

## ELECTRONEGATIVITY THROUGH THE ENERGY FUNCTION

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Received 30 November 1982; in final form 18 October 1983

The modern idea of electronegativity based on the  $E(q)$  function and the traditional chemical electronegativity are brought together in one self-contained expression. The electronegativity of a molecule is confronted with the in situ electronegativities of the component atoms.

### 1. Introduction

The concept of electronegativity has received considerable attention from chemists, obviously lured by the prospects of its quantitative application. Despite innumerable efforts, their hopes have not yet materialized and electronegativity has remained a practical, qualitative guide. Although apparently well-defined numerically, electronegativity has not avoided confusion within the very heart of its definition. Two different quantities have in fact been given the name electronegativity and, strangely enough, the distinction between them has not yet been paid sufficient attention. First, the definition of primary importance for chemists formulates electronegativity as some number allotted to each element in the periodic table. These numbers are thought to reflect the tendency of atoms to attract electrons when bonded, and were more or less equivalently derived from various experimental data by Pauling [1], Mulliken [2], Gordy [3], Sanderson [4] and many others [5,6]. This quantity will be hereafter referred to as the *chemical electronegativity*,  $\bar{X}$ . Another idea of electronegativity was first conceived by Iczkowski and Margrave [7] and further developed by Hinze et al. [8]. Recently, new impulse in this direction has come from Parr's group [9]. Iczkowski and Margrave defined the electronegativity of an atom as a derivative:

$$X(q) = -dE(N)/dN = dE(q)/dq, \quad (1)$$

where  $E$  is the energy function for an isolated atom *versus* the number of electrons,  $N$ , or the net charge  $q = Z - N$ .  $X(q)$  is called *differential electronegativity* throughout this work.

Hinze et al. [8] have noticed that numerical values of the chemical and differential electronegativities for neutral atoms were identical for the parabolic  $E(q)$  function based on the first ionization energy,  $I$ , and the electron affinity,  $A$ . Indeed,

$$E(q) = aq^2 + bq = \frac{1}{2}(I - A)q^2 + \frac{1}{2}(I + A)q, \quad (2)$$

$$X(q) = (I - A)q + \bar{X} \quad (3)$$

and hence

$$X(q = 0) = \bar{X}. \quad (4)$$

The equivalence (4) results from this particular approximation for  $E(q)$  and must not be arbitrarily generalized, as it does in fact implement a drastic assumption into an entirely obscure, if physical,  $E(q)$  function for non-integral charges.

The recent work by Parr and co-workers has flourished with a rigorous definition of the differential electronegativity [9], identified with a negative chemical potential of electrons:

$$X = -\mu = -\delta E(\rho)/\delta \rho = -\partial E/\partial N. \quad (5)$$

The energy  $E(\rho)$  is some unspecified functional of the electron density  $\rho$ . Perdew et al. [10] then derived a possible solution for  $E(N)$  as a series of straight-line segments.

A separate chapter of the history of electronegativity was written by Sanderson [4]. His electronegativity equalization principle is based in fact on the differential electronegativities, although his work actually preceded the definition of Iczkowski and Margrave. Sanderson has not avoided identity (4) for atoms. The aim of this identification, rooted in the Mulliken definition, seems to be always the same: to relate an important quantitative definition [eq. (1), (5)] to the existing electronegativity scale. Even in the recent work of Ray et al., based on the density functional approach, the authors have not resisted the temptation to seek an identity between those quantities [11].

This present work offers an answer to two questions: (i) how to relate two definitions of electronegativity to each other, and (ii) how to express rigorously the electronegativity of a molecule and of a bonded atom in terms of the energy function.

## 2. Electronegativity of a non-interacting atom

The practical definition of the differential electronegativity by means of the effective charge  $q$  [eq. (1)] implicitly admits that the energy of an atom can be expressed simply as a function of its charge, which is a rather old-fashioned oversimplification when compared with eq. (5). It may be justified if  $q$  is limited to the range  $[-1, +1]$  and only the ground electronic state of the respective ions or neutral atom are considered. Although the integral  $q$  only has a physical meaning for a non-interacting atom, we do not limit the function  $E(q)$  and assume it to be a continuous and analytic function of charge (cf. ref. [12]). To disentangle the chemical and differential electronegativities, the principal formal difference between them is to be noted.  $\bar{X}$ , the chemical electronegativity scale for atoms, contains no reference to the  $E(q)$  function, whereas  $X(q)$  is only defined through  $E(q)$  and may formally be calculated for ions of any charge  $q$ . Since they are to designate the same physical quantity and no limitations for  $E(q)$  are to be introduced, the chemical electronegativity may be viewed as an average value of  $X(q)$  over some value of charge,  $\bar{X} = \langle X(q) \rangle$ . This leads to the equation

$$\bar{X} = \int_{-1}^1 X(q) dq / \int_{-1}^1 dq = E(q)|_{-1}^1 / q|_{-1}^1 = \frac{1}{2}(I + A), \quad (6)$$

which itself justifies the suggested relationship. The

chemical electronegativity may now be calculated for an atom of any charge  $q$  if the appropriate integration limits are chosen (e.g.  $q - 1, q + 1$ ). Moreover, eq. (6) does not introduce any constraints for  $E(q)$  and the detailed form of  $E(q)$  is no longer needed to reassure the equivalence between the two definitions of electronegativity.

