

Physical Interpretation of the Electronegativity

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Received December 20, 2000

Abstract—An additivity scheme of electronegativities of univalent substituents has been proposed on the basis on the Van Vleck orbital model of valence states of atoms. The electronegativity of any organic or heteroelement-containing substituent can be calculated from the orbital electronegativities and hardnesses of atoms constituting that substituent. The proposed additivity scheme is the most consistent among those currently available for calculation of orbital electronegativities of univalent substituents. The scheme was substantiated with the aid of quantum-chemical scale of group electronegativities.

In 1916, Lewis [1] advanced an idea that the electron pair connecting two dissimilar atoms is attracted to one of these more strongly. According to Lewis, in the general case, a covalent bond has partially ionic character due to displacement of the bonding electrons to one of the atoms. Further development of this concept led to the introduction of the term *electronegativity* (EN) as a valence state parameter characterizing the ability of an atom to attract the bonding electron pair. It was postulated that ionic character of a covalent bond is determined by the difference in the atom ENs.

At present, the term electronegativity also applies to univalent polyatomic substituents and is widely used in organic and organometallic chemistry. In particular, atom and group ENs have found wide application not only in correlation analysis of reactivity of various compounds but also in interpretation and prediction of their structure and physical properties. However, quantitative data on ENs of organic and especially heteroelement-containing compounds are very few in number and unreliable; most of the proposed EN scales poorly correlate with each other. The reason is that the known methods for calculation of EN are based, as a rule, on unproved assumptions and that they make use of laborious calculation procedures. Therefore, an important problem is analysis and understanding of the available approaches rather than development of new EN systems.

First of all, a question should be raised: How should the term electronegativity be treated. There are two possible answers:

(1) Electronegativity is a physical quantity which can be calculated directly by quantum-chemical methods (at least, in principle). In this case different

EN scales should coincide with an accuracy of linear scaling, i.e., they should differ only in the zero points and units of measurements. Otherwise, one cannot assure that these scales refer to the same quantity.

(2) Electronegativity is a formal parameter which has no physical sense but can be used in correlation analysis of physical properties and reactivity of various classes of organic and heteroelement-containing compounds. Then, each EN scale should have its own scope of application, but we ought to deal (and really deal) with 20 to 30 different EN values for the same atom or substituent.

It should be emphasized that the second concept predominates: most of the proposed schemes were developed with the goal of obtaining correlation equations or formal calculation procedures for various applications. An example is our inductive EN scale developed in [2–4]. Obviously, the atom and group ENs obtained therein are formal parameters which can be used for both calculating the substituent inductive constants and establishing the structure of organophosphorus compounds on the basis of NMR data [5].

However, the first answer to the above question seems to be much more attractive from the theoretical point of view. Therefore, in the present work we tried to trace the evolution of the electronegativity term on the basis of the Van Vleck orbital model of valence states. It can be regarded as a connecting link between the phenomenological theory of covalent structures and quantum-chemical approaches. The main task of our study was to elucidate physical sense of electronegativity and analyze calculation procedures proposed in the literature for determination of orbital ENs of atoms and univalent substituents.

Orbital electronegativities of atoms. One of the first problems of the electronic valence theory was development of a phenomenological theory of Lewis–Langmuir ideal covalent structures and establishment of empirical relations between the length and energy of covalent bond, on the one hand, and valence state parameters of the atoms involved therein, on the other. The energy of formation of an ideal covalent structure, ΔE , consists of the energy of promotion of atoms into valence state, $\Delta E(A)$, and the energy of covalent bonds between them, $D(AB)$:

$$\Delta E = \sum^{\text{atoms}} \Delta E(A) + \sum^{\text{bonds}} D(AB).$$

This equation does not take into account mutual influence of atoms that are not linked directly. This influence is finally reduced to interactions between bonds and unshared electron pairs (UEP) and is considered at higher levels of the chemical perturbation theory. In terms of the given (zero) approximation, the length and energy of a covalent bond depend only on the valence states of the atoms, and these parameters remain the same for all molecules having such two-atom fragment.

An empirical relation between $D(AB)$ and valence state parameters of atoms A and B was deduced by Pauling [1] who leaned upon speculative mathematical constructs of the valence scheme procedure. Further on, these were replaced by more illustrative orbital models of covalent bonds. Therefore, we state here intuitive Pauling's ideas in terms of the qualitative theory of molecular orbitals, which underlies modern structural chemistry. According to Pauling, valence state of an atom is characterized by a set of oriented hybridized atomic orbitals (AO) which determine standard geometric bond configuration of a given atom in various molecules. The hybrid AOs are occupied by unshared electron pairs of that atom and electrons of bonds with the neighboring atoms. A covalent bond is described by localized molecular orbital consisting of singly occupied hybrid AOs of the atoms bound. Coupling of bond electrons is accompanied by interference of electronic waves and charge transfer to the atom with greater EN. Charge transfer is responsible for ionic character of a bond, which is characterized by the difference in the population of AOs of the linked atoms. It should be emphasized that ionic character of a bond is not equivalent to its polarity. The latter is characterized by dipole moment of the bond, which depends on the shape and size of hybrid AOs of the linked atoms.

On the basis of the above qualitative pattern of electron coupling, Pauling presumed that the energy

of an ordinary covalent bond can be expanded into the covalent and ionic constituents. By analyzing the energies of atomization of rigid molecules in the gas phase he found that the covalent contribution resulting from interference of coupled electrons can be given by the sum of atomic increments D_A and D_B and that the ionic contribution resulting from charge transfer is proportional to the squared difference of the atom ENs χ_A and χ_B .

$$D(AB) = (D_A + D_B) - b(\chi_A - \chi_B)^2. \quad (1)$$

Summarizing the above stated, let us stress out two important points which must be kept in mind while considering physical interpretation of EN of atoms and discussing empirical methods for estimation of EN. First, EN is an atomic parameter which was introduced to describe ionic character of bonds in *ideal covalent structures* represented by chemical structural formulas. Therefore, while developing empirical scales of EN of atoms it is necessary to use physical quantities intrinsic to ideal structures rather than real molecules whose properties inevitably depend on spatial, inductive, and resonance interactions. In this respect, the Pauling thermochemical scale limited to valence states of atoms with equivalent single bonds is the unique one, for it involves so-called average bond energies

$$E(MX) = D(MX) + \frac{1}{v} \Delta E(M) + \Delta E(X)$$

(v is the valence of atom M), which can be estimated from the energies of atomization of isovalence-substituted molecules $MX_iX'_{n-i}$. In this scale the unit of measurement will further be referred to as *thermochemical unit* (TU). Second, Pauling's atomic EN is in essence an orbital or (more exactly) one-electron quantity characterizing the ability of a given single-electron state to increase its population on bond formation. This intuitive reasoning led Hinze and Jaffe [6] to introduce the term *orbital EN of an atom*. The same authors defined Pauling's atomic EN using the following formal mathematical expression:

$$\chi_i = - \left(\frac{\partial E}{\partial n_i} \right)_{n_i = 1}. \quad (2)$$

