

Classical DFT Study on Atomic Electronegativity

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ABSTRACT

The term electronegativity was introduced by Linus Pauling, who characterized on the basis of thermodynamic data from the energies of the single bonds. In present study, the Density Functional Theory (DFT) was used to calculate electronegativity of atoms. The base of calculation is similar to Pauling and Mulliken methods. The results indicate that the largest value of electronegativity for Fluorine atom and then plotted the electronegativity values versus to atomic numbers. We have selected scale of electronegativity base on Pauling's method. Also we presented an empirical formula for electronegativity calculation that the value of the electronegativity is a function of number of valence electron, in addition to ionization potential and electron affinity. Our novel strategy designed by Natural Population Analysis (NPA) method. All calculations were performed using B3LYP method and aug-cc-pVTZ, 6-311++G(2df), SDDALL and LANL2DZ basis set in Gaussian 03W.

Keywords: Atomic Electronegativity; DFT Study; Periodic Trend; Ionization Potential; Electron Affinity

INTRODUCTION

The Electronegativity (EN) is a basic concept in chemistry. No concept more thoroughly pervades the fabric of modern chemistry than that of EN and no name is more persistently associated with its origins in the mind of the modern student of chemistry than that of Linus Pauling. In recent years were studied on EN, electron affinity (EA) and ionization potential (IP) for atoms and molecules [1-10]. EN plays an important role in Nature of chemical Bond, corrosion study and surface chemistry: hardness, softness and fraction of electrons transferred and etc. [11-14].

The history of the study of EN has been explained in theoretical and experimental works [15-17]. In Pauling's studies, the EN of atoms was determined on the basis of thermodynamic data from the energies of the single bonds in which they are involved:

$$\Delta E(A B) = E(A B)_{\text{exp}} - \frac{1}{2} [E(A A) + E(B B)]$$
$$|\chi_A - \chi_B| = 0.208 \Delta E^{1/2} \text{ (eV)}$$

Where $\Delta E(A B)$ is the additional energy of the

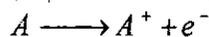
interaction of the atoms A and B above the additive covalent contribution. Having adopted EN for hydrogen as $\chi_H = 2.1$, Pauling calculated the values of χ for a large number of atoms. The data which he obtained served as the basis for the first EN scale.

Pauling's EN scale came to be generally employed and became a kind of reference standard for new methods of calculation of χ , many of the newly created scales being adjusted to Pauling's scale [18]. Furthermore, some of the modern investigators believe that Pauling's original EN scale is not only the most successful but is also adequate [19] and that his method is still one of the fundamental ones for the determination of EN.

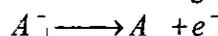
Another no less familiar approach to the determination of EN was developed in 1934 by Mulliken [20] who determined absolute EN, having

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expressed them in terms of half the sum of the ionization energies of a neutral atom:



First IP and a negative ion:



EA in the absence of the overlap of the electron shells of the interacting atoms:

$$\chi_{\text{Mulliken}} = \frac{(IP + EA)}{2}$$

Pauling's and Mulliken's scales proved to be linearly related (different workers give different parameters of the corresponding linear regression) [18, 21, 22] although the dimensions of the EN are in fact not the same.

However, in a series of succeeding studies, only one of the parameters of the Mulliken equation was employed. For example, Vereshchagin [23] assumed that the EN of an atom is expressed directly by its EA, because EN reflects the tendency of the atom in the molecule to attract electrons. On the other hand, in practice, procedures for the calculation of EN involving the use of the IP of the atom came to be most widely used [25] thus the employment of average IP for the calculation of EN by the equation:

$$\chi = \frac{IP_n}{n} + F$$

Where IP_n is the IP of an n - valent atom and EA its EA, made it possible to find the values of χ satisfactorily correlated with the EN found by Pauling [26].

In recent years, the Density Functional Theory (DFT) has become a widely used formalism for electron structure calculations of atoms, molecules, and solids. The DFT is based on the earlier

fundamental work of Hohenberg and Kohn [12] and Kohn and Sham [27]. The Kohn - Sham equations are structurally similar to the Hartree - Fock equations, but include, in principle, exactly the many - body effects through a local exchange - correlation (XC) potential.

In this paper we calculated ionization potentials, EA and EN for atoms (Li - F and Na - Cl) by DFT.

COMPUTATIONAL DETAILS

Among quantum chemical methods, DFT has some asset. DFT [28, 29] has been found to be successful in providing insights into the chemical reactivity and selectivity, in terms of global parameters such as EN, hardness and softness. We performed at the DFT level with B3LYP method and aug-cc-pVTZ, 6-311++G(2df), SDDALL and LANL2DZ basis sets. It is important that for first and second row atoms, the basis sets are cc-pVNZ where N=D, T, Q, 5, 6 ... (D=double, T=triples, etc.). The 'cc-p', a stand for "correlation - consistent polarized" and the 'V' indicates they are valence - only basis sets.