## 3. Electronegativity of an atom in a molecule

The Sanderson principle of electronegativity equalization [4] has been proved to hold for the differential electronegativities of atoms assembled in a molecule [13–15]:

$$X_1(q_1) = X_2(q_2) = \dots = X_M(q_M = 0), \quad (7)$$

where the common value is equal to the differential electronegativity of a molecule,  $X_M$ . However, even if undeniably true in a philosophical sense, the Sanderson principle has not yet been given a coherent arithmetical form that would reproduce the chemical electronegativity of a molecule, experimentally available from the Mulliken definition. The work by Ray et al. [12], Del Re [16] and the original Sanderson proposal [4] have a common shortcoming of being based on a specific, linear function  $X(q)$ , universal for a given atom, an assumption which is equivalent to accepting a parabolic function  $E^0(q)$  for isolated atoms.

The overall energy of a molecule can be formally represented as

$$E_M = \sum_i E_i^0(q_i) + e_M^{\text{ion}}(q_1, q_2, \dots) + e_M^{\text{cov}}, \quad (8)$$

where  $e_M$  stands for the interaction between individual atoms, charge dependent ("ionic") and charge independent ("covalent"), respectively. Then, the chemical potential of the  $i$ th atom is

$$\mu_i = \mu_i^0 - V_i, \quad (9)$$

where

$$V_i = \partial e_M^{\text{ion}} / \partial q_i. \quad (10)$$

Eq. (9) is virtually the same as that for the electrochemical potential in the classical thermodynamic description. The "standard chemical potential",  $\mu^0$ , is a characteristic function derived from  $E^0(q)$  for an

isolated atom. For a bonded atom,  $\mu_i \neq \mu_i^0$ , and hence the Sanderson principle does not hold for the respective standard differential electronegativities  $X^0(q) = -\mu^0$ !

The Sanderson principle and eq. (9) may be written jointly as

$$X_M(q_M = 0) = X_i^0(q_i) + V_i. \quad (11)$$

The chemical electronegativity of a molecule can be found by taking an average of the left-hand side, according to eq. (6):

$$\bar{X}_M = \frac{1}{2} \sum_i [E_i^0(q_{i,+}) - E_i^0(q_{i,-})] + \frac{1}{2}(e_{M+}^{\text{ion}} - e_{M-}^{\text{ion}}), \quad (12)$$

where the subscripts + and - refer to the net charges of individual atoms within the molecular ions  $M^+$  and  $M^-$ , respectively. This general formula might in principle lead to the numerical value of  $\bar{X}_M$ .

On the other hand, an average of the right-hand side of eq. (11) within the limits  $q_i - 1$  and  $q_i + 1$  gives an analogue of the chemical electronegativity of this bonded atom:

$$\begin{aligned} \bar{X}_{i,M} = & \frac{1}{2} [E_i^0(q_i + 1) - E_i^0(q_i - 1)] \\ & + \frac{1}{2} [e_M^{\text{ion}}(q_1, q_2, \dots, q_i + 1, \dots) \\ & - e_M^{\text{ion}}(q_1, q_2, \dots, q_i - 1, \dots)]. \end{aligned} \quad (13)$$

Neglecting for a while the change in interaction and admitting the parabolic  $E^0(q)$  function we obtain

$$\bar{X}_{i,M} \approx 2a_i q_i + \bar{X}_i, \quad (14)$$

which is exactly the result of Ray et al. and is equivalent also to the Sanderson expression.  $\bar{X}_{i,M}$  will clearly not be the same for various atoms constituting the molecule and neither will it have any general reference to  $\bar{X}_M$  as demonstrated by eqs. (12) and (13). Under these circumstances, it is rather surprising that electronegativities based on eq. (14) [11] reasonably meet expectations for the chemical electronegativities of a number of molecules. This seems to result from the peculiar property of this quantity. With the expected value between 2 and 10 eV, it appears to be rather insensitive to the details of the calculation procedure. Three available formulae [4, 11] provide quite close values. For a collection of 42 binary molecules\*, the average de-

viation from the mean value of the three formulae is only 0.36 eV. Strangely enough, the trivial formula  $\frac{1}{2}(I_{\text{donor}} + A_{\text{acceptor}})$  [10]\*\* yields results not obviously inferior to the other three. The mean of the four results is shifted by only 0.05 eV in average against the mean of the former three, with the standard deviation from the mean value changing to 0.40 eV. Statistically then, the trivial formula is as much confident as any other proposed hitherto! Unfortunately, the experimental data are not more reliable, as the electron affinity of a molecule is rarely known with an uncertainty of less than 0.3–0.5 eV. This prevents exploring the electronegativity of a molecule in more than a qualitative sense, even for donor and acceptor molecules where the need for a quantitative index of electronegativity is most clearly seen.