Here, E is the energy of valence state of an atom, and n_i is the occupation number of the i th hybrid AO occupied by bond electron. By definition (2), the quantity χ_i characterizes the rate of decrease in the energy of valence state of an atom at an infinitely

small increase of n_i relative to unity. Clearly, it is quite possible to choose such a quantity as a measure of the ability of an atom to attract bond electrons.

From the physical point of view, Eq. (2) is a formal mathematical rule which makes it possible to obtain a quantum-chemical expression for χ_i . For this purpose, it is necessary to set E as a function of occupation number of hybrid AOs and differentiate the resulting expression with respect to n_i . Hence we should specify qualitative description of valence state of an atom in terms of hybrid AOs and introduce the corresponding one- and two-species electron density functions. These points are considered below in the framework of the orbital model of valence states proposed by Van Vleck [7].

Valence state represents the electronic state of an atom in various molecules. It is a fundamental and simultaneously most speculative term in chemistry. According to the classical theory of molecular structure, valence state of an atom is characterized by a graphical descriptor indicating its formal integer charge and bond multiplicities. By definition, the valence state is transferrable, i.e., it does not depend on the environment of atom in the molecule. This property allows us to consider atoms to be primary structural elements of molecules and treat covalent bond as a relation between these elements.

Van Vleck's model is the first (and still the only) that specifies the above speculative views. Van Vleck's valence state characterized by a formal integer charge of atom and multiplicities of its bonds is regarded as a mixed state of a free atom or ion, which is described with the aid of one- and two-electron density matrices, by analogy with quantum-mechanical states of open systems. Van Vleck valence state density matrices are built up according to the graphical state descriptor in the independent species approximation. We have formulated general rules for construction of one- and two-species density matrices and deduced a generalized formula for the energy of Van Vleck's valence state. The algorithm is based on the following postulates*:

(1) Each valence stroke of a descriptor denotes an electron of a bond. An electron of a bond, which is also called *unsaturated valence of an atom*, occupies a hybrid atomic orbital and exists in a mixed spin state where both values of the spin projection are equally probable. The latter condition means that

* The term *valence state* does not follow from the first principles of quantum mechanics; therefore, any quantum-mechanical model of valence state is based on specific speculative postulates.

coupled electrons inside a molecule are indistinguishable: each bond electron behaves as a half of electron pair possessing a zero spin.

(2) Van Vleck's hybrid AOs are orthogonal in pairs, and they reproduce standard geometric configuration of bonds formed by an atom in various molecules.

Let $\varphi_i(\mathbf{r})$ be hybrid orbitals describing standard geometric configuration of bonds of a given atom. A relation is set between each electron of an atom and one-electron density matrix of the following form:

$$\varphi(\mathbf{r})\varphi^*(\mathbf{r}')\sigma(s; s'), \quad \sigma(s; s') = \omega^\alpha \alpha(s)\alpha^*(s') + \omega^\beta \beta(s)\beta^*(s').$$

The electron spin is determined by the weight vector

$$\mathbf{w} = (w^\alpha, w^\beta), \quad w^\alpha + w^\beta = 1,$$

which is set according to the following rules:

$$\mathbf{w} = \begin{cases} (1/2, 1/2) & \text{unsaturated valence} \\ (1, 0) \text{ or } (0, 1) & \text{electron of unshared pair} \end{cases}$$

The overall one-electron density matrix is given by the sum

$$\gamma_1(\mathbf{x}, \mathbf{x}') = \sum_{i=1}^N n_i \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}') \sigma_i(s; s'),$$

where N is the number of electrons, and n_i is the occupation number of one-electron state, which is equal (by definition) to unity.

Two-electron density matrix is built up as the sum of pair contributions in the independent species approximation which takes into account only spin correlation between species, postulated by the Pauli principle.

$$\gamma_2(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \mathbf{x}'_2) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N n_i n_j G_{ij}(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \mathbf{x}'_2);$$

$$\begin{aligned} & G_{ij}(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \mathbf{x}'_2) \\ &= \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i^*(\mathbf{r}'_1) \varphi_j^*(\mathbf{r}'_2) \sigma_i(s_1; s'_1) \sigma_j(s_2; s'_2) \\ &- \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i^*(\mathbf{r}'_2) \varphi_j^*(\mathbf{r}'_1) \sigma_i(s_1; s'_2) \sigma_j(s_2; s'_1). \end{aligned}$$

The average energy of Van Vleck's valence state is determined by the formula

$$E = \sum_{i=1}^N n_i \langle i | h | i \rangle + \sum_{i=1}^{N-1} \sum_{j=i+1}^N n_i n_j [\langle ij | ij \rangle - (\mathbf{w}_i, \mathbf{w}_j) \langle ji | ij \rangle]; \quad (3)$$

$$(\mathbf{w}_i, \mathbf{w}_j) = w_i^\alpha w_j^\alpha + w_i^\beta w_j^\beta; \quad (3a)$$

$$\langle i|h|i\rangle = \int \varphi_i^*(\mathbf{r}) h \varphi_i(\mathbf{r}) \partial \mathbf{r}; \quad (3b)$$

$$\langle ij|ij\rangle = \int \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \partial \mathbf{r}_1 \partial \mathbf{r}_2; \quad (3c)$$

$$\langle ji|ij\rangle = \int \varphi_j^*(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_2) \frac{1}{r_{12}} \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \partial \mathbf{r}_1 \partial \mathbf{r}_2. \quad (3d)$$

Here, $\langle i|h|i\rangle$ are one-electron integrals describing the kinetic energy of electrons and the energy of their attraction to the nucleus, and $\langle ij|ij\rangle$ and $\langle ji|ij\rangle$ are the Coulomb and exchange integrals for two-electron interaction, respectively. In the further treatment, Eq. (3) will be referred to as Van Vleck's formula, though we were the first to represent it in such a general form.