This level that makes use of Becke - Style density functional theory [30] with various correlation functional (LYP; P86 and PW91) [31]. All DFT computations were performed with the Gaussian 03W suite of programs [32]. Also Natural Population Analysis (NPA) was performed in Gaussian 03W.

RESULTS AND DISCUSSIONS

The results of the calculated for atomic EN of second and third rows are given in Table 1 and Table 2.

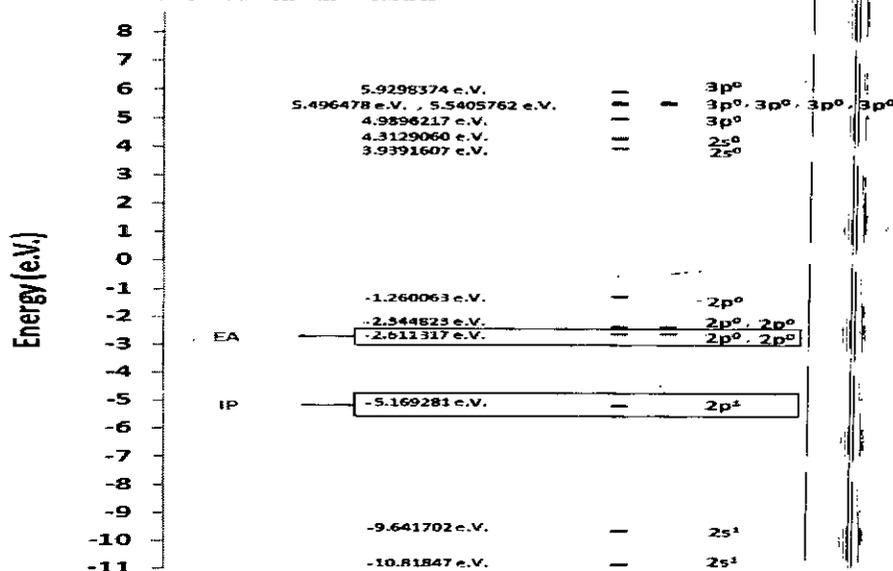


Fig. 1. Electronic Configuration of Boron and our strategy.

Our strategy for calculating of EN is based on electron energy and electron population at each atomic level by NPA tools. We have based our study such as the graph in Figure 1. The highest occupied level energy is equivalent IP and lowest unoccupied level energy is equivalent EA of atom. The important parameter in design of this strategy is determining of multiplicity, which for all atoms are considered based on Hund's rules except Beryllium and Magnesium.

According to classical studies of the average of IP and EA is equal to atomic EN, but is acceptable that we need to report EN in the

Pauling scale, and then the following empirical equation is presented:

$$\chi = 0.77 \times \sqrt[4]{N^2 \times \frac{(IP + EA)}{2}}$$

Where χ refers to the atomic Electronegativity, N is number of valence electron, IP is ionization potential and EA is equal to Electron affinity. The unit of the all parameters is electron Volts.

For both rows of the periodic table are obtained a unique EN equation, while only difference between them is constant numbers in equation of EN and atomic number:

Table 1. The Values of Atomic Electronegativity of second row / (e.V.)

Atom	Z	N	Values of Atomic Electronegativity / (e.V.)				Mulliken - Jaffe
			B3LYP/A	B3LYP/B	B3LYP/C	B3LYP/D	
Li	3	1	0.9726	0.9722	0.8816	0.9744	0.97
Be	4	2	1.4905	1.4872	1.3954	1.4911	1.54
B	5	3	1.8730	1.8740	1.8361	1.8709	2.04
C	6	4	2.3867	2.3876	2.3454	2.3813	2.48
N	7	5	2.7224	2.7242	2.6467	2.7018	2.9
O	8	6	3.0735	3.0752	3.0408	3.0342	3.41
F	9	7	3.6091	3.6110	3.5845	3.5696	3.91
R²			0.9963	0.9964	0.9958	0.9954	0.9985

A: aug-cc-pVTZ, B: 6-311+G(2df), C: SDDAll, D: LANL2DZ

Table 2. The Values of Atomic Electronegativity of third row / (e.V.)

