liu and Parr,[190] who examined the chemical potential (EN) at the orbital level, arrived at analogous conclusions and relations, but they employed the classical DFT apparatus (and evidently the principle of the total equalisation of EN).

Together with the methods based on the DFT postulates, it is necessary to point out another remarkable approach — Bader's quantum topological model, which also operates with the electron density function $\rho(r)$ and the concepts of EN and hardness but is characterised at the same time by a series of fundamental differences and characteristic features.[191–194]

Bader's concept of topological atoms is based on the subdivision of molecular space into nonoverlapping atomic regions separated by boundary surfaces corresponding to zero electron density flux.

This procedure also presupposes the classification of the interatomic interactions (chemical bonds) in terms of types of the so called 'bond critical points' (BCP) at which the condition presented above holds. It was then found that the position of the BCP and the electron density at this point reflect the polarity of the corresponding bond and make it possible to determine the EN for both atoms and groups.[36, 195, 196] One of the most significant arguments in support of this approximation is the fact that the atoms in the given valence state and the molecular fragments frequently retain an unchanged form, volume, polarisability, and other characteristics as part of the composition of various compounds. This in fact determines their chemical individuality.

Using atomic characteristics obtained on the basis of Bader's method (atomic volumes and the BCP parameters) combined with classical DFT equations, Komorowski *et al.*[197] calculated the EN and hardnesses for a large number of chemical groups.

In concluding this Section, we may emphasise that the DFT, supported by a single theoretical basis, integrates the methods for the quantitative expression of the donor–acceptor properties of chemical systems and combines Mulliken's ideas concerning absolute EN,[11] the Iczkowski and Margrave expansion of the energy of an isolated atom,[108] the Hinze–Jaffe concept of orbital EN,[99–101, 110] Sanderson's principle of the total equalisation of EN,[95] the HSAB concept, *etc*. The global and local characteristic parameters introduced within the framework of the DFT (hardness, softness, Fukui index, *etc*.) permit an adequate description of quantitative data on the reactivities and selectivities of the interaction of diverse compounds.

At the same time, the different interpretations involved in the determination of the *in situ* EN on the basis of the OFT-justified approaches have been attributed by Allen[3] to the deficiencies of the DFT definition of EN given by Parr and Pearson. Furthermore, he subjected to a well argued, in our view, criticism Mulliken's expression for EN, which has become the criterion of the validity of a whole series of approaches, including the DFT. Furthermore, Allen believes that it is illegitimate to identify EN with the chemical potential and he therefore does not accept the idea of the equalisation of EN. Parr postulates in his turn that Allen's criticism has arisen mainly from a discrepancy in the understanding of the electronic state of a bound atom.[190]

In our view, the essential feature of the contradictions has a deeper origin. One is not dealing with deficiencies in the Mulliken definition of EN and with the disagreements of various workers as regards the state of an atom in a molecule. Both in the beginning and now there is no clear idea as to what EN is (and hence as to what is the exact mathematical form of its description). Indeed the entire data described in the previous Sections indicate that the authors of different concepts of EN have no unanimous view concerning its nature even at the atomic level. Strictly speaking, the current state of this question does not even allow one to consider EN as a physical quantity. It is merely a qualitative and, in a certain sense, a conceptual notion more in the nature of a 'property' or a 'capacity' and having no rigorous dimensionality and mathematical expression. Despite this initial contradiction,

the ideas concerning EN have developed and the concepts of the EN of first a group and later of a molecule appeared. Indeed, if EN is identified with the energies of HOMO and LUMO, the EN (chemical potential) of a molecule can be easily calculated. However, it does not then become in any way better founded and more unambiguous.

The chemical potential of a molecule is known to depend on external factors such as the solvent,[198, 199] the external field,[159] *etc*. Consequently one should not speak of the EN of a molecule as a characteristic individual quantity. And, whereas in relation to Lewis acids and bases the molecular EN together with hardness can be used for the interpretation of the properties of complex formation, in the general case its physical significance is not entirely clear. Even hardness itself, used together with EN as an independent parameter, is evidently not such a parameter because both χ and η are expressed with the aid of the same parameters — the ionisation potential I and the electron affinity F.