Let us introduce Van Vleck's orbital chemical potentials (CP) of an atom, which are defined by formal derivatives like (4):

$$\mu_i = \left(\frac{\partial E}{\partial n_i} \right)_{n_i=1}, \quad i = 1, 2, \dots, v. \quad (4)$$

Here, E is Van Vleck's energy of an atom, v is its valence, and n_i is the occupation number of one-electron states (or hybrid AOs) occupied by bond electrons. Differentiation of Eq. (3) with respect to n_i gives quantum-mechanical expression (5) for the quantity μ_i :

$$\mu_i = \langle i|h|i\rangle + \sum_{j \neq i}^N n_j [\langle ij|ij\rangle - (\mathbf{w}_i, \mathbf{w}_j) \langle ji|ij\rangle]. \quad (5)$$

It follows from Eq. (5) that the orbital CP is the average energy of bond electron in Van Vleck's atom and that the orbital EN [6]

$$\chi_i = -\mu_i \quad (6)$$

coincides with the absolute value of this energy. To our knowledge, we were the first to obtain Eq. (5) which determines Van Vleck's orbital EN of an atom in the explicit form, though many authors [8, 9] stated that in the physical sense EN is an equivalent of the average energy of an electron. The term *Van Vleck's orbital chemical potential* has not been used previously, though the close relation between orbital CP and orbital EN, which is expressed by Eq. (6), underlies the principle of leveling of orbital CPs of

a bond. This principle was proposed in [10] for calculation of orbital ENs of univalent substituents.

Numerical values of orbital ENs are usually obtained by the empirical procedure based on the Mulliken quadratic interpolation formula:

$$\chi_i \approx \frac{I_{i,v}^{(1)} + A_{i,v}^{(1)}}{2}, \quad (7)$$

where $I_{i,v}^{(1)}$ and $A_{i,v}^{(1)}$ are the ionization potential and electron affinity corresponding to Van Vleck's orbital of i th electron. The quantities included in Eq. (7) refer to vertical processes, and they can be estimated from atomic electron excitation spectra [6, 11]. The spectroscopic scale of orbital ENs, developed on the basis of interpolation formula (7), is usually called Mulliken's scale.

It should be emphasized that Mulliken's formula (6) does not define orbital EN, as it is often believed. In fact, it is merely an interpolation formula derived from the complete data sample in keeping with the general quadratic interpolation rules. Had we used a more rough linear interpolation, two strongly different estimates, $\chi_i \approx I_{i,v}^{(1)}$ and $\chi_i \approx A_{i,v}^{(1)}$ would be obtained. The above "definitions" of orbital EN of an atom were also discussed in [12].

Orbital electronegativities of substituents. Van Vleck's valence state model can readily be extended to univalent substituents where the unsaturated valence occupies hybrid orbital of the central atom. The orbital EN of a substituent is determined by the formula

$$\chi_{1,G} = -\mu_{1,G}; \quad \mu_{1,G} = \left[\frac{\partial E}{\partial n_1} \right]_{n_1=1}, \quad (6)$$

where $\mu_{1,G}$ is the orbital CP characteristic of group valence state. The quantity $\mu_{1,G}$ is the average energy of unsaturated valence of substituent, which depends on its composition and structure.

The definition of $\chi_{1,G}$ allows it to be estimated by nonempirical methods of quantum chemistry [13]. Nevertheless, approximate procedures for calculation of orbital ENs of substituents are usually used, which are based on the following two assumptions:

(1) The orbital EN of a substituent may be represented by the equation

$$\chi_{1,G} = \chi_{1,M} + \sum_k^{\text{bonds of M}} \Delta \chi_k(M-X),$$

where $\chi_{1,M}$ is the orbital EN of the central atom, and $\Delta\chi_k(M-X)$ are small perturbations of the quantity $\chi_{1,M}$ resulting from polarization of bonds between the central atom and neighboring atoms. Polarization of each M-X bond is characterized by populations of hybrid AOs involved in the formation of that bond.

(2) Populations of AOs that constitute a bond can be determined according to the principle of orbital CP leveling.

In other words, the first of these assumptions suggests that influence of bonds on the unsaturated valence of a substituent is transmitted through the overlap areas of hybrid AOs of the central atom. Therefore, the substituent valence state energy in Eq. (6) may be replaced by the energy of electron motion in the vicinity of nucleus M. It is also assumed that this energy (denoted as E_M) can be expanded into a power series with respect to occupation numbers of valence orbitals, which are determined in terms of the principle of orbital CP leveling.

Unfortunately, the calculation schemes available from the literature are fairly cumbersome and unreliable since they utilize either simplified expressions for orbital CPs [10] or semiempirical expression for E_M^* [14, 15], which is not quite consistent in terms of Van Vleck's valence state model. Analysis of the above approaches led us to introduce the term *Van Vleck's orbital hardness* of an atom, and we developed an analytical additive scheme of the quantity $\chi_{1,G}$ [16]. Here, we give very briefly the main point of the developed approach and focus on discussion of the results.

Let us assume that ν is the valence of the central atom in a substituent. Expansion of the energy E_M into multiple Taylor's series with respect to occupation numbers of bond AOs gives expression (7).**

$$E - E_0 = \sum_k^{\nu} \mu_{k,M}(n_{k,M} - 1) + \sum_{k,l}^{\nu} \eta_{kl,M}(n_{k,M} - 1)(n_{l,M} - 1); \quad (7)$$

$$\mu_{k,M} = \left[\frac{\partial E}{\partial n_{k,M}} \right]_0; \quad \eta_{kl,M} = \frac{1}{2} \left[\frac{\partial^2 E}{\partial n_{k,M} \partial n_{l,M}} \right]_0. \quad (7a)$$

* In the case of integer occupation numbers this expression is not reduced to Van Vleck's formula (2) written with account taken of the assumptions made in [14, 15]; also, it does not reproduce Van Vleck's energies of atoms estimated in [6, 11].