#### 4. The energy function

The chemical potential  $\mu$  enters the density functional approach as a Lagrange multiplier whose value is not specified a priori [9, 12]. However, the very formulation of a continuous  $E^0(q)$  function implicitly introduces a model of a continuous electronic gas, and hence hints at the Thomas–Fermi model of an atom which gives  $\mu^0 = 0$  for a neutral, non-interacting atom [9]. This has been postulated to be a more general property of neutral atoms and stable molecules [18], leading to important conclusions: (i) The paradox discussed by Perdew et al. [10] is circumvented as there is no charge flow between non-interacting atoms Z and Y since  $\mu_Z^0 = \mu_Y^0 = 0$ . (ii) A new limitation for  $E^0(q)$  arises:  $(dE^0/dq)_{q=0} = 0$ . (iii) The Sanderson principle is automatically fulfilled by  $X_1(q_1) = X_2(q_2) = \dots = X_M = 0$  for a stable molecule, which, however, makes the principle not very informative. (iv) Eqs. (9) and (11) now yield

$$\mu_i^0(q_i) = -X_i^0(q_i) = V_i. \quad (15)$$

The standard differential electronegativity of a bonded atom is equal to the negative gross electrostatic potential at the site of this atom. The potential  $V_i$  is not a true local value at the nucleus ( $V_{0,i}$ ), but in fact the

\* Collected in tables 2 and 3 of ref. [11].

\*\* Including the promotion energies, when applicable. Taken from ref. [17].

point-charge approximation to atoms is hidden in it (eq. (10)). Approximately,  $V_i$  can be related to  $V_{0,i}$  by [19]

$$V_{0,i} = V_i - \int \frac{\rho_i(r) dr}{|r - R_i|} \quad (16)$$

If  $V_i$  becomes eventually accessible via eq. (16), one can explore eq. (15) to establish a realistic  $X^0(q)$  function [and  $E^0(q)$ ]. On the other hand, a reasonable choice for  $E^0(q)$  would provide insight into the interaction of an atom with the rest of the molecule simply through  $X^0(q)$ . The  $E^0(q)$  function has not only to meet conditions that warrant its physical meaning but also must lead to acceptable observables, the simplest of which are net atomic charges and binding energies. They can be calculated for systems only when the interaction term  $e_M^{\text{ion}}$  can be approximated with some degree of confidence. The most evident examples of this type are ionic crystals, where the Madelung and repulsive energies are readily available and account for almost 100% of the ionic interaction. The parabolic  $E^0(q)$  function, widely used in electronegativity considerations, leads to inadmissible net atomic charges and/or lattice energies for this class of compounds, e.g.  $q_{\text{Na}^+} = -1.37$  in solid NaCl. Recently, a novel function has been proposed [18]:

$$E^0(q) = \frac{1}{2}(I - A)q^4 + \bar{X}q^3 \quad (17)$$

This trial function is the simplest possible polynomial conforming to the  $\mu^0(q=0) = 0$  postulate that also yields correct charges and energies for a broad selection of crystals [18].

## 5. Conclusion

The two sets of differential electronegativities of a bonded atom,  $X(q)$  and  $X^0(q)$ , may be thought to reflect two different features of a molecule. The uniformity of the chemical potential is seen through  $X(q)$ , exactly as postulated by Sanderson [4] and proved by Donnelly and Parr [13]; the molecule appears to be unity, a system of joint vessels filled by the electronic gas. On the other hand, the inner chemical diversification of the molecule is observed by means of standard electronegativities,  $X^0$ . They reflect differences between

atoms in the molecule due both to their effective charges and to the fact that atoms remain different chemical individuals despite being bonded. This seems to be very much a chemical point of view.

The relationship between the standard electronegativities and electrostatic potentials (eq. (15)) points out a possible use of the former as reactivity indices in a manner similar to molecular electrostatic potentials [20]. It remains to be seen whether the striking simplicity of calculation and straightforward application to any system from an ionic molecule to the solid surface may perhaps show itself competitive enough to have standard electronegativities paid some attention in future work.

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