

Electronegativity, Hardness and Atomic number: Mutual relationships explored *via* novel isoelectronic series methodology

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ABSTRACT

The novel isoelectronic methodology proposed recently, reveals electronic configuration dependent relationship between the hardness and atomic number, and electronegativity and hardness. In eight out of the first ten isoelectronic series, the hardness measure $(I-A)/2$ is an excellent linear function of atomic number (Z), and the electronegativity measure, $(I+A)/2$ is a quadratic function of the hardness measure; Hence, it is inferred that hardness (η) is proportional to atomic number ($\eta \propto Z$) and electronegativity (χ) is proportional to square of hardness ($\chi \propto \eta^2$). In both the cases, the two inert gas series species are the exceptions where $\eta \propto Z^2$ and $\chi \propto \eta$, respectively. These relationships are slightly in discord with the previously reported mutual connections. Previous reports do not indicate electronic configuration dependency as well. The linear $(I-A)/2$ versus Z plots arises as a result of cancellation of Z^2 terms, and the slopes of these plots are sensitive indicator of the electron spin pairing and orbital change. A potential use of $(I-A)/2$ versus Z , and $(I+A)/2$ versus $(I-A)/2$ plots in pointing the incorrect ionization potentials and their evaluation has been elaborated by the striking example of the sixth ionization potential of phosphorous. The $(I-A)/2$ versus Z relations also provides us a new way to obtain hardness values of cationic and anionic atomic species.

Keywords

Isoelectronic series methodology; hardness; electronegativity; atomic number; electronic configuration.

Academic Discipline And Sub-Disciplines

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1. INTRODUCTION

Electronegativity [1-4] and hardness [5-6] are two very popular and conceptual theoretical constructs of chemistry and physics. Their extended joint or exclusive applications are found in high-temperature superconductors [7-12], nanochemistry [13], semiconductors [14-15] and several other fields. Unlike atomic number, mass, ionization energy or electron affinity they are not physical observables and do not have a quantum mechanical derivation. Their existence is like the unicorns of mythical saga [16] i.e., they exist but never seen. Without these concepts, chemistry and many aspects of condensed matter physics become chaotic and long established unique order in chemico-physical world will be disturbed. They are the gateway and the approximate solution to many problems. Parr et al. have connected them with the noumenon of Kantian philosophy [17]. Putz and his co-workers [18-23] have done significant work on electronegativity and hardness and their usefulness for theoretical prediction of several physicochemical properties-like the fundamentals of chemical bonding.

Prevalent scenario for electronegativity and hardness is based upon density functional theory (DFT). In the DFT [24-25], the electronegativity (χ) and the hardness (η) are the first and second derivative of electronic energy (E) with respect to the number of electrons (N) defined as follows [26-27]:

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_v \quad (1)$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v \quad (2)$$

Where, v is external nuclear potential.

The approximate expression for electronegativity and hardness can be written in terms of ionization potential I , and electron affinity A as [27]:

$$\chi \approx \frac{(I + A)}{2} \quad (3)$$

$$\eta \approx \frac{(I - A)}{2} \quad (4)$$

Eq. (3) and Eq. (4), though approximate, provide reliable trend and measure of electronegativity and chemical hardness, respectively. Eq. (3) is the Mulliken's electronegativity [28] measure as well.

Qualitatively, electronegativity is the electron holding power of the atoms or molecules. The more electronegative elements hold electrons more tightly and the less electronegative elements hold less tightly. Similarly, the hardness signifies the resistance towards the deformation of charge cloud of chemical systems. If the electron-charge cloud is strongly held by the nucleus, the chemical species is "hard" but if the electron cloud is loosely held by the nucleus the system is "soft" [5, 29-30]. This hardness-softness behavior has been correlated with several atomic or molecular parameters. Klopman [29-30] associates Hard-Soft behavior with the HOMO-LUMO gap of the frontier orbital theory. Komorowski [31] and Politzer [32] have identified inverse relationship between hardness and charge capacitance. Ayers [33] invokes interrelationship between the chemical hardness and size, polarizability, charge and electronegativity of the chemical systems. Ghosh et al. [34] have used most probable radii to evaluate hardness. Chattaraj et al. [35] have established a connection between softness ($1/\eta$) and magnetizability. However, in atomic species most of the properties are intern governed by the electron distribution around the nucleus. In fact, it is the binding of the surrounding electrons by the nucleus that is an important controlling factor for most of the properties; they have common origin- the atomic nucleus or the atomic number and the surrounding electrons. So, atomic number has a crucial role to play in determining the properties.