** Here, E_0 is Van Vleck's energy of the M atom.

The coefficients in this series, orbital CPs $\mu_{k,M}$ and orbital hardnesses $\eta_{kl,M}$, are parameters characterizing valence state of the central atom for which all occupation numbers are equal to unity. Empirical values of these parameters are selected in such a way that Eq. (7) would reproduce vertical ionization potentials and Van Vleck's electron affinity of the M atom, estimated in [6, 11] from spectral data. In particular, spectroscopic values of μ_k and η_{kl} (eV) for valence states with equivalent single bonds are calculated by the following formulas:

$$\mu_1 = -\frac{I_v^{(1)} + A_v^{(1)}}{2}; \quad \eta_{11} = \frac{I_v^{(1)} - A_v^{(1)}}{2};$$

$$\eta_{12} = \frac{I_v^{(2)} - 2I_v^{(1)}}{2}. \quad (8)$$

Now, we make use of the first postulate to determine the orbital EN by the equation

$$\chi_{1,G} = \chi_{1,M} + \sum_k^{\text{bonds of M}} 2\eta_{1k,M}(1 - n_{k,M}),$$

which is obtained by differentiation of interpolation formula (7) with respect to occupation number of the orbital corresponding to unsaturated valence of the substituent. Here, $\eta_{1k,M}$ is the nondiagonal orbital hardness of the central atom, which characterize the effect of ionicity of k th bond on $\chi_{1,M}$; and $n_{k,M}$ is the orbital population of the k th bond of the M atom.

The populations of atomic orbitals of bonds in a substituent can be determined using the principle of leveling of orbital CPs of a bond. According to this principle, an M-X bond is characterized by two orbital CPs, (9a) and (9b), which become leveled upon synchronous polarization of bonds of the M and X atoms.

$$\mu_{M,MX} = \frac{\partial E}{\partial n_{k,M}} = \mu_{k,M} - 2\eta_{kk,M}(1 - n_{k,M}) - \sum_{l \neq k}^{\text{bonds of M}} 2\eta_{kl,M}(1 - n_{l,M}); \quad (9a)$$

$$\mu_{X,MX} = \frac{\partial E}{\partial n_{k,X}} = \mu_{k,X} - 2\eta_{kk,X}(1 - n_{k,X}) - \sum_{m \neq k}^{\text{bonds of X}} 2\eta_{km,X}(1 - n_{m,X}). \quad (9b)$$

By equalizing expressions (9a) and (9b) for each bond of a substituent under the constraint $n_{k,M} + n_{k,X} = 2$, we arrive at a system of algebraic equations which can be solved in terms of the perturbation theory with an accuracy of up to members of first order of smallness inclusively.* As a result, we obtain additive expression (10), which relates orbital EN of a substituent to valence state parameters of its atoms:

$$\chi_{1,G} = \chi_{1,M} + \sum_k^{\text{bonds of M}} [\Delta\chi_k + \Delta\Delta\chi_{k,M} + \Delta\Delta\chi_{k,X}]; \quad (10)$$

$$\Delta\chi_k = \frac{\eta_{1k,M}}{\eta_{kk,M} + \eta_{kk,X}} (\chi_{k,X} - \chi_{k,M}); \quad (10a)$$

$$\Delta\Delta\chi_{k,M} = -\sum_{l \neq k}^{\text{bonds of M}} \frac{\eta_{1k,M}\eta_{kl,M}}{(\eta_{kk,M} + \eta_{kk,X})(\eta_{ll,M} + \eta_{ll,X})} \times (\chi_{l,X} - \chi_{l,M}); \quad (10b)$$

$$\Delta\Delta\chi_{k,X} = -\sum_{m \neq k}^{\text{bonds of X}} \frac{\eta_{1k,M}\eta_{km,X}}{(\eta_{kk,M} + \eta_{kk,X})(\eta_{mm,X} + \eta_{mm,Y})} \times (\chi_{m,Y} - \chi_{m,X}). \quad (10c)$$

Equations (10) reflect the additivity of $\chi_{1,G}$, which is postulated by the classical structural theory of organic compounds. As follows from these equations, perturbation of $\chi_{1,M}$ by M–X bond consists of three terms. The greatest contribution, $\Delta\chi_k$, corresponds to the ideal covalent structure approximation and depends only upon valence states of the bonded atoms. The quantities $\Delta\Delta\chi_{k,M}$ and $\Delta\Delta\chi_{k,X}$ are small additive corrections to $\Delta\chi_k$, which take into account the effect of neighboring bonds of M and X on charge transfer along the M–X bond. Neglecting these corrections leads to simple additive formula (11):

$$\chi_{1,G} = \chi_{1,M} + \sum_k^{\text{bonds of M}} \frac{\eta_{1k,M}}{\eta_{kk,M} + \eta_{kk,X}} (\chi_{k,X} - \chi_{k,M}), \quad (11)$$

which is equivalent to the graphical calculation scheme given in [10].**

* According to the results of our calculations [16], this approximation is almost equivalent to precise solution of the system.

** Formula (11) can be obtained by solving the equation system with respect to populations of atomic orbitals of a substituent in the zero approximation, i.e., in the ideal covalent structure approximation. In other words, Eq. (11) is obtained by taking into consideration only the first two terms of Eqs. (9a) and (9b).

Our additive formulas are interpreted very readily in terms of the Ingold electron shift theory [17]. Let us consider it as applied to methoxy group as an example. In the ideal covalent structure approximation polarization of the C–O bond is proportional to the difference in ENs of oxygen and carbon atoms and inversely proportional to the doubled sum of their diagonal hardnesses:

$$(1 - n_{\text{CO,C}})^{(0)} = \frac{1}{2} \frac{(\chi_{\text{O}} - \chi_{\text{C}})}{(\eta_{11,\text{C}} + \eta_{11,\text{O}})}.$$

This charge determines the correction $\Delta\chi_k$ to $\chi_{1,\text{C}}$. The next approximation takes into account inductive influence of geminal bonds on charge transfer along the C–O bond. Polarization of the C–H bond induces additional charge transfer along the C–O bond, thus increasing its ionicity.

$$(1 - n_{\text{CO,C}})^{(1)} = -\frac{1}{2} \frac{\eta_{12,\text{C}}(\chi_{\text{H}} - \chi_{\text{C}})}{(\eta_{11,\text{C}} + \eta_{11,\text{O}})(\eta_{11,\text{C}} + \eta_{11,\text{H}})}.$$

The inductive effect of geminal bonds of the central atom is described by the corrections $\Delta\Delta\chi_{k,M}$. Likewise, polarization of the O–H bond induces the reverse charge transfer along the C–O bond toward the carbon atom.

$$(1 - n_{\text{CO,C}})^{(1)} = -\frac{1}{2} \frac{\eta_{12,\text{O}}(\chi_{\text{H}} - \chi_{\text{O}})}{(\eta_{11,\text{C}} + \eta_{11,\text{O}})(\eta_{11,\text{O}} + \eta_{11,\text{H}})}.$$

Such effects are included in $\Delta\Delta\chi_{k,X}$.

