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The Electronegativity and the Global Hardness Are Periodic Properties of Atoms

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Abstract

The electronegativity and the hardness are two popular and useful theoretical descriptors of chemistry and physics successfully used by both chemists and physicists in correlating chemico-physical properties of atoms, molecules and condensed matter physics. We have tried to explore the fundamental nature of the hardness and electronegativity of atoms and have observed that their fundamental nature is basically lying in electrostatics and manifest as the electron attracting power emanating from the nucleus of the atom. We have tried to correlate the periodic nature of variation of the electronegativity and the hardness to the electron attracting power of the nucleus from which they are originated and developed. We have developed the formulae for evaluating both electronegativity and hardness and found that they have the direct correlation with the effective nuclear charge of the atoms and hence their periodicity.

1. Introduction

The terms electronegativity and chemical hardness are in the glossary of chemistry and the students are taught that, along with other periodic properties, both the electronegativity and the global hardness of atoms are periodic in nature. Although the rationale of the periodic nature of electronegativity can be linked to the internal constitution of atoms, the periodicity of the hardness of atoms is not that straight forward. In this report we want to explore simple algorithms that will justify the periodic nature of both electronegativity and hardness of atoms. The electronegativity and chemical hardness are two different fundamental descriptors having different fields of applications. Notwithstanding the erudite discussion of Putz [1] on the problem of observability of the electronegativity and chemical hardness, the hardness and the electronegativity are fundamentally hypothesis and conceptual structures and are not physical observables and, therefore, cannot be evaluated experimentally [2-6].

Thus, both electronegativity and chemical hardness are qualitative mental constructs and one can suggest or model their semi empirical evaluation only.

Although the periodic table does not follow from quantum mechanics, the periodic law is an indispensable tool in understanding, rationalizing and correlating the chemi-cal and physical behaviour of elements. The concept of shell structure and Pauli Exclusion Principle justifies chemical periodicity [7] of elements.

It is important to mention here some outstanding fundamental works of Putz and his coworkers [8-13] on electronegativity and hardness and their usefulness for the theoretical prediction of several physicochemical properties-like the fundamentals of chemical bonding. It is shown that the aromaticity of peripheral topological path may be well described by superior finite difference schemes of electronegativity and chemical hardness indices in certain calibrating conditions.

Although there are reports [14,15] that the electronegativity and hardness are periodic, no rationale has been put forward justifying their periodicity. We are after the quest for the origin and development of these two descriptors with an intention to correlate and justify their periodic nature. We strongly guess that the global hardness and electronegativity originate and develop from the same fundamental source within the constitution of atoms and their periodic nature would be straightforward in this rationale.

2. The Definition of Electronegativity

The attempt of scientific definition and measurement of

electronegativity was started with the seminal work of Pauling [16,17] who suggested for the first time a scientific definition of electronegativity as "the power of an atom in a molecule to attract electrons toward itself".

Though the electronegativity has been defined in many different ways after Pauling, the most logically it has been identified as electrostatic force or energy [2-6,18-20] —with which an atom holds the valence electrons. In this model, electronegativity has the origin in the electrostatic field and interaction within the volume of the atom. Thus, in the electrostatic model, electronegativity has its origin in the attraction (or influence) of the nucleus on the valence electrons or the electron cloud of the atom. For that reason, to assign the electronegativity value of any system, we have to suggest a model relying upon its fundamental nature—the holding power of the electron cloud by the chemical species for its measurement.

Because our prime motive is to rationalize the periodicity of electronegativity, we lay emphasis on such scales of measurement that are based upon electrostatic concept and periodicity can be easily included and justified. In 1946, the direct relation between electronegativity and the effective nuclear charge was suggested by Gordy [20]. Recently, Ghosh and Chakraborty [3] modified Gordy's electrostatic scale of electronegativity. They

[3] suggested that the electronegativity of an atom is equal to the electrostatic potential felt by one of its valence electrons at a radial distance equal to its absolute radius or most probable radius. Justifiably, such potential is created by the conjoint action of the nucleus and the remaining electrons in the atom.