Another piece of evidence for the ambiguity of the parameters χ and η is the interrelation (and in a series of approaches also the identity), mentioned in this review, of the parameters a and b in the quadratic equations relating E and q, subsequently identified with EN and hardness. Furthermore, it is logical to postulate (and this has already been noted above) that the parameters I and F are themselves determined by identical factors involving the elementary structure of the atom and constitute merely one of the many manifestations of EN as a more fundamental property.

In our view, EN has received an unduly extensive and hence diffuse treatment, which does not reflect its initial physical significance. The reason is that, as a fundamental characteristic determining the electronic properties of atoms and molecules, EN cannot be measured in a way other than through these (measured) properties, *i.e*. cannot be determined directly. This is in fact why fundamental importance is frequently attributed to a measured parameter (for example, the ionisation potential).

We believe that the vital problem at the present stage of development of EN is that of the 'return to sources': it is necessary to restrict the concept of EN as a fundamental unchanging property of a chemical element and to create on this basis simple and understandable methods for the quantitative determination of the electronic properties of atomic-molecular *ensembles* (substituents, groups, molecules, *etc*.). The next Section of the review is devoted to one of such possible approaches.

V. The concept of 'inductive' electronegativities

A wide variety of numerous methods for the estimation of EN have been developed (the main ones were described in previous Sections of the review). Several tens of EN scales have been created on their basis and these are widely employed in the analysis of physicochemical properties and reactivities of compounds.

At the same time, the general methods for the estimation of EN from reactivity data have been scarcely employed. In our view, such direct approaches are in fact the most interesting and promising for the estimation of the electronic properties of atoms and groups, just as inductive, steric, and other constants of substituents are determined on the basis of the principle of the linearity of free energies.[14, 15, 200, 201]

The view that the values of EN and inductive constants reflect a general fundamental property, determining the distribution of electron density in the molecule, has been firmly established in the literature.[15] This is confirmed by the existence of numerous correlations of inductive constants and EN with the same parameters. Furthermore, numerous examples of the employment of EN of atoms and groups for the quantitative interpretation of the reactivities of molecules, especially in the chemistry of organometallic compounds, are known.[15]

In this connection, attempts have frequently been undertaken to relate the quantities σ and χ, but the correlations obtained were of a local character, which rules out the establishment of a functional interrelation between these parameters.[202]

1. A new model of the inductive effect

In a series of communications [203–206] we proposed a new method of determining the EN of 'inductive' atoms and groups from the inductive constants of substituents, which are directly related to the reactivity of molecules.

The method has been developed on the basis of a new model of the inductive effect, which makes it possible to calculate with a high degree of accuracy the inductive constants of various substituents at any reaction centres. The calculated Taft inductive constants for 427 substituents are linearly related to the corresponding experimental data with a correlation coefficient of 0.99.[206]

Using the model of the inductive effect, it is possible to solve a series of important theoretical problems associated with that of inductive interactions, such as the inductive influence of alkyl substituents,[207] the inductive effect in the chemistry of organoelement compounds,[208] *etc*., which cannot be done within the framework of any other approaches. Some of the rules derived in the new model made possible a new look at the problem of the quantitative determination of EN and of its physical significance.[209] The principal results obtained by means of the approach which we have developed have been surveyed in a review.[202]

The fundamental postulate of the model of the inductive effect involves the consideration of inductive constants at the atomic level of additivity:

$$\sigma^* = \sum_i^n \frac{(\sigma_a)_i}{r_i^2}, \qquad (31)$$

where σ^* is the inductive constant of the substituents on Taft's scale, n is the number of atoms in the substituent, $(\sigma_a)_i$ is an empirical quantity, which we introduced, defining the inherent power of the ith atom of the substituent to exhibit the inductive effects and depending on the chemical nature of the element and its valence state, and r_i is the distance from this atom to the reaction centre for which a tetracoordinate carbon atom was chosen in constructing the model.