Analytical formulas (10) make it possible to calculate EN of any univalent substituent provided that spectroscopic ENs and hardnesses of its atoms are known. Using Eq. (8) and the data of [6, 10, 11, 18], we estimated spectroscopic values of $\chi_{1,\text{A}}$, $\eta_{11,\text{A}}$, and $\eta_{12,\text{A}}$ (eV) for some elements (Table 1). The values of $\chi_{1,\text{A}}^{\text{S}}$ and $\eta_{11,\text{A}}^{\text{S}}$ were calculated from $I_{\text{v}}^{(1)}$ and $A_{\text{v}}^{(1)}$ taken from [6, 11], and nondiagonal hardnesses of atoms N($te^2tetete$, V_3), P(s^2ppp , V_3), and O(te^2te^2tete , V_2) were estimated by Eq. (11) using $\chi_{1,\text{G}}^{\text{S}}$ (G = NH₂, PH₂, OH) taken from [10]. An analogous estimation of nondiagonal hardness $S(s^2p^2pp$, V_2) for the sulfur atom gives an unreal $\eta_{12,\text{S}}^{\text{S}}$ value of –24.2 eV. Therefore, $\eta_{12,\text{S}}^{\text{S}}$ was estimated by formula (8c) using $I_{\text{v}}^{(2)} = 34.2$ eV [18]; as a result, we obtained $\eta_{12,\text{S}}^{\text{S}} = 5.1$ eV. It should be noted that variation of $\eta_{12,\text{S}}^{\text{S}}$ from –24.2 to 5.1 eV reduces $\chi_{1,\text{SH}}^{\text{S}}$ by only 0.1 t.u. The reason

is that spectroscopic ENs of the S and H atoms, $S(s^2p^2pp, V_2)$ and $H(s, V_1)$ differ by only 0.2 eV. Hence $\chi_{1,SH}^S$ almost coincides with $\chi_{1,S}^S$.

It is important that Van Vleck's orbital EN of an atom strongly depends on the s order of the bond electron orbital. The hybridization of AO is defined unambiguously only for univalent atoms, such as $H(s, V_1)$, $F(s^2p^2p^2p, V_1)$, $Cl(s^2p^2p^2p, V_1)$, and valence states like $B(trtrtr, V_3)$, $C(tetetete, V_4)$, and $Si(tetetete, V_4)$ with a trigonal or tetrahedral bond configuration. These valence states of elements were used to define scaling transformation (12):

$$\chi^S(\text{t.u.}) = 2.1 + 0.4[\chi^S(\text{eV}) - 7.2], \quad (12)$$

which converts spectroscopic ENs of atoms and substituents from eV to t.u. The data in Table 1 show that spectroscopic ENs of $H(s, V_1)$, $F(s^2p^2p^2p, V_1)$, $Cl(s^2p^2p^2p, V_1)$, and $C(tetetete, V_4)$ coincide with the corresponding Pauling values (given in parentheses) within the error of determination (0.1 t.u.). The difference between the spectroscopic and thermochemical ENs of trivalent boron and quadrivalent silicon is 0.3 t.u. Valence states of the N(III), P(III), O(II), and S(II) atoms should be drawn using hybrid orbitals with a partial s -character, which reproduce standard geometric bond configuration of the atom in its compounds. There are no published data on ionization potentials and electron affinities of such valence states. Therefore, Table 1 contains spectroscopic parameters of the $N(te^2tetete, V_3)$ and $O(te^2te^2tete, V_2)$ states with overestimated s order of bond orbitals and of the $P(s^2ppp, V_3)$ and $S(s^2p^2pp, V_2)$ states built up from nonhybridized orbitals. As expected, spectroscopic ENs of $N(te^2tetete, V_3)$ and $O(te^2te^2tete, V_2)$ are much greater than thermochemical ENs of N(III) and O(II), for increase of the s -character of the bond electron orbital leads to sharp increase of Van Vleck's orbital EN.* The same factor is responsible for the reduced spectroscopic ENs of $P(s^2ppp, V_3)$ and $S(s^2p^2pp, V_2)$ relative to the corresponding thermochemical values. According to our assessments,* the difference between spectroscopic and thermochemical ENs of the N, P, O, and S atoms should be negligible provided that hybrid orbitals reproducing standard bond configuration are used.

The proposed additive scheme is applicable to any organic and heteroelement-containing substituents if

* In particular, EN of trivalent nitrogen increases from 2.2 t.u. for p orbitals to 3.8 t.u. for sp^3 -hybridized orbitals. Even stronger effect is observed for bivalent oxygen: Its EN varies from 3.1 to 5.3 t.u.

Table 1. Spectroscopic orbital electronegativities and hardnesses of atoms

Atom (A)	$\chi_{1,A}^S$		$\eta_{11,A}^S$	$\eta_{12,A}^S$
	eV	t.u.	eV	
$H(s, V_1)$	7.2	2.1 (2.1)	6.4	0.0
$B(trtrtr, V_3)$	6.3	1.7 (2.0)		
$C(tetetete, V_4)$	8.0	2.4 (2.5)	6.6	2.5
$Si(tetetete, V_4)$	7.3	2.1 (1.8)		
$F(s^2p^2p^2p, V_1)$	12.2	4.1 (4.0)	8.7	0.0
$Cl(s^2p^2p^2p, V_1)$	9.4	3.0 (3.0)	5.6	0.0
$Br(s^2p^2p^2p, V_1)$	8.4	2.6 (2.8)	4.7	0.0
$N(te^2tetete, V_3)$	11.5	3.8 (3.0)	7.4	4.0
$P(s^2ppp, V_3)$	6.1	1.7 (2.1)	4.7	5.0
$O(te^2te^2tete, V_2)$	15.2	5.3 (3.5)	9.1	8.6
$S(s^2p^2pp, V_2)$	7.4	2.2 (2.5)	5.0	5.1

valence states of their atoms could be described in terms of Van Vleck's model. This also applies to "normal" valence states of nontransition elements and almost all valence states of transition metals. Exceptions are so-called hypervalent states of nontransition elements belonging to the 3rd and 4th Period (e.g., quinquivalent phosphorus in PF_4 and hexavalent sulfur in SF_5).**

