

ON DEFINITION OF ELECTRONEGATIVITY WITHIN THE FRAMEWORK OF MO METHODS

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The possibility of generalization of the electronegativity concept to valence states of atom in molecule has been studied by semiempirical CNDO and INDO approximations. It is shown that the concept of electronegativity as the property of a given atom in molecule can be defined only on the basis of the simplest CNDO approximation.

The concept of electronegativity is one of basic concepts of general theoretical chemistry, the origin of which dates back to the Berzelius definition of electronegative and electropositive elements. For a long time this concept has been intuitive. The first generally accepted definition of electronegativity has been proposed by Pauling¹ and Mulliken². In the initial stage of its development, the electronegativity was considered as general invariant property of the element, irrespective of whether this atom had or had not been bound in a chemical compound. The detailed experimental verification of the original Pauling value by a number of authors had shown^{3,4}, however, that the electronegativity of elements changes with the compound, depending *e.g.* on the oxidation state of the given atom. This result initiated undoubtedly further attempts at supporting this concept theoretically.

With the aim to explain the dependence of electronegativity of the atom on the structure of molecule in which the atom is bonded, Mulliken⁵ has proposed that in his original definition, the values of the ionisation potential and electron affinity should be regarded as the values corresponding to valence state of the atom in a given molecule. Important contribution to the development of the electronegativity concept is due to Iczkowski and Margrave⁶ who suggested to define electronegativity as the derivative of the energy of the atom (in ground or valence state) with respect to the charge on this atom. This approach constituted the basis for all the recent attempts at theoretical interpretation of electronegativity concept. In recent years this approach has been used by Parr and coworkers in the form of the so called density functional theory⁷ and of Slater's X_a method⁸. Hinze and Jaffé⁹ generalized the Iczkowski approach by introducing the concept of the so called orbital electronegativity.

The key point of the Mulliken as well as Iczkowski electronegativity concept as the property of the atom in molecule is the concept of valence state, since the reliability of calculated values of electronegativities depends in general on the extent to which this valence state can be determined. The problem arises from that the so called valence state does not represent any of stationary states of the atom and cannot be therefore characterized experimentally. It is hence the hypothetical state whose definition is always connected with a certain degree of subjective approach. The situation is clear enough for isolated atoms where the so called valence state can be obviously characterized by integer numbers m and n which describe a certain configuration $s^m p^n$, providing

that the sum $m + n$ denotes the total number of electrons on the atom. The sp^3 configuration on carbon can serve as example. Somewhat less clear is the case of the atom bound in molecule. By analogy to the previous case, one can attempt to characterize the valence state by means of occupation numbers x, y belonging to the $s^x p^y$ configuration. However, the x, y values can now be in general non-integer numbers. The sum $x + y$ denotes the net electron density on the atom and represents the parameter characterizing nonuniformity of the charge distribution in the molecule. Hence, this parameter is not known *a priori* and has to be obtained by *e.g.* quantum chemical calculations of the molecule. Another possibility of defining the valence state of the atom in molecule has been recently proposed *e.g.* by Parr⁷ with the use of the condition of minimalisation of the sum of atom promotion energies.

The aim of this work is to analyze the possibility of calculation of electronegativities in general valence states of the atom in molecule on the basis of semiempirical CNDO and INDO methods.

RESULTS AND DISCUSSION

CNDO Approximation

Within the framework of CNDO approximation, the energy of neutral atom with configuration $s^m p^n$ can be described by relation (1).

$$E(A, s^m p^n) = mU_s^A + nU_p^A + \frac{1}{2}(m + n)(m + n - 1)\gamma_{AA}. \quad (1)$$

In this expression the quantities m and n are integer occupation numbers of s and p orbitals, providing that their sum equals to the core charge Z_A . Formal derivative of Eq. (1) with respect to variables m and n gives the values of orbital electronegativities χ_s and χ_p of the isolated atom ((Eqs (2) and (3)):

$$\chi_s = -\frac{\partial E}{\partial m} = -U_s^A - (m + n - \frac{1}{2})\gamma_{AA} = \frac{Is + As}{2} \quad (2)$$

$$\chi_p = -\frac{\partial E}{\partial n} = -U_p^A - (m + n - \frac{1}{2})\gamma_{AA} = \frac{Ip + Ap}{2} \quad (3)$$

As it is seen from Eqs (2) and (3), this approach leads to the same values of electronegativities as the original Mulliken definition. On deriving these equations we have, however, assumed that the expression for energy (Eq. (1)) in the point m_0, n_0 is the differentiable function of variables m and n . In order to fulfill this condition and thus make it possible to calculate electronegativity, it is necessary to define the function $E(s^m p^n)$ also for m and n in the vicinity of the point m_0, n_0 , *i.e.* to ensure that the equation is valid at least locally also for non-integer values of m and n . It appears

that within the framework of CNDO approximation this condition is fulfilled. This makes it possible to calculate the electronegativity of not only the isolated atoms but also the atoms bound in molecule. This possibility is based on the finding that in the CNDO approximation, the total molecular energy can be divided into the sum of mono- and biatomic contributions ((Eq. (4)).