At first sight it appears that electronegativity and hardness have a conceptual and philosophical connection and similarity. They are associated with how strongly the valence electron or the electron cloud is held by the atomic nucleus. Considering these facts, connections and unifications of the two have been suggested and advocated.

Pearson [36] has suggested that for donor atoms, the electronegativity can be taken as a measure of the hardness of the base. Ayer [33], and Putz [37] have opined that the hardness and electronegativity are proportional to each other i.e.

$$\chi \propto \eta \quad (5)$$

Nazmul Islam et al. [38], arguing that the values of A are either very small tending to zero or in most cases are unknown have recently, suggested that

$$\chi = \eta = I \quad (6)$$



Recently, we have suggested a potential use of isoelectronic series to explore relationships [39], as they are the fundamental periodic properties [40] and possess equal number of electrons. There have been several types of studies, involving atomic and molecular isoelectronic species. In relation with atomic isoelectronic series, significant work has been done by Sen and co-workers [41-49]. There have been some works involving electronegativity and hardness as well [50-51]. There has been some work on isoelectronic variation [50-51] of hardness with the nuclear charge as well. However, the nature of those works has entirely been different from the present work. Recently, relationship between electronegativity and atomic number has been explored *via* the isoelectronic series methodology [52] and justified the previously suggested connection [38]. Here, *via* the novel isoelectronic methodology, the mutual relationships between the hardness and fundamental property-atomic number, and between electronegativity and hardness have been investigated, for the first ten isoelectronic series.

2. METHODOLOGY

The novel isoelectronic series methodology is very simple and does not require rigorous computation. It consists of some statistics and is based on the fact that every atomic (neutral or ionic) species is also a part of some isoelectronic series. As the isoelectronic species possess equal number of electrons, the variation in a property is mainly governed by the atomic number and from the isoelectronic trend one can infer about the neutral, cationic or anionic atomic species, provided a smooth trend is there. Therefore, from the isoelectronic trend of the hardness measure, $(I-A)/2$ with atomic number one can infer about the mutual relationship between the hardness and atomic number for neutral atom. Similarly, from the isoelectronic trend of the electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ one can establish connection between the two. Here, I and A need not to be the first ionization potential and electron affinity; one just needs successive ionization potentials that can be depicted as I and A . Moreover, through such approach, one will also come to know about the mutual relationships of $(I+A)/2$, $(I-A)/2$ and atomic number, irrespective of the fact whether $(I+A)/2$ and $(I-A)/2$ serve as the measures of electronegativity and hardness or not.

3. RESULTS

The isoelectronic trend of the hardness measure, $(I-A)/2$ with atomic number, Z (up to $Z=20$), for the first ten isoelectronic series, is presented in Fig.1-3. The Fig. 1 includes **H** ($1s^1$), **Li** ($1s^2 2s^1$), **Be** ($1s^2 2s^2$) and **B** ($1s^2 2s^2 2p^1$) isoelectronic series. The Fig. 2 is for **C** ($1s^2 2s^2 2p^2$), **N** ($1s^2 2s^2 2p^3$), **O** ($1s^2 2s^2 2p^4$), and **F** ($1s^2 2s^2 2p^5$) isoelectronic series. The Fig. 3 is for **He** ($1s^2$) and **Ne** ($1s^2 2s^2 2p^6$) isoelectronic series. The Fig. 1 and Fig. 2 include the plots which are apparently linear, and can be represented by (7)

$$(I+A)/2 = sZ + i \quad (\text{in eV}) \quad (7)$$

The slope (s), intercept (i) and the determination coefficients (r^2) obtained by least square fitting are presented in Table 1.