Table 2 contains orbital ENs of substituents, calculated by Eqs. (11) and (10) (the latter takes into account mutual effect of geminal bonds), and also the corresponding values taken from [10, 15]. Mulliken's values of $\chi_{1,G}^S$ calculated from $\chi_{k,A}^S$ and $\eta_{kl,A}^S$ (Table 1) were converted to thermochemical units through Eq. (12) which interrelates Mulliken's and Pauling's scales. It can be seen that orbital EN of a substituent is determined mainly by EN of the central atom (cf. $\chi_{1,A}^S$, t.u., in Table 1); additive corrections in formulas (11) and (10) give an appreciable contribution to $\chi_{1,G}^S$ only for substituents whose atoms are characterized by ENs much exceeding that of the central atom. Group ENs calculated by formula (11) almost coincide with those obtained in [10] by the graphical method. Small deviations (0.03 to 0.07 t.u.) are likely to result from roundoff errors in the graphical procedure which are inevitable in such calculations. These errors attain

** In terms of Van Vleck's model, description of such valence states requires electron excitation to high-lying vacant d orbitals. Thermochemical estimates suggest that in these cases the promotion energy cannot be equalized by the energy of covalent bonds.

Table 2. Spectroscopic electronegativities of substituents

Substituent	$\chi_{1,G}^S$		$\chi_{1,G}^S$		Published data	
	Eq. (11)	Eq. (10)	Eq. (11)	Eq. (10)	[10]	[15]
	eV		t.u.			
CH ₃	7.54	7.72	2.24	2.31	2.30	2.32
CH ₂ F	8.38	8.22	2.57	2.51	2.61	2.55
CHF ₂	9.22	8.78	2.91	2.73	2.94	
CF ₃	10.06	9.39	3.24	2.98	3.29	3.10
CH ₂ Cl	7.98	7.99	2.41	2.42	2.47	
CHCl ₂	8.42	8.26	2.59	2.52	2.63	
CCl ₃	8.86	8.51	2.76	2.62	2.79	
CH ₂ Br	7.78	7.87	2.33	2.37	2.40	
CHBr ₂	8.02	8.02	2.43	2.43	2.49	
CBr ₃	8.27	8.15	2.53	2.48	2.57	
CH ₂ CH ₃	7.69	7.72	2.30	2.31		2.35
CHFCH ₃	8.53	8.24	2.63	2.52		
CHClCH ₃	8.13	8.00	2.47	2.42		
CHBrCH ₃	7.93	7.88	2.39	2.37		
CH(CH ₃) ₂	7.85	7.73	2.36	2.31		2.38
C(CH ₃) ₃	8.00	7.74	2.42	2.32		2.41
CH ₂ OH	8.84	7.80	2.76	2.34		2.50
CH ₂ OCH ₃	8.84	7.88	2.76	2.37		
CH ₂ SH	7.56	7.72	2.24	2.31		
CH ₂ SCH ₃	7.56	7.79	2.24	2.34		
CH ₂ NH ₂	8.32	7.75	2.55	2.32		2.42
NH ₂	9.01	9.73	2.82	3.11	2.82	3.15
NHCH ₃	9.25	9.77	2.92	3.13		3.19
N(CH ₃) ₂	9.50	9.81	3.02	3.14		3.24
PH ₂	7.09	6.64	2.06	1.88	2.06	
PHCH ₃	7.44	6.63	2.20	1.87		
OH	10.76	10.76	3.52	3.52	3.53	3.97
OCH ₃	11.26	11.00	3.72	3.62		4.03
SH	7.31	7.31	2.14	2.14	2.35	2.42
SCH ₃	7.66	7.46	2.28	2.20		2.46

a maximum (0.2 t.u.) for $\chi_{1,SH}$. As noted above, the quantity $\chi_{1,SH}$ is especially sensitive to such errors because of similarity in spectroscopic ENs of sulfur and hydrogen atoms. Therefore, the value of $\chi_{1,SH}^S$ in [10] is slightly overestimated. The perfect coincidence of the analytical and graphical values of $\chi_{1,G}^S$ for NH₂, PH₂, and OH groups is explained by the fact that the nondiagonal hardness of nitrogen, phosphorus, and oxygen was estimated by us via reverse calculation with the aid of Eq. (11) using the corresponding group ENs from [10].

Formula (11) takes into account only the transferable part of perturbation of orbital EN of the central

atom, which originates from polarization of its bonds in the ideal covalent structure approximation. Insofar as bond increments $\Delta\chi_k$ depend only on the valence states of the linked atoms, they remain the same in isovalence-substituted molecules. Perturbations arising from mutual influence of geminal bonds are taken into account by the next approximation of the chemical perturbation theory, given by Eq. (10). The nontransferable perturbations were also considered in [14, 15]. However, the authors did not made attempts to obtain an analytical additive scheme of group ENs. Numerical values of $\chi_{1,G}$ were determined by direct solution of algebraic equation system derived on the basis of the principle of orbital CPs leveling for each bond of a substituent.

Proceeding to analysis of geminal contributions to $\chi_{1,G}$, it should be noted that in the calculation of group ENs [15] the following array of atomic ENs [14] was used: H(*s*, V_1) 2.1, C(*tetetete*, V_4) 2.5, F(*s²p²p²p*, V_1) 4.0, N(*te²tetete*, V_3) 3.4, O(*s²p²pp*, V_2) 3.2, S(*s²p²pp*, V_2) 2.5. These values differ from both spectroscopic (Table 1) and Pauling's thermochemical ENs. Orbital ENs of the oxygen atom used in our calculations and in those performed in [15] differ so strongly that comparison of the results for oxygen-containing substituents makes no sense. The reason is that Mullay [15] used ENs of the *p* orbital of O(*s²p²pp*, V_2) while we, as well as Hinze *et al.* [10], utilized the data for the valence state O(*te²te²tete*, V_2) with tetrahedral hybrid orbitals. However, neither the former nor the latter choice of the valence state is correct. In terms of the spectroscopic model of atom valence states, according to which Van Vleck's atom is regarded as a mixed state of free atom and parameters of this state (orbital ENs and hardnesses) are estimated from spectral data using quadratic interpolation formula, the state of bivalent oxygen atom should be built up from hybrid orbitals having a partial *s* order and reproducing the standard geometric configuration of bonds formed by oxygen in its compounds. Our data suggest that EN of such state should coincide with or at least be very similar to Pauling's thermochemical EN. However, this is the case for neither O(*te²te²tete*, V_2) nor O(*s²p²pp*, V_2). The same also applies to the nitrogen atom and, to a lesser extent, to phosphorus and sulfur.