Evidently this approach is in essence formal. However, the high quality of the correlations between the calculated inductive constants and experimental data shows that the constants σ_a really reflect the ability of atoms to exhibit the inductive effect. As a consequence of this, the question of the factors responsible for such ability, *i.e*. the physical significance of the elementary constants σ_a, is of current interest.

In order to solve this problem, we investigated the quantitative dependence of the constants σ_a on various physical and geometrical parameters and established in this connection a series of important rules.

In particular, an expression relating the quantity σ_a to the difference between the EN of the given element and carbon (the reaction centre) and the square of the covalent radius of the element in the corresponding valence state was obtained:

$$\sigma_a = 7.840(\Delta\chi + 0.45)R^2 . \qquad (32)$$

This relation explains satisfactorily both the magnitude and the sign of the inductive constants.

In order to eliminate the systematic correction of 0.45 from Eqn (32), we adopted a value of 2.1 for the 'inductive' EN of the carbon atom. Eqn (32) then assumes a simpler form:

$$\sigma_a = 7.840\Delta\chi R^2. \qquad (33)$$

This value of the 'inductive' EN of carbon ($\chi_C = 2.1$) differs appreciably from the corresponding value on Pauling's scale ($\chi_C = 2.55$), which is not fortuitous. The value which we proposed reflects the real donor–acceptor properties of carbon manifested in its reactivity. An argument in support of this claim is the fact

that the data obtained are based on concrete characteristics of the reactivity of molecules — inductive substituent constants. That the EN of carbon on Pauling's scale are somewhat too high is indicated also by the fact that the quantity $\chi_C = 2.55$ presupposes the existence of electron–accepting properties in carbon in relation to iodine ($\chi_I = 2.4$) and phosphorus ($\chi_P = 2.2$) and this is not the case. Furthermore, the insignificant polarity of the C–H bond indicates the similarity of the electronegativities of carbon and hydrogen atoms, which is also inconsistent with their values on Pauling's scale ($\chi_H = 2.1$).

By analysing Eqn (33), it is possible to understand the physical significance of inductive interactions. The constant σ_a, reflecting the ability of the atom to exhibit the inductive effect, depends not only on the EN — the driving force of the shift of electron density — but also on the area of its valence shell (R^2), *i.e.* its ability to delocalise the charge generated. Thus the inductive effect of a particular element (substituent) is determined by the 'difference between the potentials' ($\Delta\chi$) of this element and the reaction centre and by the 'capacity' of the latter.

We may also note that Eqn (33) makes it possible to express the EN of the element in terms of its constant σ_a and the square of the covalent radius.

$$\Delta\chi = a\sigma_a R^{-2}$$

Evidently this method of expressing EN is in essence identical with the 'geometrical' EN systems, while the empirical constants σ_a are similar, in terms of their physical nature, to the effective nuclear charges of atoms. Furthermore, we obtained a correlation, with a similar significance, between the constant $\sigma_a(C)$ of the element E, linked to a carbon atom as the reaction centre, and the dipole moment μ of the C_{sp^3}–E bond:[203]

$$\sigma_a(C) = 9.370R^2\frac{\mu}{l}, \tag{34}$$

where l is the bond length.

Since $\mu/l = q$, one can postulate that the superposition of relations (33) and (34) will 'disclose' the correspondence of the difference between the EN of the partner atoms in the formation of the bond ($\Delta\chi$) to the partial charge q arising on them:

$$q = 0.836\Delta\chi .$$

We have already mentioned analogous relations between the atomic charges in the X–H and X–Me systems, calculated by quantum-chemical methods, and the EN of the element χ quoted by Marriott *et al.*[38] Relations between q and χ are also known for alkali metal halides.[8]

The fact that Eqns (31) and (33) make it possible to express the inductive constant of the substituent via the fundamental physical and geometrical parameters of its constituent atoms in accordance with the additive scheme

$$\sigma^* = 7.840\frac{\sum\Delta\chi_i R_i^2}{r_i^2} \tag{35}$$

is particularly remarkable. This method of determining inductive constants permits the solution of many theoretical problems concerning the quantitative determination of the inductive effect (for a more detailed system, see the relevant review [202]).