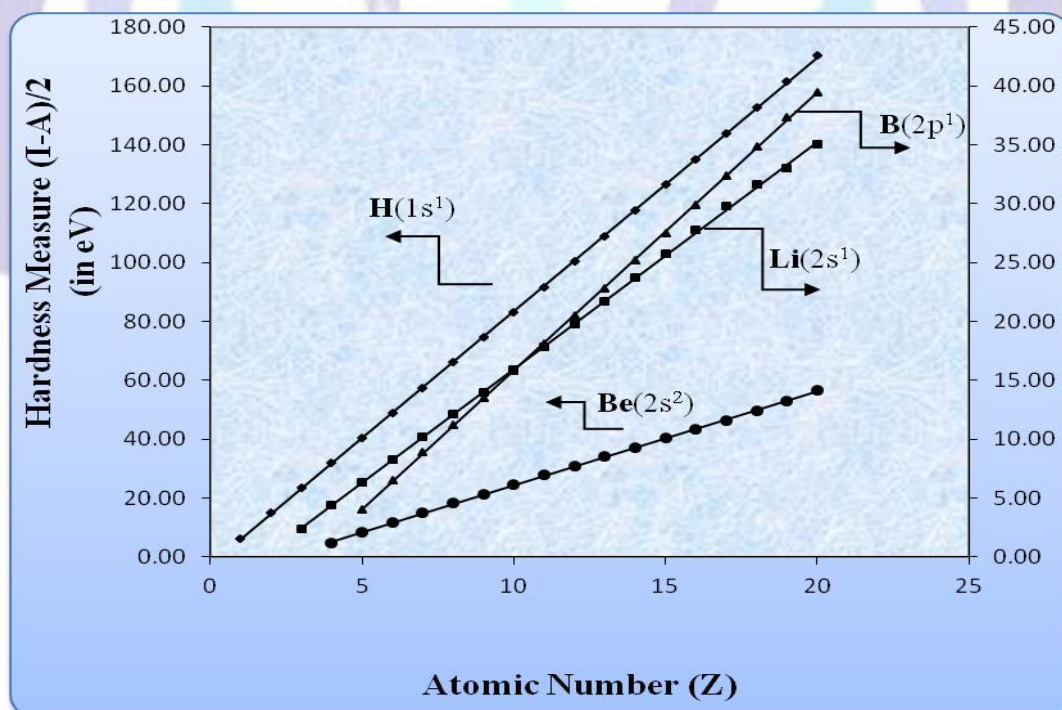


Fig. 1: Isoelectronic trend of the hardness measure, $(I-A)/2$ with atomic number for **H** ($1s^1$), **Li** ($1s^2 2s^1$), **Be** ($1s^2 2s^2$) and **B** ($1s^2 2s^2 2p^1$) isoelectronic series. The solid lines are the least square lines. The $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

