# A new equation based on ionization energies and electron affinities of atoms for calculating of group electronegativity

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## ARTICLE INFO

## ABSTRACT

In particular, in organic chemistry, the electronegativity of functional groups are taken into consideration significantly to predict reaction mechanism and to explain inductive effects of functional groups. In the present study, considering the relationship with charge of the electronic energy for atoms, Sanderson's electronegativity equalization principle and Density Functional Theory (DFT), we have obtained a new equation by which group electronegativity can be calculated from ionization energies ($I$) and electron affinities ($A$) of atoms that constitute the group, where the results obtained were compared with equation of Sanderson who proposed that group electronegativity is the geometric mean of atomic electronegativities. For a large number of groups, it was found to be a very close agreement with a standard deviation of 0.12. The advantage of the present equation is that it can be used for ionic groups. In addition, the derived equation can be used to calculate Mulliken and Pauling electronegativities of molecules.

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## 1. Introduction

The principal aim of theoretical chemistry is to develop rules to explain chemical reactions and molecules in a quantitative and predictable way. The electronegativity is a useful theoretical descriptor in correlating chemico-physical properties of atoms and molecules. The idea of group electronegativity is historically important because the electronegativity concept evolved largely from the desire of organic chemists to understand reaction mechanisms in terms of the inductive effects of various functional groups. In recent years, there has been a considerable amount of work done that deals with the evaluation and use of group electronegativity [1–6].

A significant development in the electronegativity concept has been provided by Sanderson's electronegativity equalization principle [7,8]. According to this principle, when two or more atoms initially different in electronegativity combine chemically, their electronegativities have become equalized. The equalized value gives the electronegativity of the formed molecule and is equivalent to the geometric mean of the electronegativity values of the constituent atoms, as in Eq. (1). Electronegativity was originally introduced by Pauling as a measure of an atom in a molecule to attract electronic charge. Considering the Sanderson's electronegativity equalization principle it can be said that when two or more

different atoms combine to form a molecule, their electronegativities change to a common intermediate value and become equalized. If so, group electronegativity that is a measure of inductive effects of functional groups can be defined as final electronegativity values of atoms in a molecule.

$$\chi = \left(\prod_{i=1}^{N}\chi_i\right)^{1/N} \tag{1}$$

where $\chi$ is the electronegativity of molecule or combined atom, $\chi_i$ is the electronegativity of pre-bonded $i$-th atom, $N$ is the total number of atoms in the molecule. For the calculation of group electronegativity, apart from geometric mean method of Sanderson, the arithmetic mean method [9–11] is also used for this purpose. According to arithmetic mean method, the electronegativity of any group is equivalent to the arithmetic mean of the electronegativity values of the constituent atoms in the group and can be calculated via following equation.

$$\chi_G = \frac{\sum_{i=1}^{N}\chi_i}{N} \tag{2}$$

$X_G$ represents the electronegativity of molecule or combined atom, $\chi_i$ is the electronegativity of pre-bonded $i$-th atom, $N$ is the total number of atoms in the molecule.

In a study related to metal oxides, F. Di. Quarto and his colleagues [11] proposed that the results of arithmetic mean method for calculation of group electronegativity are compatible with

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experimental data. Therefore, arithmetic mean method is also a valid useful method in the calculation of group electronegativity.

Another important study for the electronegativity concept has been made by Iczkowski and Margrave [12]. They proposed that the electronegativity of an atom may be expressed as linear function of the charge on the atom:

$$\chi = a + 2b\delta \tag{3}$$

where $a = (I + A)/2$ and $b = (I - A)/2$, $I$ and $A$ are the valence-state ionization energy and electron affinity of the atom, respectively, $\delta$ is partial charge. Many workers have been used Eq. (3) for calculating the partial charges of atoms in functional groups and molecules [13–16].

In estimating group electronegativity and partial charges, Huheey [13] suggested a simple scheme based on the Iczkowski–Margrave equation and Sanderson's principle. In his study, the following expressions were used for the substituent $AB_n$:

$$\chi_{AB_n} = \chi_A = a_A + 2b_A\delta_A \tag{4}$$

$$\chi_{AB_n} = \chi_B = a_B + 2b_B\delta_B \tag{5}$$

$$\delta_A + n\delta_B = q \tag{6}$$

where $q$ is the charge of the substituent.

Another group electronegativity equation was derived by Bratsch [17],

$$\chi_G = \frac{N + q}{\sum\left(\frac{v}{\chi}\right)} \tag{7}$$

here, $\chi_G$ is the electronegativity as equalized through Sanderson's principle, $N = \Sigma(v)$ is the total number of atoms in the species formula, $q$ is the charge of the species and $\chi$ is the Pauling electronegativity of pre-bonded or isolated atoms in the species.