It is remarkable that Eqn (35) relates two terms — the driving force for the displacement of electron density (EN) and the ability to delocalise the charge generated (R_i^2/r_i^2, actually the softness). However, these parameters are frequently used as independent parameters for the description of reactivity within the framework of the DFT (see, for example, Langaenaeker and coworkers [210–213]). Thus an analogy may be traced in which the parameter R_i^2/r_i^2 acquires the significance of an 'effective softness'.

Furthermore, the reproducibility and stability of the solutions indicate the constancy of the physical nature of the additive model of the inductive effect. This permits the analysis of the physical significance of the established rules on the basis of fundamental physical laws. Thus the evident analogy between the mathematical procedures of the model under discussion and the familiar equations of the theory of electrostatic induction is noteworthy. In particular, within the framework of this theory the flux of the electrostatic induction vector $\vec{N}$ through a spherical surface is defined as follows:

$$\vec{N} = \frac{q}{4r^2}R_s^2 , \tag{36}$$

where R_s is the radius of the sphere, q is the point charge, and r is the distance from the centre of the sphere to this charge.

If the inductive influence of the substituent is considered within the framework of the fundamental equation (31) taking into account Eqn (34) obtained, then, for the inductive constant of a monatomic substituent on Taft's scale, it is defined by

$$\sigma^* = 9.370\frac{q}{r^2}R^2 , \tag{37}$$

where q is the charge arising on the atom when the latter forms a covalent bond, r is the distance from the atom to the reaction centre, and R is the covalent radius of the atom.

The similarity of Eqns (36) and (37) imparts to the inductive constant of a monatomic substituent the physical significance of the flux of the electromagnetic induction vector, passing through the surface of the corresponding atom and generated by the charge on the reaction centre. The physical significance of the inductive effect has been analysed.[209] Without going into the details of this investigation, we shall only mention that the following expression has been established for the calculation of the charge arising on the ith atom in a nonconjugated molecule:

$$q_i = 0.172\sum_j\frac{\Delta\chi_{i-j}(R_i^2 + R_j^2)}{r_{i-j}^2}, \tag{38}$$

where the values of q_i are expressed in units of the elementary charge e, while the distances r_{i-j} between the ith and jth centres and the radii of the atoms i and j are expressed in Å.

We may note a clear analogy between the relation obtained and Eqn (25) expressing the charge in terms of the EN and the hardness of the partner atoms involved in the bond. In the model of the inductive effect, the charge and its inductive constant are directly proportional to $\Delta\chi$ and the ability of the system to delocalise the charge [the ratio $(R_i^2 + R_j^2)/r_{i-j}^2$]. In the DFT, the quantity q is also directly proportional to $\Delta\chi$ and inversely proportional to the sum of the hardnesses $\sum\eta$, *i.e.* actually to the ability to delocalise the charge mentioned above.

We shall demonstrated by the following example the possibility of calculating the partial charges in the molecule on the basis of the relations which we have obtained. Table 1 presents the effective atomic charges (δ) in the molecules of hydrogen halides obtained by Sanderson's method,[214] the reduced dipole moments of the hydrogen halide molecules μ/l, and the charges q calculated by Eqn (38). Evidently δ and q are fairly close. Furthermore, the reduced dipole moments of the H–Hal molecules and the distribution of their electron density are correlated with the calculated value of q:

$$\frac{\mu}{l} = (-1.351 \pm 0.071) + (19.523 \pm 0.645)q .$$

Table 1. The charges on the atoms in the molecules of hydrogen halides calculated by Sanderson's method and within the framework of the new model of the inductive effect together with the reduced dipole moments.

Molecule	δ /e	q /e	(μ/l)/Å
HF	0.16	0.177	2.09
HCl	0.09	0.108	0.81
HBr	0.06	0.099	0.56
HI	0.04	0.084	0.26

Thus one may say that the empirical rules established within the framework of the model developed permit a fairly adequate estimation of the shift of electron density in molecules.