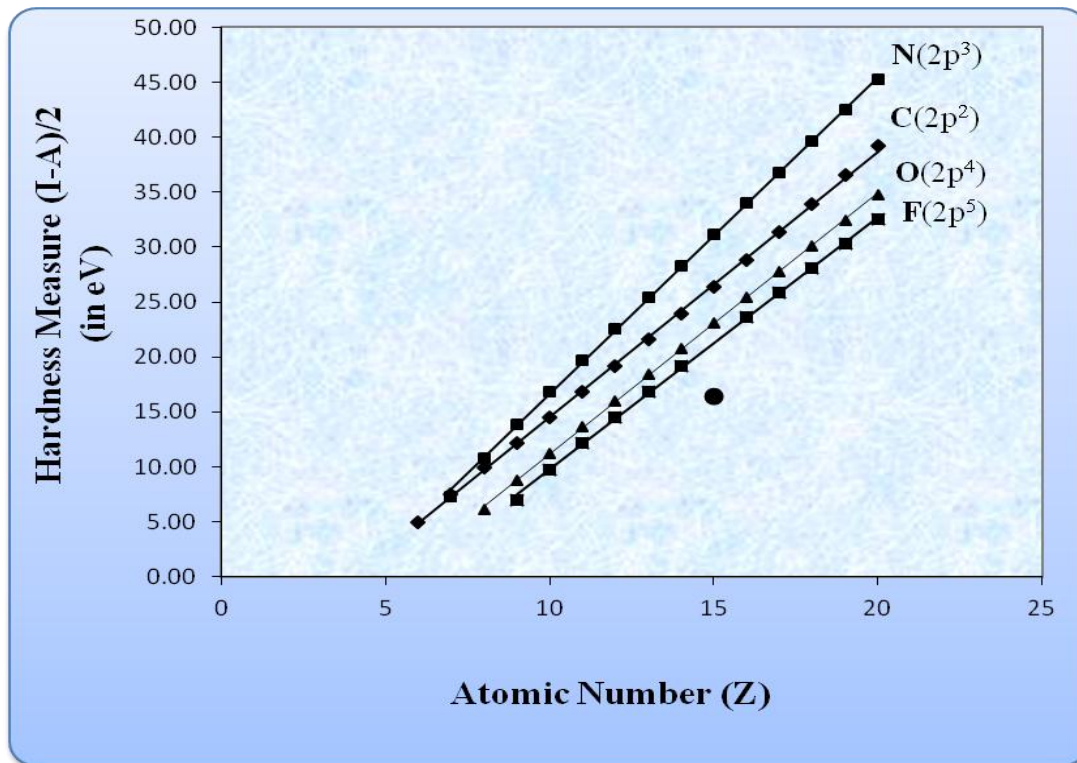


Fig. 2: Isoelectronic trend of the hardness measure, $(I-A)/2$ with atomic number for C ($1s^2 2s^2 2p^2$), N ($1s^2 2s^2 2p^3$), O ($1s^2 2s^2 2p^4$) and F ($1s^2 2s^2 2p^5$) isoelectronic series. The solid lines are the least square lines. The dark point at atomic number 15 just below Fluorine-like isoelectronic series corresponds to sixth I.P. of Phosphorous and not included in the least square fit (see discussion). The $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

Table 1: Slopes (s), Intercepts (i) and determination coefficients (r^2) of the hardness measure vs. atomic number linear isoelectronic trend of Fig. 1-2 and Eq. 7.

Isoelectronic Series	s	i	r^2
H-like($1s^1$)	8.618 ± 0.012	-2.682 ± 0.015	0.9999
Li-like($1s^2 2s^1$)	1.929 ± 0.007	-3.301 ± 0.09	0.9998
Be-like($1s^2 2s^2$)	3.189 ± 0.013	-7.435 ± 0.17	0.9998
B-like($1s^2 2s^2 2p^1$)	2.357 ± 0.006	-7.700 ± 0.08	0.9999
C-like($1s^2 2s^2 2p^2$)	2.419 ± 0.014	-9.630 ± 0.19	0.9996
N-like($1s^2 2s^2 2p^3$)	2.890 ± 0.017	-12.279 ± 0.24	0.9996
O-like($1s^2 2s^2 2p^4$)	2.377 ± 0.009	-12.612 ± 0.13	0.9998
F-like($1s^2 2s^2 2p^5$)	2.300 ± 0.0174	-13.242 ± 0.25	0.9995

* regression analysis carried out by excluding sixth ionization potential of phosphorous(see discussion)

The plots of Fig. 3, which are nonlinear, can be represented by (8)

$$(I-A)/2 = aZ^2 + bZ + C \quad (\text{in eV}) \quad (8)$$

In Table 2 the correlation coefficients a , b and c , obtained by least square fit are listed.