Ghosh and Chakraborty [3] argued that the electronegativity, χ, is no equal but proportional to the ratio of effective nuclear charge, Z_{eff} and absolute radius or most probable radius, r of the atoms and proposed the electronegativity equation as follows:

$$\chi = a\frac{Z_{eff}}{r} + b \qquad (1)$$

where "a" and "b" are the constants to be determined by least square fitting and these are different for different periods.

We have plotted the electronegativity values of Ghosh and Chakraborty [3] as a function of their atomic number in **Figure 1** to demonstrate the periodic behaviour of the atoms of the 103 elements of the periodic table.

3. The Definition of Hardness

It is apparent that the hardness fundamentally signifies
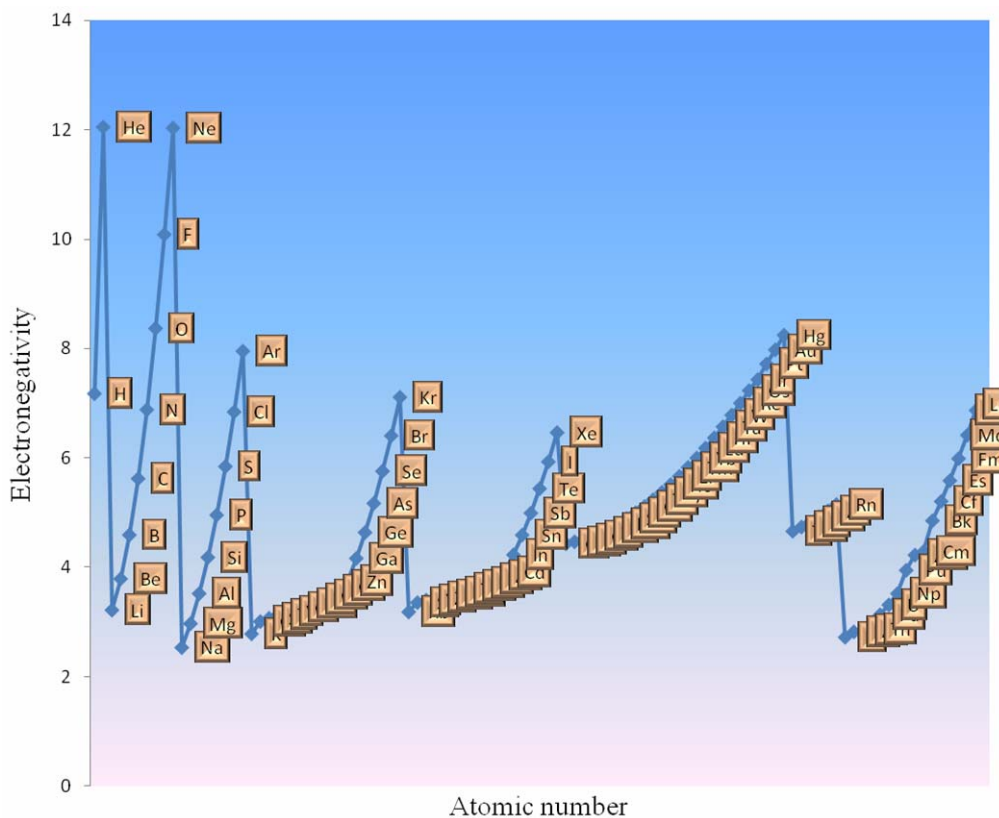

Figure 1. Plot of the electronegativity (eV) values of 103 elements of the periodic table as a function of their atomic number.

the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical response. Thus, the hardness as conceived in chemistry signifies the resistance towards the deformation of charge cloud of chemical systems under small perturbation encountered during chemical processes. Still there is another notion of hardness—the physical hardness' originated in solid-state condensed matter physics signifying the resistance of a structure towards deformation [21]. But in case of atoms, the chemical hardness and physical hardness have fundamentally evolved with time to converge to the one and single concept—the hardness in general.