2. Determination of the 'inductive' electronegativities of atoms and groups

The results of our investigations have shown that the model developed elucidates to a considerable degree the nature and physical significance of the inductive effect, relating it to the fundamental laws of electrostatics and electromagnetic induction. This leads in its turn to new possibilities for the quantitative theoretical estimation of the intramolecular distribution of electron density and of the reactivities of organic and organoelement compounds.

Furthermore, the expressions obtained for the inductive constant [Eqns (33)–(35)] permit the converse procedure involving the calculation of the group 'inductive' EN.[215–217]

Thus we found the values of χ for a series of the commonest atoms in different valence states by a converse recalculation based on Eqn (33). We created in this way a scale of 'inductive' EN. The values obtained reproduce Pauling's scale with an adequate accuracy (with the exception of the carbon atom) and are quite well correlated with a series of other familiar scales.[215]

Proceeding to the determination of group EN on the basis of Sanderson's total equalisation principle, we postulated that the $\Delta\chi_i$ in Eqn (35) for the atoms of the substituent is a constant quantity reflecting the EN of the entire substituent. One can then write

$$\Delta\chi = \frac{\sigma^*}{7.84 \sum R_i^2/r_i^2} .$$

Comparison of this expression and Eqn (33) yielded the final formula for the calculation of group 'inductive' EN.

$$\Delta\chi_g = \frac{\sum_i^n \Delta\chi_i R_i^2/r_i^2}{\sum_i^n R_i^2/r_i^2} . \qquad (39)$$

It is remarkable that an evident analogy with Eqn (33) for the group EN in the DFT is observed in this case too. This confirms yet again the legitimacy of identifying the parameter R_i^2/r_i^2 with the effective softness of the atom.

Equation (39) permits the calculation of the group EN for any groups, substituents, or ligands at any reaction centres from the fundamental characteristics of their constituent atoms. At the same time, it is evident that this expression for the group EN has a series of undoubted advantages.

Firstly, it makes it possible to reveal in an analytical form, other conditions being equal, the decisive role of the central atom of the substituent. It is in fact in this instance that the parameter r_i is a minimum and the contribution of the corresponding term is the most significant. Furthermore, the expression presented makes it possible to obtain the values of EN of both groups and individual atoms on a single scale, because the latter can be regarded in this case as monatomic substituents.

Secondly, the 'inductive' EN of the most diverse nonconjugated substituents,[216] calculated in terms of the approximation of a carbon reaction centre within the framework of Eqn (39), are correlated satisfactorily with the known scales based on the principle of the total equalisation of EN (for examples, the scales of Mullay,[115] Sanderson,[218] and De Proft *et al.*[219]). A fairly good qualitative correspondence is observed with other χ scales (correlation coefficients of 0.91–0.95).[216] In contrast to other equations, Eqn (39) takes into account the steric structure of the substituent, which permits a correct calculation of the group EN for isomeric fragments, avoiding one of the most significant deficiencies of the principle of the equalisation of EN.

Thirdly, in analysing the expression for the group EN one cannot disregard the question of the dependence of the EN of the substituent on its conformation. The existence of this dependence for the inductive effect has been frequently noted and is not open to doubt.[15] Electronegativity has never been considered in this context, although the EN of the substituent and its inductive influence have the same physical nature.

Fourthly, Eqn (39) makes it possible to discover the relation between the three principal characteristics of substituents — the inductive (σ^*) and steric (R_s) constants and the group EN (χ_g).

The following expression defining the steric constant has been proposed within the framework of the model of the frontal steric effect which we have developed:[220–222]

$$R_s = 30\lg\left(1 - \sum_i^n \frac{R_i^2}{4r_i^2}\right) , \qquad (40)$$

where R_i is the radius of the ith atom of the substituent and r is the distance from this atom to the reaction centre.

The scale of the constants R_s thus obtained is satisfactorily correlated with various experimental scales (for example, E_s, E_s^0, and V), describing adequately the steric effects of various substituents. The model permits the calculation with a high degree of accuracy of the steric effect of any substituent at any reaction centre.