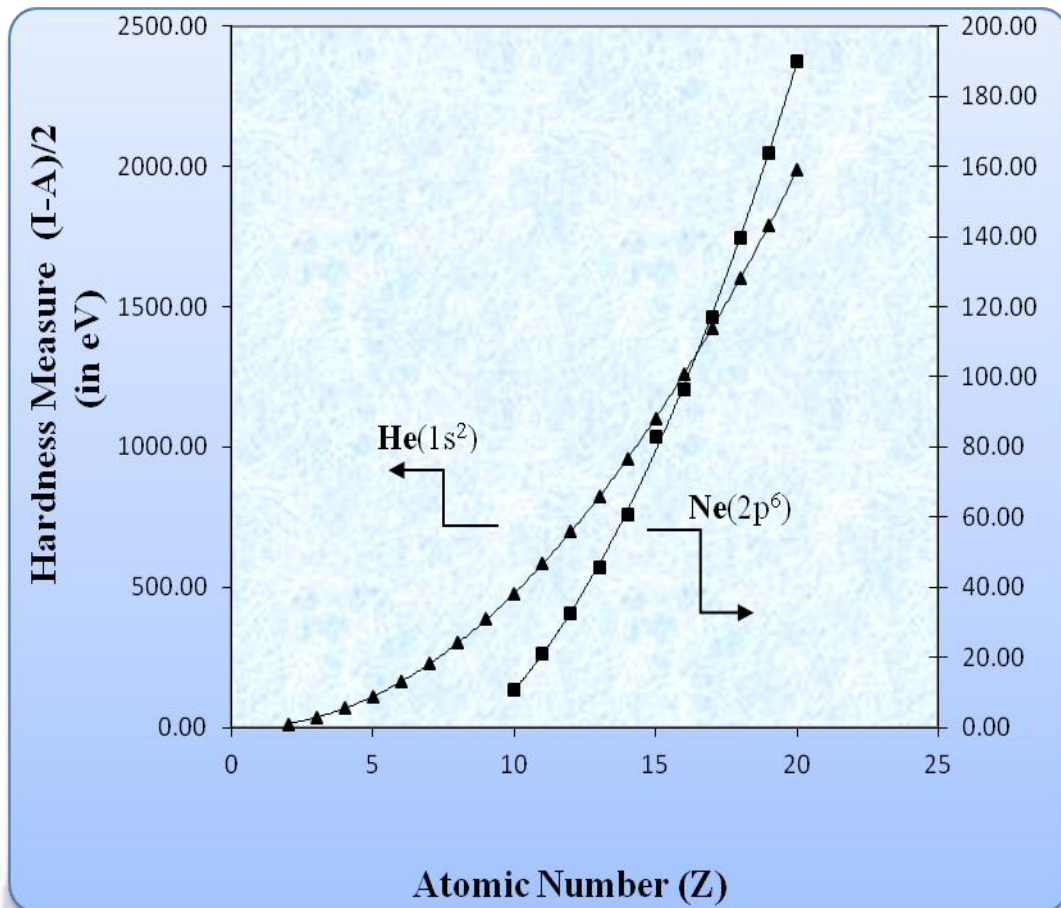


Fig. 3: Isoelectronic trend of the hardness measure, $(I-A)/2$ with atomic number for He ($1s^2$) and Ne ($1s^22s^22p^6$) isoelectronic series (inert gas configuration). The solid curved lines are least square curves. The dark point at atomic number 15, just above Ne series corresponds to sixth ionization potential of phosphorous (see discussion). The $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

Table 2: The coefficient a, b and c of the hardness measure vs. atomic number quadratic isoelectronic trend of Fig. 3 and Eq. 8.

Isoelectronic Series	a	b	C
He-like($1s^2$)	5.114	-3.14	-1.60
Ne-like($1s^22s^22p^6$)	0.85	-7.6	-2.06

The isoelectronic trend of electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ (up to $Z=20$), for the first ten isoelectronic series (H-Ne), is presented in Fig. 4-8. The Fig. 4 includes He($1s^2$) and Ne($1s^22s^22p^6$), Fig. 5 includes H($1s^1$), Fig. 6 includes Li($1s^22s^1$), Be($1s^22s^2$) and C($1s^22s^22p^2$), Fig. 7 includes B($1s^22s^22p^1$), N($1s^22s^22p^3$) and O($1s^22s^22p^4$) and Fig. 8 includes F($1s^22s^22p^5$) isoelectronic series, respectively. The plots of Fig. 4, which are apparently linear, can be represented by (9)

$$(I+A)/2 = s(I-A)/2 + i \quad (\text{in eV}) \quad (9)$$

The slope (s), intercept (i), and the determination coefficients (r^2) of the Fig. 4 plots are presented in Table 3.

