Theoret. Chim. Acta (Berl.) 59, 629–637 (1980)

THEORETICA CHIMICA ACTA

Generalization of Electronegativity Concept

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A generalization of the original method introduced by Hinze and Jaffé for calculating the orbital electronegativities is proposed. This generalization is based on a new energy partitioning scheme within the framework of CNDO approximation and permits the orbital electronegativities to be calculated for atoms in actual valence states in which they occur in real molecules.

Key words: Electronegativity – Valence states – CNDO.

1. Introduction

The concept of electronegativity is one of the most frequently used concepts in chemistry which has had a considerable success in systematizing the huge amount of experimental chemical data. None the less it has never been satisfactorily defined. The most widely accepted definitions of electronegativity are due to Pauling [1] and Mulliken [2, 3]. Both these and also other definitions [4–6] implicitly assumed the electronegativity to be an intrinsic property of the element independent of whether its atom is isolated or bonded in a molecule. Careful reinvestigation of experimental data has however shown that the electronegativity of the element in fact varies, e.g. with varying oxidation state of the atom [7–9]. These experimental findings emphasized the need for further theoretical development of the electronegativity concept.

Mulliken [10] and Moffit [11] reinvestigated the original Mulliken's definition [2] and have drawn attention to the fact that valence state ionization potentials and electron affinities should be used instead of experimental values of corresponding ground state atomic quantities to describe the character of the atom in a molecule. Valence state ionization potentials and electron affinities can be determined from experimental data only for isolated electroneutral atoms or

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0040-5744/81/0059/0629/$01.80

their ions. However the atoms in molecules are not electroneutral but generally carry a fractional net charge. Their actual valence states therefore differ from valence states of neutral atoms. For illustration of this difference let us recall that whereas the configuration of the valence state of the neutral carbon atom is sp^3, the same atom bonded in a molecule is generally characterized by a configuration $s^x p^y (x+y \leq 4)$. In order to respect the partial ionicity of real bonds the values of electronegativities should depend in some way on the actual electronic configuration of the atom in a molecule.

These ideas were quantitatively expressed by Hinze and Jaffé [12] who emphasized that the electronegativity should be considered as an orbital rather than global atomic property. Orbital electronegativities are defined as a negative derivative of the energy of the atom with respect to the charge in the orbital. Nevertheless this at first sight clear and simple definition contains a good deal of arbitrariness because of the concept of energy of the atom. This energy is unequivocally defined only for isolated atoms but for atoms bonded in molecules it becomes a rather hypothetical quantity the definition of which is always more or less arbitrary. The formula originally proposed by Hinze and Jaffé is not entirely satisfactory since it requires additional a priori assumptions to be made about the actual functional dependence of energy of the atom on the charge in the orbital.

The aim of this article is to generalize the original method of Hinze and Jaffé for calculating the atomic energies. It is shown that starting from a properly defined energy partitioning scheme in the framework of the CNDO approximation, the energy of the atom can be expressed analytically as a function of orbital charge densities. This generalization permits to calculate the orbital electronegativities of atoms in molecules (these are termed bond electronegativities by Hinze and Jaffé) starting from atomic data and calculated orbital charge densities. On the basis of these orbital electronegativities we reintroduce again the concept of global atomic electronegativity. It is shown that this new definition leads to electronegativities for isolated atoms identical with Mulliken scale but for atoms in molecules it is able to characterize the variation of electronegativity with the changes in atomic valence states.

2. Results and Discussion

The definition of orbital electronegativities introduced by Hinze and Jaffé [12] requires to know how the energy of the atom varies with the change in orbital occupation numbers. In their original treatment they solved the problem by postulating the expressions for energy of atom for integer occupation numbers $n_j = 0, 1, 2$ (Eqs. 1a–1c)

$$E(j^0) = 0 \tag{1a}$$

$$E(j^1) = -I_j \tag{1b}$$

$$E(j^2) = -I_j - A_j \tag{1c}$$

in terms of orbital ionisation potential I_j and orbital electronaffinity A_j which were determined from atomic data for isolated atoms.

For fractional occupation numbers characterizing the configuration of the atom in a molecule the parabolic extrapolation was proposed. Then the electronegativity χ_j^A of the orbital j on atom A depends linearly on the occupation number n_j of orbital j and is given by Eq. (2)

$$\chi_j^A = (A_j^A - I_j^A)n_j + (3I_j^A - A_j^A)/2. \tag{2}$$

This method of calculating the orbital electronegativities is not however entirely satisfactory since after postulating the Eqs. 1a–1c it was further necessary to choose the analytic form of the dependence of atomic energy on n_j. The proposed parabolic interpolation is probably the simplest one but not necessarily the most realistic one.