Comparison of group ENs calculated by Eqs. (11) and (10) (Table 2) shows that corrections for geminal interactions are as a rule much smaller than transferable polarization contributions to $\chi_{1,G}$. However, for substituents with a large number of geminal bond pairs the contribution of nontransferable perturbation may be as large as ~0.2 t.u., i.e., it cannot be

neglected. Here, we do not consider oxygen-containing groups since spectroscopic EN of $O(te^2te^2tete, V_2)$ is strongly overestimated, as compared to ENs of the other atoms, so that a considerable reestimation of perturbations is necessary.

The difference between the $\chi_{1,G}$ values calculated by Eq. (10) and those given in [15] does not exceed ~ 0.15 t.u. provided that the data for oxygen-containing groups are excluded. The only exceptions are SR groups, but in this case the discrepancies (~ 0.3 t.u.) result mainly from the difference in ENs for $S(s^2p^2pp, V_2)$. Thus Eq. (10) and the scheme proposed in [15] give similar results when spectroscopic ENs do not differ strongly from atomic ENs [15].

We believe that the additive scheme proposed by us is the most consistent among the known schemes for calculation of orbital ENs of substituents. However, before bringing the developed approach to practical application, it is necessary to substantiate speculative assumptions forming its basis. For this purpose, we tried to take advantage of nonempirical quantum-chemical methods.

Nonempirical scale of orbital electronegativities of substituents. Variation procedures of molecular quantum mechanics are designed for studying stationary states of atoms, molecules, or radical species, primarily in the ground electron state. The applicability of variation procedures to such imaginary molecular systems as substituents requires special discussion, for the fact that valence state of an atom or substituent should fit some variation principle follows from nowhere. At present level of theory development we can rest only upon Van Vleck's orbital model of valence states. In the framework of this model, the application of quantum-chemical methods for calculation of group ENs of univalent substituents is justified if their ground electronic state is described by a single-determinant wave function allowing localization of molecular orbitals of a closed shell [19]. In these cases orbital EN of a valence state is numerically equal to the absolute value of electronic CP of the ground state of a substituent, and it can be calculated by interpolation formula (13):

$$\chi_{1,G} \approx \frac{E(G^+) - E(G^-)}{2}. \quad (13)$$

Here, $E(G^+)$ and $E(G^-)$ are electronic energies of cation and anion, respectively, which are calculated by the restricted Hartree-Fock (RHF) procedure with and without account taken of electron correlation. The calculations are performed for geometric configuration

Table 3. Quantum-chemical electronegativities of substituents (eV)

Substituent	$\chi_{1,G}^{OC,a}$	Substituent	$\chi_{1,G}^{OC,a}$	Substituent	$\chi_{1,G}^{OC,a}$
CH ₃	5.20	CHClCH ₃	4.65	COCl	5.69
CH ₂ F	5.18	CHBrCH ₃	4.67	CO ₂ H	5.77
CHF ₂	5.44	CH ₂ OH	4.24	CCH	8.36
CH ₂ Cl	5.06	CH ₂ OCH ₃	4.11	CN	8.84
CHCl ₂	5.20	CH ₂ SH	4.26	NH ₂	6.21
CH ₂ Br	5.05	CH ₂ SCH ₃	4.02	NHCH ₃	5.20
CHBr ₂	5.18	CH ₂ NH ₂	3.50	OCH ₃	6.84
CH ₂ CH ₃	4.49	CHCH ₂	5.24	SCH ₃	5.88
CHFCH ₃	4.68	CHO	4.55		

^a Group ENs calculated by Eq. (13) in terms of the CCSD method using 6-311++G(*d,p*) basis set and geometric parameters of substituent G in molecule HG.

corresponding to standard geometry of a substituent in compounds containing it.

Generally speaking, the choice of the calculation scheme is ambiguous: The only necessary condition is the use of an extended basis set including diffuse functions for proper description of anionic systems. On the basis of the results of test calculations of alkyl and haloalkyl groups we selected the coupled cluster procedure CCSD/6-311++G(*d,p*) with account taken of one- and two-electron excitations in optimized geometric configuration of nuclei, which reproduces the geometry of substituent in its hydrogen compound [19]. Using the above procedure we calculated orbital ENs of 26 organic and heteroelement-containing substituents (Table 3).

However, the results of quantum-chemical calculations still do not give nonempirical scale of orbital ENs of substituents. In order to built up such a scale it is necessary to define a scaling transformation to convert quantum-chemical ENs from eV to t.u., since the latter units are traditionally regarded as standard ones for measurement of EN. For this purpose the effect of orbital compression on Van Vleck's atomic ENs should be estimated.

Remind that the original formulation of Van Vleck's model reflects the concepts specific for 1930s, when interference and polarization were considered to be the only effects of electron coupling which influence the energy of a covalent bond between atoms. Detailed analysis of the energy of covalent bonding shows [20] that the above ideas are generally inaccurate. Interference of coupled electrons induces compression of orbitals of the linked atoms; as

Table 4. Recommended spectroscopic values (eV) of orbital electronegativities and hardnesses of atoms

Atom (A)	$\chi_{1,A}^S$	$\chi_{11,A}^S$	$\chi_{12,A}^S$
H(<i>s</i> , V_1)	7.2	6.4	0.0
C(<i>tetetetete</i> , V_4)	8.2	6.6	2.5
F($s^2p^2p^2p$, V_1)	12.0	8.7	0.0
Cl($s^2p^2p^2p$, V_1)	9.4	5.6	0.0
Br($s^2p^2p^2p$, V_1)	9.0	4.7	0.0
N(<i>te²tetete</i> , V_3)	9.4	7.4	4.0
P(s^2ppp , V_3)	7.2	4.7	5.0
O(<i>te²te²tete</i> , V_2)	10.7	9.1	8.6
S(s^2p^2pp , V_2)	8.2	5.0	5.1