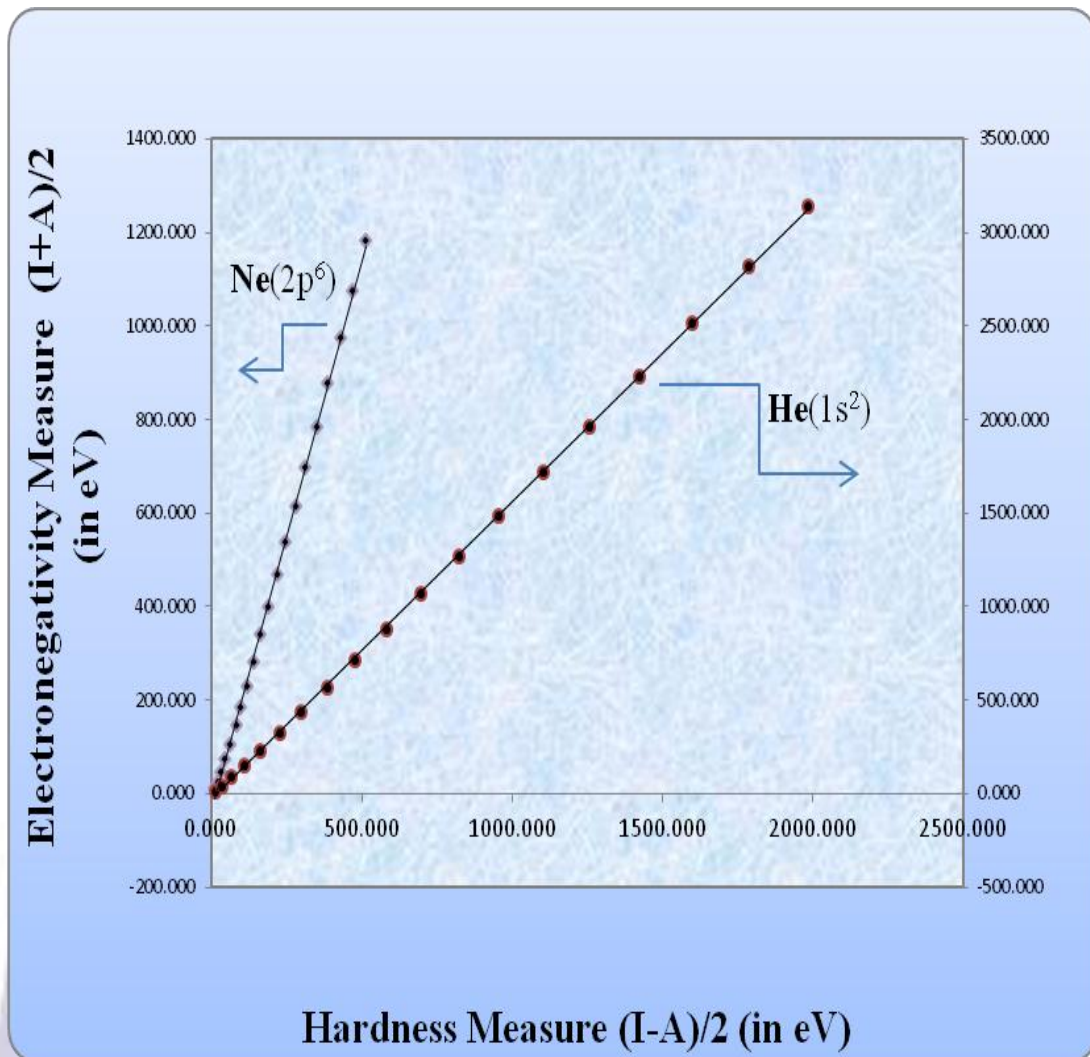


Fig. 4: Isoelectronic trend of the electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ for He ($1s^2$) and Ne ($1s^2 2s^2 2p^6$) isoelectronic series. The solid lines are the least square lines. The $(I+A)/2$ and $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

Table 3: Slopes (s), Intercepts (i) and the determination coefficient (r^2) of the electronegativity measure vs. the hardness measure linear isoelectronic trend of Fig. 4 and Eq. 9.