Parr and Pearson [22] using the density functional theory [23,24] as basis, defined the term "absolute hardness, η" as

$$\eta = 1/2 \left[\partial^2 E / \partial N^2 \right]_v \qquad (2)$$

Although the hardness was rigorously defined by Parr and Pearson [22], evaluation of accurate hardness value of atoms through the rigorous theoretical calculation using Equation (2) is not easy [25], because the numerical method is the only route of evaluating global hardness of the atoms. Moreover, Reed [26] has pointed out that there is inherent mathematical inconsistency in evaluat-

ing global hardness by finite difference approximation method of Parr and Pearson [22]. Moreover, since hardness is not an observable, the possibility of its quantum mechanical evaluation is ruled out. Thus there is ample scope of venturing for semi-empirical methods of evaluating global hardness of atoms. These ventures require relying upon the fundamental nature of the hardness again—the holding power of the electron cloud by the chemical species. We [5] developed a semi-empirical algorithm relating hardness with the radius of the atom. We have suggested and evolved an algorithm of evaluating the global hardness of atoms presented below:

$$\eta = a \frac{7.2}{r} + b \quad (\text{in eV}) \qquad (3)$$

where r is the absolute (most probable) radius of atoms in proper unit and a and b are constants.

We have computed the global hardness of 103 elements of the periodic table through the Equation (3) using atomic radii computed by us [27]. Since the absolute of atoms are periodic, the periodic nature of hardness is follows from Equation (3).

We have plotted the atomic hardness values, computed through the Equation (3), as a function of their atomic number in **Figure 2** to demonstrate the periodic behaviour
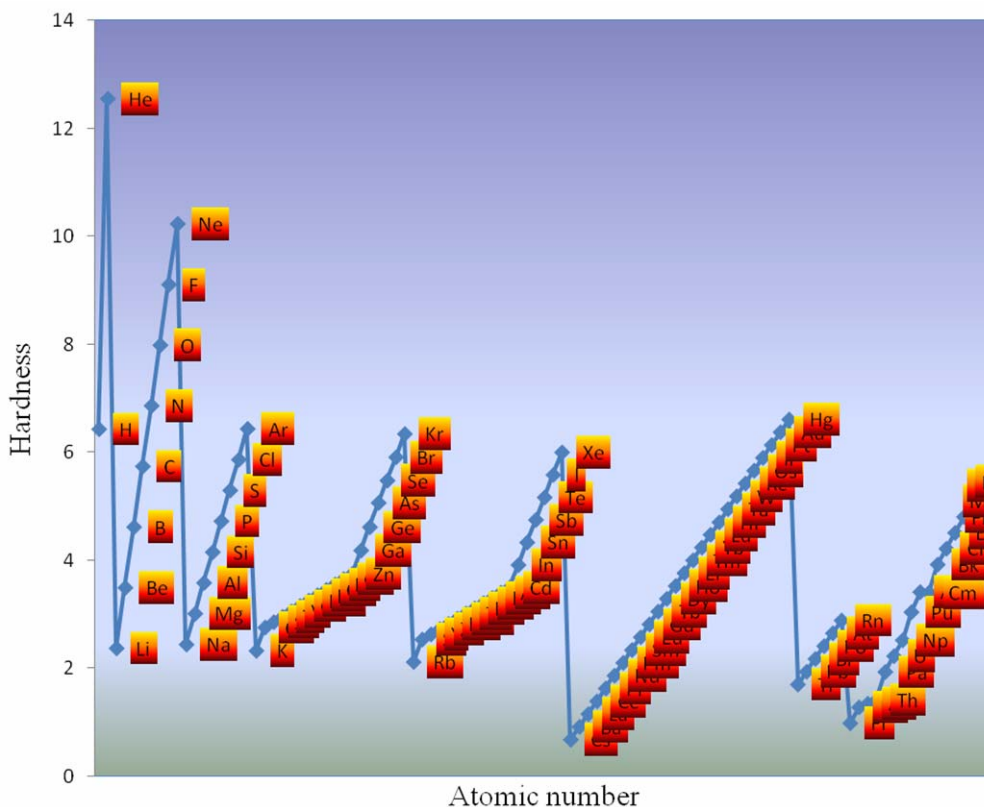

Figure 2. Plot of the hardness (eV) values of 103 elements of the periodic table as a function of their atomic number.

of the atoms of the 103 elements of the periodic table.