To avoid all such a priori prerequisites and to minimize thus the inevitable arbitrariness we propose here a new physically justified method for calculating the atomic energies based on the formalism of the semiempirical CNDO approximation.

The energy of the electroneutral atom with configuration $s^m p^n$ is given by Eq. (3)

$$E(A, s^m p^n) = mU_{ss}^A + nU_{pp}^A + Z_A(Z_A - 1)\gamma_{AA}/2 \tag{3}$$

where $U_{\mu\mu}$ represents the one electron energy of the orbital μ and $Z_A (Z_A = m + n)$ the core charge of the atom A. By differentiating this expression with respect to m or n one could obtain the orbital electronegativities χ_s^A or χ_p^A of the isolated atom.

In order to calculate the electronegativity of the atom in a molecule it is necessary to define what is to be considered to be the energy of this atom. Natural basis for such definition is offered by the possibility of partitioning of total molecular energy into mono and biatomic components (Eq. 4)

$$E = \sum_A \varepsilon_A + \sum_{A<B}\sum \varepsilon_{AB}, \tag{4}$$

since just the monoatomic term ε_A represents the energy of the atom A in a molecule. The original partitioning scheme was proposed by Pople [13]. According to him the monoatomic term ε_A is given by Eq. (5)

$$\varepsilon_A = \sum_\mu^A p_{\mu\mu} U_{\mu\mu}^A + \sum_\mu^A \sum_\nu^A p_{\mu\mu} p_{\nu\nu} \gamma_{AA}/2 - \sum_\mu^A \sum_\nu^A p_{\mu\nu}^2 \gamma_{AA}/4. \tag{5}$$

This equation is not however appropriate for calculating the electronegativity since it expresses the energy of the atom not only in terms of orbital occupation numbers $p_{\mu\mu}$ but also in terms of "bond orders" $p_{\mu\nu}$. To overcome this difficulty, these cross terms should be eliminated. This can be simply accomplished by a set of following rearrangements.

Let us complete the exchange part of the monoatomic contribution by the additional term ε_{add} (Eqs. 6).

$$\varepsilon_{\text{add}} = \sum_{\mu}^{A} \sum_{\nu}^{B \neq A} p_{\mu\nu}^{2} \gamma_{AA}/4 \tag{6a}$$

$$\sum_{\mu}^{A} \sum_{\nu}^{A} p_{\mu\nu}^{2} \gamma_{AA}/4 + \varepsilon_{\text{add}} = \sum_{\mu}^{A} \sum_{\nu}^{\text{all}} p_{\mu\nu}^{2} \gamma_{AA}/4. \tag{6b}$$

Then by the use of identity (7)

$$\sum_{\nu}^{\text{all}} p_{\mu\nu}^{2} = 2p_{\mu\mu} \tag{7}$$

the original monoatomic contribution ε_A transforms into the form (8)

$$\varepsilon'_A = \sum_{\mu}^{A} p_{\mu\mu} U_{\mu\mu}^{A} + \sum_{\mu}^{A} \sum_{\nu}^{A} p_{\mu\mu} p_{\nu\nu} \gamma_{AA}/2 - \sum_{\mu}^{A} p_{\mu\mu} \gamma_{AA}/2. \tag{8}$$

Since the total energy must remain constant the additional terms ε_{add} have to be substracted from biatomic contributions ε_{AB}. Then, by the use of identity (9), one obtains the modified expression for biatomic contributions ε'_{AB} (10).

$$\begin{aligned}\sum_{A} \varepsilon_{\text{add}} &= \sum_{A} \sum_{\mu}^{A} \sum_{\nu}^{B \neq A} p_{\mu\nu}^{2} \gamma_{AA}/4 \\ &= \sum\sum_{A<B} \sum_{\mu}^{A} \sum_{\nu}^{B} p_{\mu\nu}^{2} (\gamma_{AA} + \gamma_{BB})/4 \end{aligned} \tag{9}$$

$$\begin{aligned}\varepsilon'_{AB} &= \sum_{\mu}^{A} \sum_{\nu}^{B} p_{\mu\nu} S_{\mu\nu} (\beta_0^A + \beta_0^B) \\ &\quad + (\gamma_{AA} - 2\gamma_{AB} + \gamma_{BB}) \sum_{\mu}^{A} \sum_{\nu}^{B} p_{\mu\nu}^{2}/4 \\ &\quad + (P_A - Z_A)(P_B - Z_B)\gamma_{AB} + Z_A Z_B (1/R_{AB} - \gamma_{AB}). \end{aligned} \tag{10}$$

From the above derivation it follows that Eqs. (8 and 10) offer an alternative possibility of partitioning of molecular energy. Which one of the possibilities is actually to be preferred is a matter of convenience dictated only by the physical nature of the studied problem. For calculating the orbital electronegativities we prefer the modified partitioning since the atomic energies ε'_A are expressed solely in terms of occupation numbers $p_{\mu\mu}$ as required by Hinze's and Jaffé's definition.