$$E = \sum_A \varepsilon_A + \sum_{A < B} \varepsilon_{AB}. \quad (4)$$

In our previous work¹⁰ we have proposed to modify the distribution suggested by Pople¹¹ in such a way that new monoatomic contributions ε_A depend only on diagonal elements of density matrix ((Eq. (5)).

$$\varepsilon_A = \sum_{\mu}^A p_{\mu\mu} U_{\mu}^A + \frac{1}{2} \sum_{\mu}^A \sum_{\nu}^A p_{\mu\mu} p_{\nu\nu} \gamma_{AA} - \frac{1}{2} \sum_{\mu}^A p_{\mu\mu} \gamma_{AA}. \quad (5)$$

With respect to formal similarity, Eq. (5) can be considered as the generalization of the original expression (1) to the case of arbitrary occupation numbers m, n . On the basis of this equation we can calculate the values of orbital electronegativities χ_s^*, χ_p^* of the atom in the valence state characterized in a given molecule by the configuration $s^x p^y$ ($x = p_{ss}, y = p_{xx} + p_{yy} + p_{zz}$) and by the total net charge P_A . From comparison of relations for χ_s^*, χ_p^* ((Eqs (6) and (7)) with analogous relations^{2,3} for the electronegativity of isolated atom it is seen that the difference between CNDO

$$\chi_s^* = - \frac{\partial \varepsilon_A}{\partial x} = - U_s^* - (P_A - \frac{1}{2}) \gamma_{AA} \quad (6)$$

$$\chi_p^* = - \frac{\partial \varepsilon_A}{\partial y} = - U_p^* - (P_A - \frac{1}{2}) \gamma_{AA} \quad (7)$$

electronegativities for isolated atom and the atom in molecule is proportional to the charge on this atom in the molecule ((Eq. (8)).

$$\chi_j^* - \chi_j = (Z_A - P_A) \gamma_{AA} \quad (8)$$

However, for correlations with many physical or physico-chemical characteristics it is often more advantageous to describe atom by one global quantity rather than by the set of several orbital characteristics. This idea is also more closely related to the original electronegativity concept. One of the possibilities leading from orbital electronegativities to some global quantity is illustrated *e.g.* by Eq. (9).

$$\xi_A = \frac{\sum_{\mu}^A p_{\mu\mu} \chi_{\mu}^*}{\sum_{\mu}^A p_{\mu\mu}} \quad (9)$$

According to this relation, the total electronegativity ξ_A is defined as the weighted mean of the corresponding orbital electronegativities with the weighting factors proportional to orbital occupation numbers $p_{\mu\mu}$. This relation is analogical to the expression reported by Parr⁷.

As shown in Fig. 1, the ξ values for isolated atoms are proportional to the original Pauling values. The advantage of the presented definition is, however, that it generalizes the electronegativity also for the case of the atom in molecule and describes naturally its changes in dependence on the change in the valence state of the atom.

INDO Approximation

Similarly as in the previous case, we will analyze first the electronegativity of isolated atoms. Here, the situation is more complex compared to the CNDO approximation, since due to the preservation of monoatomic differential overlap, the atom with $s^m p^n$ configuration is characterized by several states differing in orbital moment, multiplicity and energy. In order to eliminate the dependence of energy on the atomic state the INDO method introduces the mean energy of the $s^m p^n$ configuration as the weighted mean of energies of all the states which are compatible with a given configuration. This energy is then expressed by relation (10).

$$\bar{E}(A, s^m p^n) = mU_s^A + nU_p^A + \frac{1}{2}(m+n)(m+n-1)\gamma_{AA} - \frac{1}{6}mnG_1 - \frac{1}{2\cdot 5}n(n-1)F_2 \quad (10)$$

Formal derivative of this equation with respect to m and n gives again expressions for the orbital electronegativity χ_s , χ_p of isolated atoms ((Eqs (11) and (12)).

$$\chi_s = -\frac{\partial \bar{E}}{\partial m} = -U_s^A - (m+u-\frac{1}{2})\gamma_{AA} + \frac{1}{6}G_1 \quad (11)$$

$$\chi_p = -\frac{\partial \bar{E}}{\partial n} = -U_p^A - (m+n-\frac{1}{2})\gamma_{AA} + \frac{1}{6}G_1 + \frac{2}{2\cdot 5}(n-\frac{1}{2})F_2 \quad (12)$$

To perform the above derivatives, it is, however, necessary to investigate again the question of differentiability of Eq. (10). In contradistinction to CNDO approximation, it becomes evident that Eq. (10) does not hold for non-integer occupation

numbers. This conclusion can be proved again by partitioning the total molecular energy to mono- and biatomic contributions. Within the framework of INDO method, monoatomic contribution E_A is described by Eq. (13).

$$E_A = \sum_{\alpha}^A p_{\alpha\alpha} U_{\alpha}^A + \frac{1}{2} \sum_{\alpha}^A \sum_{\beta}^A p_{\alpha\alpha} p_{\beta\beta} ((\alpha\alpha/\beta\beta) - \frac{1}{2}(\alpha\beta/\alpha\beta)) + \\ + \frac{1}{2} \sum_{\alpha}^A \sum_{\beta \neq \alpha}^A p_{\alpha\beta}^2 ((\alpha\beta/\alpha\beta) - \frac{1}{2}(\alpha\alpha/\beta\beta)). \quad (13)$$