4. Rationale of the Formulae of Evaluation of Electronegativity and Hardness and Their Commonalities and Periodicity

We are trying to posit that the electronegativity and the hardness originate and develop from the same fundamental source in the atom. They must have originated from the atomic nucleus. It is fundamentally explored that the electronegativity and the global hardness have two different labels or legends of the same fundamental property of atoms. In a recent work, we [6] found that the algorithms for the evaluation of the electronegativity and the hardness are identical. Now, before discussing the periodicity of electronegativity and hardness we have to establish the relation between these two descriptors with the fundamental property—the effective nuclear charge that determines their magnitudes.

Following Slater's suggestion, the atomic radius is the value of r for which r f(r) has the extrema, Ghosh *et al.* [27,28] calculated the most probable radii (r_{max}) of the atoms of 103 elements of the periodic table using suggestion of Slater that r = r_{max}, using the following Equations

$$r = r_{max} = n/\xi \qquad (4)$$

or

$$r = r_{max} = \frac{n^*}{\xi} \qquad (5)$$

where ξ is the orbital exponent related to the screening constant and to the effective nuclear charge; n^* is effective principal quantum number.

The orbital exponent, ξ is defined as

$$\xi = \frac{Z_{eff}}{n^*} \qquad (6)$$

Hence, putting the value of ξ in Equation (5), we rearranged the formula for computing the most probable radii as

$$r = \frac{n^{*2}}{Z_{eff}} \qquad (7)$$

Now, we can rearrange the formula for computing atomic electronegativity of Ghosh and Chakraborty [3] using the above Equation (7) as follows:

$$\chi = a\frac{Z_{eff}^2}{n^{*2}} + b \qquad (8)$$

or,

$$x \propto Z_{eff}^2 \qquad (9)$$

As a, b and n^* are the constant in a period.

Thus the electronegativity is intimately connected to its originator, the effective nuclear charge.

Again, putting this value in our suggested formula of hardness, Equation (3) above, we can write:

$$\eta = 7.2a\frac{Z_{eff}}{n^{*2}} + b \qquad (10)$$

As a, b and n^* are the constant in a period, from the above Equation (10) we can say that the hardness is proportional to the effective nuclear charge:

$$\eta \propto Z_{eff} \qquad (11)$$

Above Equation (11) clearly shows that the hardness is directly related to the electron attracting power of the nucleus—the effective nuclear charge.

Thus the problem of correlating the periodicity of the electronegativity and the hardness boils down to the fundamental nature of the variation of the effective nuclear charge.

5. The Effective Nuclear Charge—Is It Periodic?

In a multi-electronic species, the electrons don't experience the full positive charge of the nucleus due to the shielding of the inner electrons. The effective nuclear charge is the charge felt by the valence electrons after taken into account the number of shielding electrons that surround the nucleus. It is an empirical parameter, which depends on both the nuclear charge and the number of shielding electrons. The nuclear charge keeps increasing. Meanwhile, the shielding electrons stay constant while we are going across s and p parts of the period, and increase gradually across the d part of the period. Then in the next period, they jump in number. Consequently, the effective nuclear charge drops at that point. Therefore, the effective nuclear charge increases as we go across a period and then drops and starts over again at +1 when we start the next period. Within a period the effective nuclear charge increases as we go across the periodic table. As we go down a group, the increase in the nuclear charge is cancelled out by the increase in shielding electrons and the effective nuclear charge stays pretty much the same. Effective nuclear charge is quite often referred to as the kernel charge. The "kernel" includes the nucleus and all shielding electrons but does not include the valence electrons.

Ghosh and Biswas [28] following Slater [29], have evaluated the screening constant, S and the orbital exponent, ξ, for the topmost electrons of the atoms of the 103 elements of the periodic table. However, there are other sources [30,31,32] we rely upon the work of Ghosh and

Biswas [28] to explore the periodicity of the effective nuclear charge of the atoms.