Eq. (3) can be used directly without any need for parabolic extrapolation to determine the electronegativity. The general expression for their calculation is given by Eq. (11)

$$\chi_j^A = -\frac{\partial \varepsilon'_A}{\partial p_{jj}} = -U_{jj}^A - (P_A - \tfrac{1}{2})\gamma_{AA}. \tag{11}$$

For electroneutral atoms ($P_A = Z_A$) this expression becomes identical with Mulliken's formula

$$\chi_j^A(0) = -U_j^A - (Z_A - 1/2)\gamma_{AA} = (I_j + A_j)/2. \tag{12}$$

From the comparison of these two equations it follows that the orbital electronegativities depend on the total net charge Q_A on atom ($Q_A = Z_A - P_A$). The proportionality constant is equal to the monocentric repulsion integral γ_{AA}

$$\chi_i^A - \chi_i^A(0) = Q_A \gamma_{AA}. \tag{13}$$

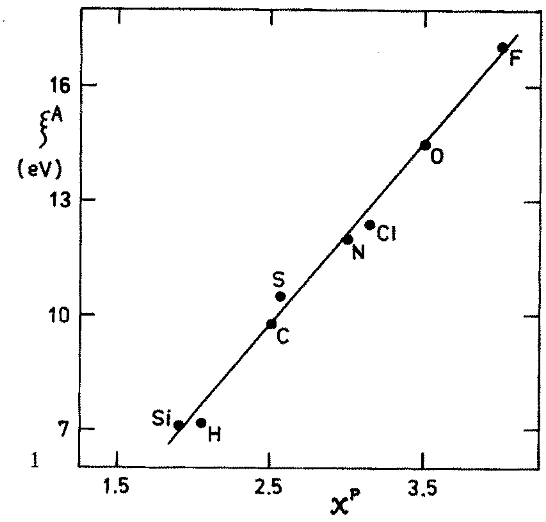
Having defined the orbital electronegativities in the framework of the CNDO approximation it is natural to attempt at extending this definition also to more sophisticated MO methods such as INDO, MNDO etc. Unfortunately, described or similar modification of energy partitioning cannot be performed for these methods. The reason for it lies in the fact that the formula for the energy of the atom with configuration $s^m p^n$ e.g. in the framework of INDO method cannot be generalized for noninteger values of m and n. This is due to the fact that the INDO energy of the configuration $s^m p^n$ represents the weighted mean of energies of all the states arising from this configuration. For noninteger values of m and n it is not possible to determine how many states of a given multiplicity and l will arise from the configuration $s^m p^n$ and consequently it is not possible to perform the averaging process. From this it follows that the concept of valence state orbital electronegativity remains restricted only to the most simple CNDO approximation.

The problem of electronegativity was recently treated also by Parr with coworkers [14, 15] from the point of view of density functional theory. They concluded that for the molecular ground state the orbital electronegativity is the same for all orbitals which seems to be in contradiction to our results. As it was however pointed out by the authors the conclusion about the equalization of orbital electronegativities is valid only for natural orbitals. In the framework of the Hartree–Fock model as in our case here this condition does not hold.

For correlations of different physico-chemical data with electronegativity it is frequently more convenient to characterize the atom by one quantity rather than by several values of orbital electronegativities. For that reason we propose here to reintroduce again the global atomic electronegativity as a weighted mean of individual orbital electronegativities (Eq. 14)

$$\xi^A = \frac{\sum_{\mu}^{A} p_{\mu\mu} \chi_{\mu}^{A}}{\sum_{\mu}^{A} p_{\mu\mu}}. \tag{14}$$

The individual orbital charge densities $p_{\mu\mu}$ play the role of weighting factors. The electronegativity introduced in this manner is no longer invariant property of the atom and its variations on going from one molecule to another reflect the changes in valence states of atoms in different molecules. Since as it has already been emphasized the individual orbital electronegativities of neutral atoms are identical with Mulliken values (Eq. 12), the global electronegativity ξ^A of the neutral atom is proportional to Mulliken electronegativity. Moreover since there is a rough proportionality between Mulliken and Pauling's electronegativity



