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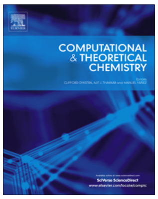

A new method for calculation of molecular hardness: A theoretical study

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ABSTRACT

The chemical hardness introduced by Pearson in 1960s is an extremely useful theoretical descriptor. It is apparent that principles such as hard and soft acids and bases (HSAB) and maximum hardness principle (PMH) related with the chemical hardness provide theoretical justifications and explanations for many issues in chemistry. In the present report, a new molecular hardness equation to calculate chemical hardness of functional groups and molecules is derived utilizing the relationship with charge of the electronic energy for atoms, Density Functional Theory, and Datta's global hardness equalization principle. The reliability of the new equation is assessed by comparison with experimental data, the results of Datta's geometric mean equation, and molecular hardness values obtained in the present work. The new equation provides the opportunity to calculate the chemical hardness of molecules from first ionization energies (IE_1), first electron affinities (EA_1) and second ionization energies (IE_2) of atoms in the molecules.

1. Introduction

Density Functional Theory (DFT) [1–3] has been widely used for the prediction of molecular properties and to ensure theoretical explanations in many topics in chemistry. In this theory, important reactivity indices such as chemical potential (μ), chemical hardness (η) [4–7], electronegativity (χ) [8,9], and softness (σ) [10] are defined as derivatives of electronic energy (E) with respect to number of electrons (N) at a constant external potential $\upsilon(r)$. Quantitative expressions related to these concepts are as follows [11]:

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(r)} \tag{1}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(r)} = \left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(r)} \tag{2}$$

$$\sigma = \frac{1}{\eta} \tag{3}$$

Operational definitions for chemical hardness and electronegativity were obtained by Pearson and co-workers using finite difference methods, assuming that there is a quadratic relationship between E and N. Thus, electronegativity and chemical hardness of any chemical species can be calculated via the following equations which use the first vertical electron affinity (EA) and the first vertical ionization energy (IE) of said chemical species [12–14].

$$\chi = \frac{\mathrm{IE} + \mathrm{EA}}{2} \tag{4}$$

$$\eta = \mathrm{IE} - \mathrm{EA} \tag{5}$$

Koopman's theorem [15,16] provides an alternative molecular orbital theory method to calculate the ionization energies and electron affinities of molecules. According to this theorem, the negative of the highest occupied molecular orbital energy and the negative of the lowest unoccupied molecular orbital energy correspond to ionization energy and electron affinity, respectively ($-E_{HOMO} = \mathrm{IE}$ and $-E_{LUMO} = \mathrm{EA}$). Consequently, chemical hardness and electronegativity are given as follows:

$$\chi = -\left(\frac{E_{HOMO} + E_{LUMO}}{2}\right) \tag{6}$$

$$\eta = E_{LUMO} - E_{HOMO} \tag{7}$$

Electronegativity, the negative of chemical potential, is an important concept in understanding the nature of chemical interactions [17]. Sanderson postulated the electronegativity equalization principle [18–20] which states that electronegativities of atoms in a molecule are equilibrated during molecule formation. Sanderson further suggested the geometric mean principle, that molecular

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electronegativity is the geometric mean of the electronegativities of atoms in the molecule. Thus, molecular electronegativity, χ_M, can be calculated using the following equation [21–23].

$$\chi_M = \left(\prod_{i=1}^{N} \chi_i\right)^{1/N} \tag{8}$$

where N represents the number of atoms in the molecule, and χ_i ($i = 1, 2, \ldots N$) is the isolated atom electronegativity.

Following Sanderson, Datta [24] demonstrated that the hardness of all the atoms in a molecule is indeed equalized, and molecular hardness is the geometric mean of the chemical hardness of constituent atoms. Molecular hardness, η_M, can be calculated via following equation.

$$\eta_M = \left(\prod_{i=1}^{N} \eta_i\right)^{1/N} \tag{9}$$

where N represents the number of atoms in any molecule, and η_i ($i = 1, 2, \ldots N$) are the isolated atom hardnesses.

Pearson divided ions and molecules into four categories: hard acids, hard bases, soft acids and soft bases, and showed that species from the same categories prefer to react between themselves (the Hard and Soft Acid/Base (HSAB) Principle [25–27]). According to this Principle, hard acids prefer to coordinate to hard bases; soft acids prefer to coordinate to soft bases. Unpolarized chemical species are described as "soft" while polarized chemical species are expressed as "hard". It is clear that hard-hard interactions are mainly ionic and soft–soft interactions are mainly covalent. Chemical reactions always involve transfer of electrons between the chemical species. Soft molecules are sensitive to charge transfer in contrast to hard molecules. Chemical stability is closely associated with chemical hardness and hard molecules are less reactive (the Principle of Maximum Hardness (PMH) [28]). It should be clear that molecular hardness values of chemical species in a reaction provide important clues to prediction of reaction mechanism and estimation of the products formed in the reaction [29].