In **Figure 3** the physical process of screening is depicted.

Figure 4 depicts the periodicity in atomic effective nuclear charge values [28] plotted against the effective atomic number (Z_{eff}) taken from reference (28).

On moving form left hand side to right hand side of any period of the periodic table, charge periodically is added to the outermost orbital, therefore, it can be assumed that attraction of nucleus on the outermost shell is increased periodically as "n" or "n^*" remains constant in a period. As a consequence, Z_{eff} increases monotonically without any exception in a period. Thus the effective nucleus charge of elements must be a periodic property.

In **Figure 5** we made a comparative study of electronegativity and hardness with their originator—the effective nuclear charge.

6. Results and Discussion

Looking on **Figures 1**, **2**, **4** and **5** reveals that in any period the values of electronegativity, hardness and effecttive nuclear charge is the lowest for alkali metal and highest for the noble gas atoms.

As there is repetition of shell structure as one proceeds down ward in the periodic table, a new shell is started after it is completely filled up. Of course, some new orbital appears in lanthanoids and actinoids but it steadily happen that the effective nuclear charge increases monotonically in each period without any exception.

When we look at the whole **Figure 5** at a glance we are convinced that in a period the effected nuclear charge, electronegativity and hardness would increase monotonically to be maximum at the noble gas elements and in the pattern is repeated next period.

7. Conclusions

Thus, we reach to a converging point that the electronegativity and hardness have the same fundamental nature *i.e.*, the electron attracting power although they are applied to different fields for the shake of convenience. Their common property—the electron attracting power and periodicity are controlled by the atomic nucleus creating electrostatic field of attraction. Their origin and development are unequivocally the same and similar. The physical process of screening is a reality but the proper operation and manifestation is mysterious to the common sense. We hope that the puzzle of inter electronic screening can be rationalized by invoking the quantum field theory. Thus, the periodicity of electronegativity and hardness find justification in the periodicity of the electron
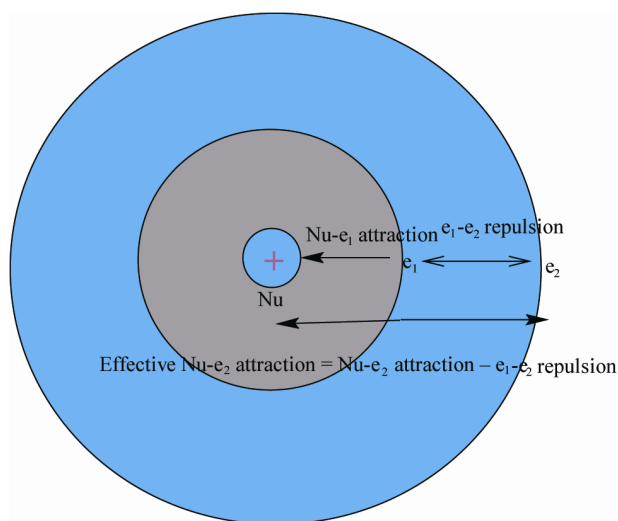

Figure 3. The physical process of screening and the effective nuclear charge.
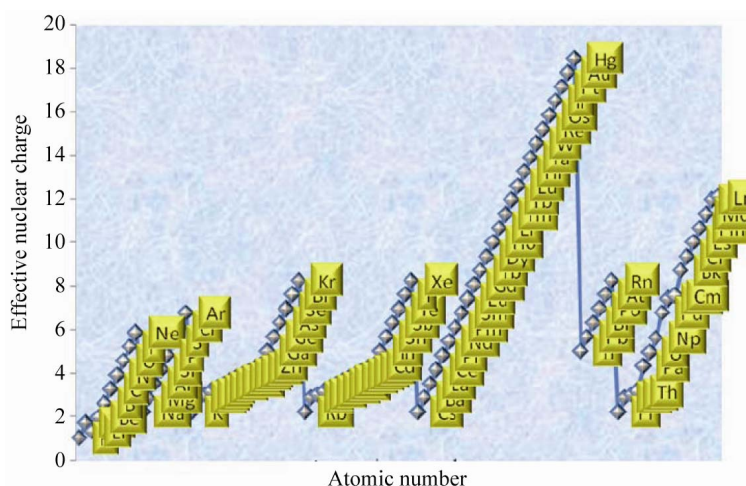