Equation (40) may be simplified by taking into account the fact that, for low values of x, the function $\log(1-x)$ is linear. For the vast majority of substituents (with the exception of unduly bulky ones), the sum in brackets is small and one can therefore write

$$R_s = \text{const} \sum \frac{R_i^2}{r_i^2} . \qquad (41)$$

Since the difference between the atomic and covalent radii of the elements (used respectively in the steric and inductive models) is as a rule insignificant, the following final formula relating the fundamental physical parameters of the substituent is obtained from Eqns (35) and (41):

$$\sigma^* = A\Delta\chi_i R_s , \qquad (42)$$

where A = const.

In order to confirm the correctness of this expression and to determine the normalised value of the multiplier, we calculated the group EN also for a series of other groups frequently encountered in organic and organoelement compounds and not containing multiple bonds. Within the framework of regression analysis, all the values of $\Delta\chi_i$ obtained were compared with the corresponding constants σ^* and R_s. The theoretical values of the latter for substituents at a carbon reaction centre were taken from Cherkasov *et al.*[202] This yielded a relation[216] confirming the validity of the above considerations at an experimental level and indicating the universality of relation (42):

$$\sigma^* = (0.067 \pm 0.034) + (0.435 \pm 0.024)\Delta\chi_i R_s \qquad (43)$$

(the correlation coefficient is 0.9868 for 64 points).

The exact value of the normalising coefficient in expressions of type (43) can vary somewhat on passing from one reaction series to another depending on the nature of the specific reaction centre.[217]

The existence of relation (43) makes it possible to justify Eqn (39), avoiding the direct employment of the equalisation principle.

Since the steric constant R_s, defined by Eqn (41), is additive, we can write

$$R_{s\,i} = B\frac{R_i^2}{r_i^2} , \qquad (44)$$

where B = const. and R_{si} is a parameter describing the shielding of the reaction centre by the ith atom of the group.

Using Eqns (44) and (45), it is possible to express the inductive constant of the substituent in the following form:

$$\sigma^* = \text{const} \sum_i^N \Delta\chi_i R_{s\,i} .$$

However, bearing in mind Eqn (43), the inductive constant of the substituent can be expressed in terms of the EN of the group and its steric shielding constant:

$$\sigma^* = \text{const}\, \Delta\chi_g R_{s\,g} . \quad (45)$$

Thus, taking into account Eqns (35) and (45), we obtain an expression for the group EN, more correctly for the difference between the EN of the substituent and the reaction centre $\Delta\chi_g = \chi_g - \chi_{RC}$, which agrees fully with Eqn (39), but this time does not involve the employment of the principle of the total equalisation of EN:

$$\Delta\chi_g = \frac{\sum_i^n \Delta\chi_i R_i^2/r_i^2}{R_{s\,g}} = \frac{\sum_i^n \Delta\chi_i R_i^2/r_i^2}{\sum_i^n R_i^2/r_i^2} . \quad (46)$$

It is remarkable that Eqn (45) is analogous also to the relation between the principal characteristics of the substituent — the inductive constant σ, the group EN, and the steric shielding constant R_s — obtained on the basis of the total equalisation principle.

Taking into account the relations obtained, one may conclude that the mathematical principle of the total equalisation of the EN of all the atoms constituting the substituent is capable of yielding correct results as a computational method. The problem consists only in the need to establish the optimum algorithm for the averaging of the atomic EN, taking into account the chemical nature of the atoms and the steric structure of the substituent. Evidently, our approach is fully consistent with these requirements.

3. The 'inductive' electronegativities of substituents at different reaction centres

In the expression which we obtained for the 'inductive' EN, there are parameters which depend on the choice of the specific reaction centre — the distance from the *i*th atom of the substituent to this centre and the difference between their EN. It therefore appeared logical and useful to calculate using Eqn (39) the values of $\Delta\chi_g$ for the commonest nonconjugated substituents at different reaction centres.[217]

We compared them with the corresponding 'inductive' EN [$\Delta\chi_g$(C)] which we had obtained earlier in terms of the approximation of a carbon reaction centre [216] using a linear regression of the type

$$\Delta\chi_g(E) = a\Delta\chi_g(C) + b . \quad (47)$$

This made it possible to show that there is a rigorous linear relation between the $\Delta\chi_g$ for substituents at different reaction centres; the correlation coefficients are 0.98–0.99. The coefficients a then proved to be virtually unity and the coefficients b were found to be equal to the difference between the EN of carbon and the element E ($\chi_C - \chi_T$), whence it follows that χ_g is a constant quantity. This leads to the unambiguous conclusion that the 'inductive' EN of the substituents χ_g are constant regardless of the nature of the reaction centre, which is consistent with the established view concerning the universal nature of the concept of 'electronegativity'.