The present work uses Density Functional Theory (DFT), the relationship with charge of electronic energy, and the global hardness equalization principle to develop a new molecular hardness equation which provides a method to calculate molecular hardness from first ionization energies, first electron affinities and second ionization energies of atoms in the molecules.

2. Theoretical method

One of the most significant methods for determination of the electronegativities of atoms is due to Iczkowski and Margrave [30]. They find an initial parabolic relationship of the energy of any atom (A) with its charge (q) (Fig. 1) as in the following equation, where the energy of the neutral atom is assumed to be zero [31,32].

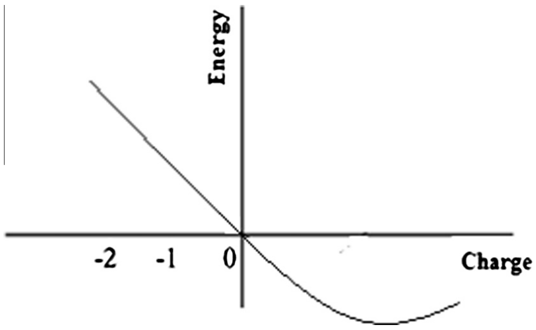

Fig. 1. Atomic energy change with charge for any atom. The energy of neutral atom is assumed to be zero.

$$E(A) = aq + bq^2 + cq^3 + dq^4 + \cdots \tag{10}$$

where E is the total energy of the A atom, q is the charge of the atom and a, b, c, d are coefficients. The electronegativity is the first derivative with respect to charge of the total energy.

$$\partial E/\partial q = a + 2bq + 3cq^2 + 4dq^3 + \cdots \tag{11}$$

For the any A atom, the a, b, c, d coefficients can be determined in terms of successive ionization and electron affinity reactions of the A atom, assuming that the energy of the neutral atom is zero. Iczkowski and Margrave used only the first two terms of Eq. (10). Thus, the energy and electronegativity of atoms are represented, respectively, as

$$E = aq + bq^2 \tag{12}$$

$$\partial E/\partial q = a + 2bq \tag{13}$$

In the present study, a new atomic hardness (η_a) equation is obtained using a similar approach to that of Iczkowski and Margrave. The new equation by which to calculate the chemical hardness of functional groups and molecules is derived in terms of the atomic hardness equation and the global hardness equalization principle. The atomic hardness equation is obtained using only the first three terms of Eq. (10) with atomic hardness as the second derivative with respect to charge of the electronic energy.

$$E = aq + bq^2 + cq^3 \tag{14}$$

$$\chi = \left(\frac{\partial E}{\partial q}\right) = a + 2bq + 3cq^2 \tag{15}$$

$$\eta_a = \left(\frac{\partial^2 E}{\partial q^2}\right) = 2b + 6cq \tag{16}$$

As mentioned above, for the any A atom, the a, b, and c coefficients can be determined by considering successive ionization and electron affinity reactions of the A atom while assuming that the energy of neutral atom is zero. Ionization energy and electron affinity reactions are given below.

$$A \rightarrow A^+ + e^- \quad \mathrm{IE}_1$$

$$A^+ \rightarrow A^{2+} + e^- \quad \mathrm{IE}_2$$

$$A^- \rightarrow A + e^- \quad \mathrm{EA}_1$$

We can now write the following expressions.

$$E(A^+) - E(A) = [a + b + c] - [0] = a + b + c = \mathrm{IE}_1 \tag{17}$$

$$\begin{aligned} E(A^{2+}) - E(A^+) &= [2a + 4b + 8c] - [a + b + c] = a + 3b + 7c \\ &= \mathrm{IE}_2 \end{aligned} \tag{18}$$

$$E(A) - E(A^-) = [0] - [-a + b - c] = a - b + c = \mathrm{EA}_1 \tag{19}$$

Solving for $2b$ and $6c$, we find

$$2b = \mathrm{IE}_1 - \mathrm{EA}_1 \tag{20}$$

$$6c = \mathrm{IE}_2 - 2\mathrm{IE}_1 + \mathrm{EA}_1 \tag{21}$$

For chemical hardnesses of atoms in a molecule that contains N atoms, we can write in terms of Eqs. (16), (20) and (21) that