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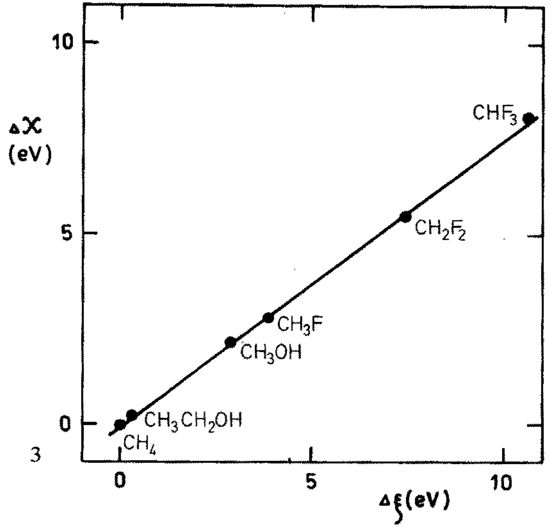

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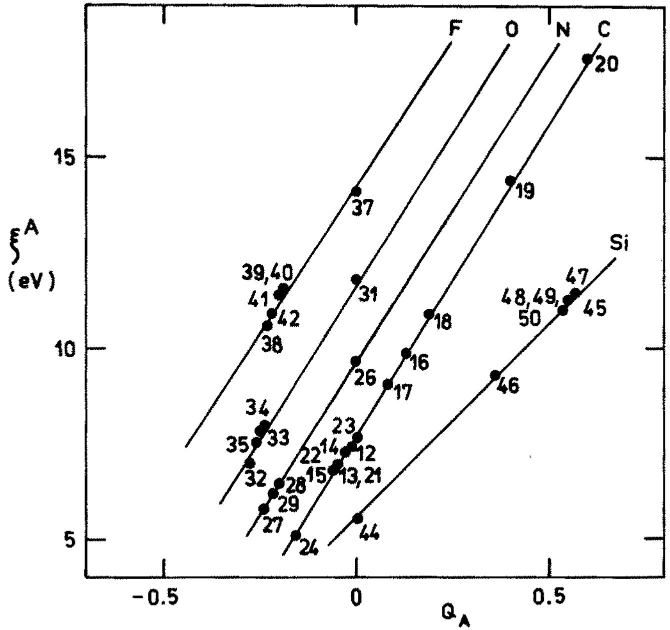

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Fig. 1. Comparison of atomic electronegativities ξ^A of isolated atoms[a] with the Pauling scale[b]

[a] The values of ξ^A correspond to ground state (and not to valence state) configurations of atoms

[b] Pauling electronegativities taken from the work [16]

Fig. 2. The dependence of atomic electronegativities ξ^A for several molecules on the atomic net charge Q_A [a]

[a] Numeration see Table 1

Fig. 3. Dependence of C(1*s*) ESCA chemical shifts (relative to CH$_4$) for some simple molecules on the atomic electronegativities ξ^A [a]

[a] Experimental values taken from the works [21, 22]

Table 1. Calculated values of atomic electronegativities ξ^A (in eV) in some simple molecules

Element	No.	Compound	ξ^A (eV)	$Q_A(Z_A - P_A)$
H	1	H (s^1)	7.17	0
	2	H_2	7.17	0
	3	HF	11.91	0.23
	4	H_2O	10.13	0.14
	5	NH_3	8.85	0.08
	6	CH_4	7.42	0.01
	7	C_2H_4	7.48	0.01
	8	C_2H_2	8.46	0.06
	9	SiH_4	4.37	−0.14
	10	Si_2H_6	4.73	−0.12
C	11	C (s^2p^2)	9.81	0
	12	C* (sp^3)	7.69	0
	13	CH_4	7.00	−0.05
	14	C_2H_4	7.29	−0.03
	15	C_2H_2	6.85	−0.06
	16	CH_3OH	9.91	0.13
	17	CH_3NH_2	9.04	0.08
	18	CH_3F	10.88	0.19
	19	CH_2F_2	14.38	0.40
	20	CHF_3	17.58	0.60
	21	CH_3CH_2F	6.98	−0.05
	22	CH_3CH_2OH	7.31	−0.02
	23	$CH_3CH_2NH_2$	7.43	−0.01
	24	CH_3SiH_3	5.10	−0.16
N	25	N (s^2p^3)	12.09	0
	26	N* (sp^4)	9.68	0
	27	NH_3	5.77	−0.24
	28	CH_3NH_2	6.53	−0.20
	29	$Me_3SiCH_2NH_2$	6.23	−0.22
O	30	O (s^2p^4)	14.54	0
	31	O* (sp^5)	11.82	0
	32	H_2O	7.01	−0.28
	33	CH_3OH	7.88	−0.25
	34	CH_3CH_2OH	7.98	−0.24
	35	Me_3SiCH_2OH	7.56	−0.26
F	36	F (s^2p^5)	17.13	0
	37	F* (sp^6)	14.11	0
	38	HF	10.58	−0.23
	39	CH_3F	11.63	−0.19
	40	CH_2F_2	11.53	−0.19
	41	CHF_3	11.45	−0.20
	42	Me_3SiCH_2F	10.92	−0.22
Si	43	Si (s^2p^2)	7.08	0
	44	Si* (sp^3)	5.60	0
	45	SiH_4	11.28	0.55
	46	Si_2H_6	9.28	0.36
	47	SiH_3CH_3	11.43	0.57
	48	Me_3SiCH_2F	11.04	0.54
	49	Me_3SiCH_2OH	10.95	0.53
	50	$Me_3SiCH_2NH_2$	11.04	0.54