Figure 4. Plot of the effective nuclear charge values of 103 elements of the periodic table as a function of their atomic number.
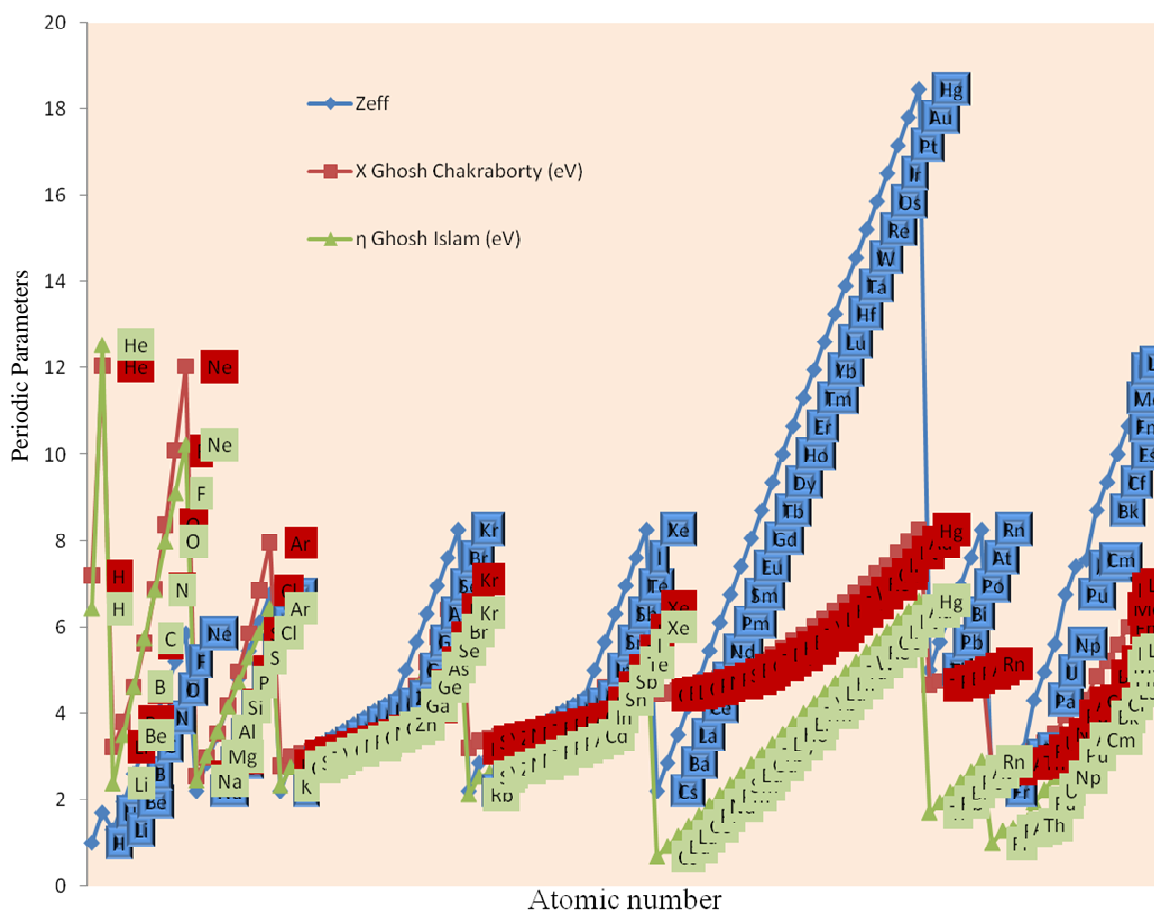
Figure 5. Comparative plot of the effective nuclear charge, electronegativity and hardness values of 103 elements of the periodic table as a function of their atomic number.

attracting power originated from the nuclei of the atoms.

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