A similar equation was proposed by Mullay [18],

$$\chi_G = \frac{N + 1.5q}{\sum\left(\frac{v}{\chi}\right)} \tag{8}$$

In the present report, it was derived a new equation which enables us to calculate group electronegativity directly from ionization energies and electron affinities of pre-bonded atoms. In order to the applicability of the derived equation, our results were compared with those obtained from the other methods given in the literature.

## 2. Methodology

One of the most important works related to electronegativity has been demonstrated by Iczkowski and Margrave. They defined electronegativity as the derivative of ionization energy with respect to charge. Later on, Jaffe and co-workers introduced the idea of orbital electronegativity considering the study of Iczkowki and Margrave. Assuming that the energy of neutral atom is zero, the following curve that gives the relationship between atomic energy and charge is obtained [19,20]. Such a curve for oxygen atom is given in Fig. 1. For all atoms, same curve is not the case but it should be expressed that the correlation between atomic energy and charge is parabolic as indicated in Eq. (9) [21]. In Fig. 1, it is seen that the energy of atom is zero at $\delta$(charge) = 0 point.

The function of the curve may be described rather accurately by the quadratic formula for small $\delta$ values [12],

$$E = a\delta + b\delta^2 \tag{9}$$

where $E$ is the total energy of the atom, that is found from $\Sigma I$ or $\Sigma A$, $I$ and $A$ are ionization energy and electron affinity of the atom. In
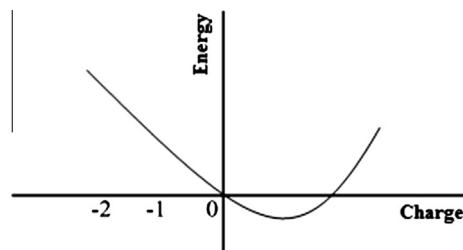


**Fig. 1.** Atomic energy ($E$) change with charge ($\delta$) for oxygen atom. (The energy of neutral atom is assumed to be zero.)

Eq. (9), if $\delta$ is taken (+1), $E$ will be the energy of the (+1) cation energy or first ionization energy. Likewise, for $\delta = -1$, the energy will be negative of the first electron affinity (Note that the definition of electron affinity does not follow the usual thermodynamic convention in that a positive electron affinity is exothermic). This argument leads to the following relations:

$$I = a + b \tag{10}$$

$$-A = -a + b \tag{11}$$

From these equations, the following relations are obtained:

$$a = (I + A)/2 \tag{12}$$

$$b = (I - A)/2 \tag{13}$$

As suggested by Iczkowski–Margrave, the first derivative of the energy with respect to the charge may be defined as the electronegativity of the atom:

$$\chi = a + 2b\delta \tag{14}$$

As can be seen from this equation, $a$ is equal to electronegativity of neutral atom. Eq. (12) is similar to that of Mulliken, but he used valence-state ionization energy and electron affinity whereas we employed here those of ground-state. Therefore, the electronegativity concept in this paper may be defined as absolute electronegativity, as proposed by Parr and co-workers [22,23].

Considering equation (14), for each atom in a chemical species (molecule or group) that contains $N$ atoms, we can write

$$\chi_1 = a_1 + 2b_1\delta_1$$
$$\chi_2 = a_2 + 2b_2\delta_2$$
$$\chi_3 = a_3 + 2b_3\delta_3$$
$$\vdots \quad \vdots \quad \vdots$$
$$\chi_N = a_N + 2b_N\delta_N$$

On the basis of Sanderson's principle, one can write the following relation:

$$\chi_1 = \chi_2 = \chi_3 = \cdots = \chi_N = \chi_G \tag{15}$$

where $\chi_G$ is the electronegativity of the species. Using the condition for the species to be $q$ charge, namely

$$\delta_1 + \delta_2 + \delta_3 + \cdots + \delta_N = q \tag{16}$$

The partial charge of any atom in the species can be given as follows;

$$\delta_i = \frac{\chi_G - a_i}{2b_i} = \frac{\chi_G}{2b_i} - \frac{a_i}{2b_i} \tag{17}$$

From Eqs. (16) and (17) one can obtained the following equation:

$$\chi_G = \frac{\sum_{i=1}^{N}\left(\frac{a_i}{b_i}\right) + 2q}{\sum_{i=1}^{N}\left(\frac{1}{b_i}\right)} \tag{18}$$