The method which we have developed takes into account the evident dependence of the difference between the EN of the group and the reaction centre $\Delta\chi_g$ on the nature of the latter, but the 'inductive' EN themselves do not vary under these conditions, in contrast to the constants σ characterising the electronic pair interaction between the substituent and the reaction centre.

In analysing the relations obtained, the question arises of the universality of the relation between the inductive constant, the group EN, and the steric constant [Eqn (45)] and of its dependence on the nature of the reaction centre. Thus, we showed previously [202] that, on passing from one reaction centre to another, the constants R_s vary in proportion, but the inductive constants are not linearly related in the general case. Furthermore, the linear relation established in the above investigation between the $\Delta\chi_g$(E) presupposes the existence of a significant constant term in relations of type (47). In order to estimate the universality of Eqn (45) and to determine its normalising multiplier, we tested experimentally the validity of Eqn (45) on a wide range of different reaction centres E. The constants σ and R_s were taken from Cherkasov and coworkers.[202, 220]

Analysis of the data obtained demonstrated the validity of a rigorous linear relation between the parameters investigated and the constancy of the slopes in all the correlation equations. Consequently Eqn (45) is universal and valid regardless of the choice of the reaction centre. Having averaged the values of a obtained, it is possible to formulate the following final expression:

$$\sigma^* = -2.1\Delta\chi_g R_s .$$

Thus the methods for expressing the steric (R_s) and inductive (σ) constants as well as EN in terms of fundamental physical and geometrical parameters [Eqns (35), (40), and (46)] which we have proposed not only permit a correct theoretical calculation of these characteristics but also reveal their genetic interrelation.

The possibility of a simple description of the electronic steric influence of substituents within the framework of the models developed is determined by the fact that they are based on extensive experimental data — inductive and steric constants. This 'extremely empirical' basis of the theoretical approaches which we have developed constitutes a significant argument in support of their adequacy. This is also indicated by the agreement between the experimental substituent constants and their values calculated by Eqns (35) and (44).

The concept of 'inductive' EN revealed a series of new aspects of the application of group EN: its interrelation with conformations, the absence of a dependence on the nature of the reaction centre, and 'the genetic relationship' with the inductive and steric constants. The quantitative interrelation of the 'inductive' EN and the partial atomic charges, which we have discovered, as well as consistency with other known methods for the calculation of EN must be specially emphasised. This makes it possible to throw light on certain controversial questions and to emphasise new aspects in the concept of EN.

Thus the expression for group EN [Eqn (46)] has been obtained within the framework of the approach which we have developed by two independent procedures, one of which presupposes the equalisation of the EN of the substituent atoms. On the one hand, this makes it possible to explain the existing diversity of the views on the principle of the equalisation of EN. As a mathematical computational procedure, it undoubtedly 'works', although Eqn (46) presupposes a more complex equalisation formula than simple geometrical, arithmetical, *etc.* averaging. On the other hand, the existence of an expression which permits the calculation of the EN of the group from the EN of its constituent atoms taking into account the geometry of the system throws doubt on the usefulness of employing the principle of the equalisation of EN. We agree with the criticism by Allen,[3] who pointed out that the equalisation of the *in situ* EN conflicts with the constancy of the chemical nature of the atom and who rejected the identification of EN with the chemical potential.