scales, there is also a simple linear relationship between ξ^A and Pauling electronegativities (Fig. 1). For isolated atoms thus this new definition does not bring any improvement over ordinary electronegativity scales. The main advantage of this definition lies in the fact that it permits to calculate the electronegativity of the atom in a molecule.

The actual dependence of electronegativity on the type of the molecule is documented by several values collected in Table 1. These values show that the electronegativity of the element increases with increasing positive net charge on the atom. This result is reasonable since it is clear that the greater is the positive charge on the atom, the greater will be its tendency to attract electrons. As it is shown in Fig. 2, the dependence of the electronegativity ξ^A on the net charge Q_A on the atom is practically linear. Moreover it is interesting to mention that the slope of regression line is roughly constant for the elements of the same period.

The electronegativities calculated by this generalized methods can be used in all situations as the ordinary values e.g. in estimating the degree of ionicity of chemical bonds, in correlations with ESCA chemical shifts, or C^{13} NMR chemical shifts etc. For example we have found perfect linear correlations of our electronegativities with the ESCA 1*s* chemical shifts of carbon atom in a series of some simple molecules (Fig. 3). Similar correlations were recently discussed by Gasteiger [17]. This simple example demonstrates the usefulness of the new generalized method of calculating the electronegativity. We believe however that the new definition may give even a more realistic description than the ordinary scales. As an example illustrating the applicability of the new definition in a situation where ordinary scales lead to erroneous conclusion let us mention the case of the so called alpha effect in organosilicon chemistry [18, 19]. Under the name of alpha effect is recognized the fact that in contrast to smaller electronegativity of silicon with respect to carbon, silyl groups in alpha functional derivatives exhibit rather strong electronaccepting behavior. As can be seen from Table 1 the electronegativity of silicon in carbofunctional derivatives Me_3SiCH_2X ($X = NH_2$, OH, F) is, in harmony with experimental results, really greater than the electronegativity of carbon (in CH_3 group) in analogous ethyl-derivatives CH_3CH_2X. For electroneutral atoms the order of electronegativity of carbon and silicon is of course reversed.

This result simply documents the fact that the concept of electronegativity as an invariant property of the element may lead in some cases to erroneous conclusions. On the other hand when the variation of the electronegativity with the changes in atomic valence states is properly described even the order of atomic electronegativity may change in dependence on the type of the studied molecule.

Values of repulsion integrals γ_{AA} along with the values of atomic parameters $U_{\mu\mu}$ for the elements of the first two periods are collected in Table 2. The values of $U_{\mu\mu}$ were calculated from standard CNDO/2 parameters [20].

Table 2. Values of parameters $U_{\mu\mu}$ and repulsion integrals γ_{AA} for elements of first two periods (in eV)

Element	U_{ss}	U_{pp}	γ_{AA}
H	−17.38	—	20.41
Li	−6.32	−4.47	6.42
Be	−20.41	−17.02	9.64
B	−41.72	−36.13	12.85
C	−70.26	−61.78	16.06
N	−106.03	−93.99	19.27
O	−149.08	−132.81	22.49
F	−199.32	−178.13	25.70
Na	−5.38	−3.88	5.15
Mg	−15.13	−12.06	6.67
Al	−28.25	−23.47	8.19
Si	−44.05	−38.15	9.72
P	−64.61	−56.04	11.24
S	−87.83	−77.17	12.76
Cl	−114.41	−101.53	14.28

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Received April 14, 1980/September 16, 1980/February 27, 1981