Atom	Z	N	Values of Atomic Electronegativity / (e.V.)				Mulliken - Jaffe
			B3LYP/A	B3LYP/B	B3LYP/C	B3LYP/D	
Na	11	1	0.9775	0.9765	0.8707	0.8464	0.91
Mg	12	2	1.3338	1.3424	1.3452	1.3505	1.37
Al	13	3	1.7361	1.7333	1.7321	1.7324	1.83
Si	14	4	2.2314	2.2303	2.2246	2.2396	2.28
P	15	5	2.5912	2.5901	2.5745	2.5668	2.3
S	16	6	2.9556	2.9521	2.9442	2.9249	2.69
Cl	17	7	3.4282	3.4319	3.4488	3.4065	3.1
R²			0.9984	0.9984	0.9981	0.9968	0.9741

A: aug-cc-pVTZ, B: 6-311+G(2df), C: SDDAll, D: LANL2DZ

$$\text{Second Row: } \chi = 0.77 \times \sqrt[4]{N^2 \times \frac{(IP + EA)}{2}} = (0.4259 \times Z) + 0.2513$$

$$\text{Third Row: } \chi = 0.77 \times \sqrt{N^2 \times \frac{(IP + EA)}{2}} = (0.4089 \times Z) + 3.5462$$

The data presented in Table 1 and Table 2 show that value uttermost of EN is referring to Fluorine. The atomic EN calculated by the DFT methods for B3LYP/A, B, C, D. The B3LYP/C values have the bigger deviation from Mulliken - Jaffe.

We plotted the atomic EN versus atomic number Z Figure 2 and Figure 3. The correlation coefficient for third row at B3LYP/A is better than second row at B3LYP/A (Table 1 and Table 2). With increasing atomic number, Mulliken - Jaffe EN values in the third row of the periodic table shows an obvious deviation at the phosphorus atom to after, while the calculated values is continued its trend line, the cause of this phenomenon is EN dependence to the number of valence electrons.

CONCLUSION

In this study, atomic EN for second and third row of periodic table in Pauling scale was calculated and compared with Mulliken - Jaffe values. We obtained these results:

(1) The values calculated in terms of quantitative are good agreement with Mulliken - Jaffe values. In terms of Qualitative all computational ways are introduced fluorine as the most electronegative element in the periodic table.

(2) In the second row of periodic table, aug-cc-pVTZ, 6-311++G(2df) and LANL2DZ basis sets results the similar values, while in the third row of the periodic table, all of the basis sets are harmonious together.

(3) In the third row of periodic table, Mulliken - Jaffe values are diverted after the phosphorus atom, while the calculated values have a direct trend, because our formula is dependence on the number of valence electrons.

In this historical study is presented an empirical formula to imitation the work of Pauling, according to this formula, the value of the EN is a function of number of valence electron in addition to IP and EA.

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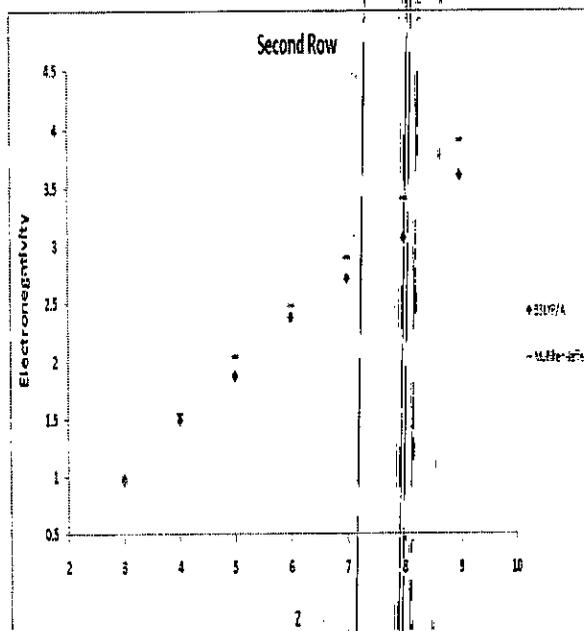


Fig. 2. Linear dependence of Atomic Electronegativity versus Z for second row of periodic table.

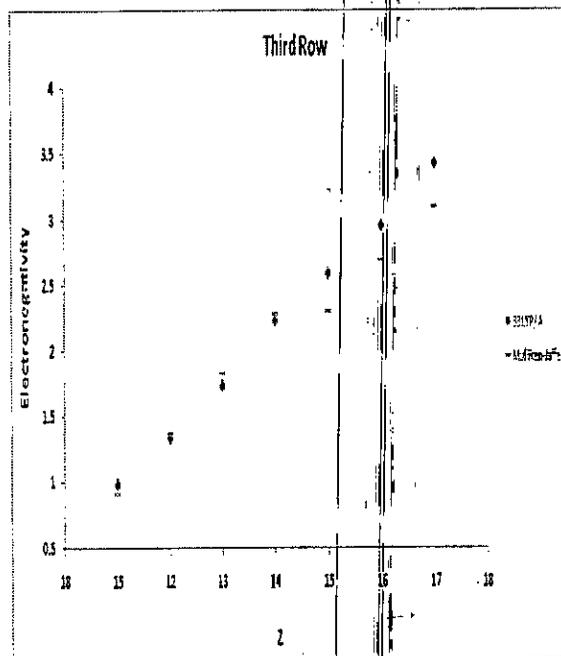


Fig. 3. Linear dependence of Atomic Electronegativity versus Z for third row of periodic table.

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