We have already emphasised that the 'inductive' EN have been obtained from the corresponding empirical atomic constants σ_a. This suggests that the calculated 'inductive' EN of atoms reflect their real electron-donating (electron-accepting) properties. However, since σ_a is an inherent unchanging atomic characteristic (this in fact permits its employment in additive calculations), we arrive inevitably at the conclusion that EN

should also be a constant quantity for an atom, regardless of its environment (and, incidentally, regardless of any external factors in general).

$$\chi = \frac{\sigma_a}{R} = \text{const}\ .$$

Thus one may conclude that the transition from the set of accumulated methods for the determination of χ (including also procedures within the framework of our approach) and also of procedures for the treatment of the term 'electronegativity' itself to a qualitatively new representation of its essential nature, not as a concept but as a property determined solely by the nature of the element and its valence state, has been achieved.

VI. Conclusion

Within the limited space of a review article, we were unable to cover the entire wide variety of the studies carried out in the field of the quantitative determination of EN and its practical employment.

From our point of view, the entire experience gained in the course of the historical development of the concept of EN has shown that it is a universal property of a chemical element, which depends solely on its nature and valence state and remains unchanged on formation of a molecule. Indeed, in all the existing scales, with all their diversity, the EN of chemical elements are constant quantities within the limits of each scale, differing only as regards the valence state. They describe satisfactorily the physical and chemical properties of diverse molecular systems. On the other hand, the majority of the scales, which have been frequently created on the basis of significantly (sometimes also fundamentally) different approaches, are satisfactorily correlated, emphasising the universality of EN as a property of a chemical element.

On the other hand, all the known methods for the 'averaging' or equalisation of EN when the donor — acceptor properties of groups and molecules are considered nevertheless operate in one way or another with 'intrinsic' (or 'null') values of the EN of their constituent chemical elements. Thus the basic sets of EN are entirely sufficient for an adequate quantitative description of the electronic properties of any atomic *ensembles*, while the equalisation principle (whatever the specific algorithm on which it is based) is only a successful instrument for such description. The attribution to it of a real physical significance actually leads to the blurring of the concept of EN and to its replacement by other (perhaps similar) concepts.

One should add to the foregoing that electronegativities are introduced methodologically as constants: an intrinsic unchanging value of χ is assigned to each abstract atom or substituent; their sets constitute EN scales.

Thus EN is a fundamental property of an atom — its power to attract electrons, which is manifested on formation of a molecule. We suggest that it is just as fundamental and unchanging as the chemical nature of an element and its nuclear charge and mass are constant in any molecules. As a fundamental property in a similar category, EN should be regarded, in our view, as a characteristic of a chemical element which depends on its nature and valence state. In its turn, EN generates the remaining electronic properties of atoms and molecules — ionisation potential, electron affinity, chemical potential, charge distribution, hardness, softness, *etc*, (the group EN should be included here also), which are determined by the balance of the EN of the chemical elements constituting the given system.

These properties may vary and may be equalised, but EN itself should remain unchanged. As soon as we allow a dependence of the EN of the element on its environment in the molecule, its charge, *etc*, we inevitably blur the very concept of EN, replacing it by other derived quantities (for example, the chemical potential) which are perhaps logically non contradictory. Yet another important cause of such 'mixing' of concepts is the fact that EN may be measured only in terms of measured properties, as a consequence of which an unjustifiably great importance is attributed to the measured parameter. Pauling's definition of EN is most correct in this connection: 'EN is the force with which an atom in a molecule attracts electrons'.

However, when account is taken of the postulate, described above, of the constancy of EN as a fundamental property of a chemical element in a given valence state, we tend to understand by the term 'atom in a molecule' in Pauling's formulation the state of the atom in the initial instant of the interaction. From our point of view, such an interpretation is simpler, logical, and rational if only because it is definite and unambiguous. Pauling's definition, which is essentially correct, therefore requires refinement in each specific instance. We believe that it can be formulated as follows: 'EN is the ability of an element to attract electrons on formation of chemical bonds, which depends on its nature and valence state'.

This revised definition of EN is the most complete and unambiguous and makes it possible to distinguish it from other similar parameters characterising the electronic state of atomic-molecular systems, and implies the constancy of EN as a fundamental property of an element in the given valence state.

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