Table 5. Orbital electronegativities (t.u.) of substituents

Substituent	$\chi_{1,G}^S$ ^a	$\chi_{1,G}^{QC}$ ^b	Substituent	$\chi_{1,G}^S$ ^a	$\chi_{1,G}^{QC}$ ^b
CH ₃	2.36	2.51	CH ₂ SH	2.38	2.35
CH ₂ F	2.56	2.50	CH ₂ SCH ₃	2.42	2.31
CHF ₂	2.77	2.55	CH ₂ NH ₂	2.37	2.22
CF ₃	3.00		CHCH ₂		2.51
CH ₂ Cl	2.48	2.48	CHO		2.40
CHCl ₂	2.58	2.51	CO ₂ H		2.60
CCl ₃	2.69		SOCl		2.59
CH ₂ Br	2.46	2.48	CCH		3.05
CHBr ₂	2.54	2.50	CN		3.13
CBr ₃	2.62		NH ₂	2.63	2.68
CH ₂ CH ₃	2.37	2.39	NHCH ₃	2.65	2.51
CHFCH ₃	2.56	2.42	N(CH ₃) ₂	2.67	
CHClCH ₃	2.48	2.41	PH ₂	2.10	
CHBrCH ₃	2.46	2.41	PHCH ₃	2.09	
CH(CH ₃) ₂	2.37		OH	2.73	
C(CH ₃) ₃	2.38		OCH ₃	2.83	2.79
CH ₂ OH	2.38	2.34	SH	2.33	
CH ₂ OCH ₃	2.42	2.32	SCH ₃	2.40	2.62

^a Group ENs calculated by Eq. (10) with the use of refined spectroscopic parameters of valence states from Table 4.

^b Group ENs calculated by Eq. (13) in terms of the CCSD method using 6-311++G(*d,p*) basis set and geometric parameters of substituent G in molecule HG.

a result, the potential energy of the bonding electron pair decreases, providing the main contribution to the covalent bond energy. This conclusion explains why the interference contribution to the bond energy is additive, so that it may be approximated by the sum of atomic increments [see formula (1); Pauling's interference increments originate mainly from reduc-

tion of the potential energy of coupled electrons in the vicinity of nuclei which they link together. Therefore, Van Vleck's hybrid orbitals should reflect compression of the electron shell depending on the valence state of the atom, and they cannot be regarded as atomic orbitals in the exact sense.

The effect of orbital compression is automatically included into quantum-chemical calculations of orbital ENs of substituents, performed with the use of extended basis sets, but it is not taken into account in spectroscopic ENs of atoms and substituents. With the above in mind, we compared quantum-chemical ENs of univalent substituents, calculated by the coupled cluster procedure, with those derived from spectroscopic parameters using formulas (10). In keeping with our data (Tables 2, 3), the difference between spectroscopic and quantum-chemical ENs almost does not change in the series of substituents with the same central atom. This means that it is determined mainly by the nature and valence state of the central atom rather than by its environment in the group. For example, this difference is 3.1 ± 0.3 eV in the series of alkyl and haloalkyl substituents. We presumed that the average value of $\chi_{1,G}^{QC} - \chi_{1,G}^S$ is determined mainly by orbital compression of the central atom and that it can be used for correction of spectroscopic ENs of elements. Then, approximate quantum-chemical EN of quadrivalent carbon is 4.9 eV. Analogous estimates corrected for orbital compression were found for nitrogen (7.5 eV), oxygen (11.0 eV), and sulfur atoms (5.7 eV). However, quantum-chemical data necessary for determination of orbital ENs of the above atoms are very limited; therefore, the corresponding estimates are less reliable than for quadrivalent carbon.

If electronegativity is a physical quantity defined with an accuracy including the origin and units of measurement, any valid scale of orbital ENs of elements should be linearly related to Pauling's thermochemical scale. By correlating the quantum-chemical estimates of atomic ENs with the corresponding Pauling's values we obtained scaling transformation (14) which is necessary to convert quantum-chemical data to thermochemical units:

$$\chi^{QC}(\text{t.u.}) = 2.1 + 0.17[\chi^{QC}(\text{eV}) - 2.8]. \quad (14)$$

Correlation of the quantum-chemical scale of orbital ENs of substituents with Mulliken's scale is complicated, for the available spectroscopic values of orbital ENs and hardnesses of many elements have been determined with the aid of improper valence state models and are to be refined. Our estimates [19]

suggest that the error in the calculation of spectroscopic ENs of substituents by additive formulas (10) may be reduced considerably through the use of thermochemical atomic ENs converted into eV scale by formula (12). The orbital ENs of elements, obtained in such a way, are given in Table 4. We recommend these values for use in the calculation of group ENs according to the proposed additive scheme. Clearly, our recommendations reflect the present state-of-the-art and will lose validity when orbital ENs and hardnesses of elements will be determined for correct Van Vleck's valence state models based on orbitals with intermediate hybridizations.

Table 5 contains corrected spectroscopic and quantum-chemical ENs of univalent substituents, expressed in thermochemical units using scaling transformations (12) and (14), respectively.* It is seen that spectroscopic and quantum-chemical values of EN for 20 substituents coincide within 0.2 t.u. A greater error could be expected only for trifluoromethyl group since the effect of C–F bonds on orbital EN of the central atom in the series of fluoromethyl groups is slightly overestimated in terms of the principle of orbital CP leveling.

In keeping with our results, the principle of orbital CP leveling and the additive scheme of group ENs based thereon provide a qualitatively valid physical pattern of the influence of bond polarization on orbital EN of the central atom and reproduce the results of rigorous nonempirical calculations with a sufficient accuracy. Therefore, we recommend the developed approach for wide practical application in the calculations of orbital ENs of any organic and heteroelement-containing substituents.

This work was financially supported by the St. Petersburg Competitive Center for Fundamental Natural Sciences and by the "Materials and Technologies of the XXIth Century" Scientific-Educational Center at the Kazan State University ["Basic Research and Higher Education" (BRHE) joint Russian-American program, grant no. REC-007].

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* Electronegativities expressed in thermochemical units are rounded to one decimal point. The other decimal digits have no physical sense.

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