In this relation, the energy of the atom is expressed not only by occupation numbers $p_{\alpha\alpha}$, $p_{\beta\beta}$ but also by cross terms of the type of bond orders $p_{\alpha\beta}$. In CNDO approximation these cross terms could be eliminated on the basis of the validity of identity ((Eq. (14)).

$$\sum_{\beta} p_{\alpha\beta}^2 = 2p_{\alpha\alpha}. \quad (14)$$

Similar transformation cannot be, however, performed within the framework of INDO method, since the multiplicative repulsion term appearing at $p_{\alpha\beta}^2$ is not constant and depends on the type of orbitals α and β . From this it follows that one cannot derive an equation analogical to Eq. (10) which holds for integer occupation numbers. This means that the values of electronegativities χ_s , χ_p cannot be obtained by

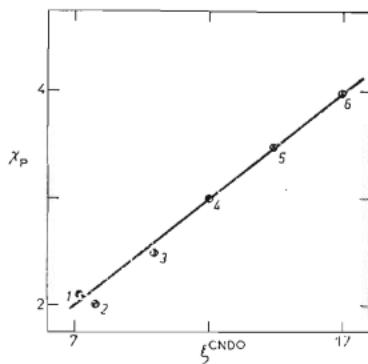


FIG. 1

Dependence of global CNDO electronegativities on the corresponding Pauling values for Period 1 elements; 1 H, 2 B, 3 C, 4 N, 5 O, 6 F

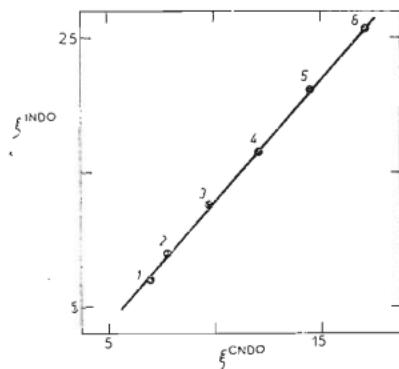


FIG. 2

Dependence of global electronegativities ξ calculated by INDO method on the corresponding CNDO quantities; for numbering see Fig. 1

derivation of relation (10), since the function $E(m, n)$ in the point m_0, n_0 is not differentiable.

If the values of derivatives cannot be calculated analytically, one can attempt at their approximation by means of the finite difference method. For example, in this approximation, the derivative $\partial\bar{E}/\partial n$ is given by the value of differential quotient (15).

$$\left. \frac{\partial \bar{E}}{\partial n} \right|_{m_0, n_0} \approx (E(s^{m_0}, p^{n_0+1}) - E(s^{m_0}, p^{n_0-1})) / 2 \quad (15)$$

It is, however, evident that such a finite difference approach cannot be applied generally. Thus, for calculating the electronegativity χ_s for configuration s^2 , the energies of configurations s^3 and s^1 should be known, but the former configuration is forbidden due to the Pauli principle. Similar problems are encountered not only in INDO approximation but they are quite general. It was *e.g.* Iczkowski and Margrave⁶ who found that the derivative $\partial E/\partial n$ shows discontinuity for some configurations. To overcome these problems and to introduce an unambiguous scale of atom electronegativities, further complementary assumptions should be introduced. Thus, for example, Parr⁸ in his recent X_s study has proposed to define atom configuration in such conflict cases with the use of Slater's transition state method. As far as our INDO approach is concerned, for this purpose it is possible to make advantage of the fact that the value of differential coefficient (15) equals to the value of formal derivative. In this sense, in such cases the orbital electronegativities of isolated atoms are substituted by the values of the corresponding derivatives ((Eq. (11), (12)). As found, this approach leads to reasonable results. When using χ_s, χ_p values in calculating total electronegativities ξ^{INDO} by means of Eq. (9), the resulting values correlate linearly very closely with the corresponding CNDO quantities which in turn are essentially equivalent to the Pauling scale (Fig. 2). The relation between global electronegativities ξ^{INDO} and ξ^{CNDO} is given by Eq. (16).

$$\xi^{\text{INDO}} = \xi^{\text{CNDO}} + \frac{1}{3} \frac{mn}{m+n} G_1 + \frac{2}{25} \frac{n(n-\frac{1}{2})}{m+n} F_2. \quad (16)$$

The above analysis has clearly shown that the concept of electronegativity as the property of the atom in molecule can be substantiated quantitatively and unambiguously by quantum chemistry only within the framework of the simplest MO methods. With more realistic MO approximations, starting from INDO to "accurate" *ab initio* SCF methods, it becomes clear that one can speak of the electronegativity only for isolated atoms and only at the expense of some further complementary assumptions (averaging of energy, *etc.*). Within the framework of the more accurate MO methods one cannot find an adequate theoretical index which would correspond to the electronegativity.

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