Isoelectronic Series	s	i	r^2
He-like($1s^2$)	1.590	- 32.32	0.999
Ne-like($1s^2 2s^2 2p^6$)	2.354	- 37.30	0.999

The plots of Fig. 5-8 can be represented by (10)

$$(I+A)/2 = a \{(I-A)/2\}^2 + b(I-A)/2 + C \quad (\text{in eV}) \quad (10)$$

The coefficients a , b and c of the Fig. 5-8 plots are presented in Table 4.

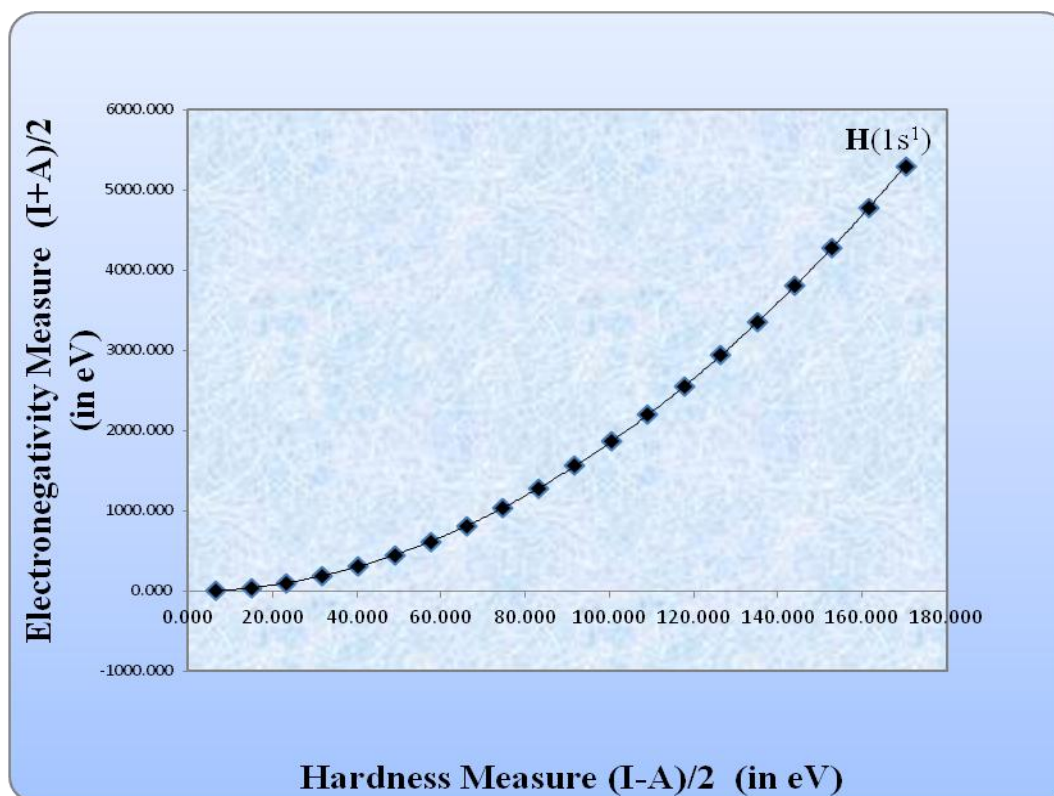


Fig. 5: Isoelectronic trend of the electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ for H ($1s^1$) isoelectronic series. The solid curved lines are the least square curves. The $(I+A)/2$ and $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

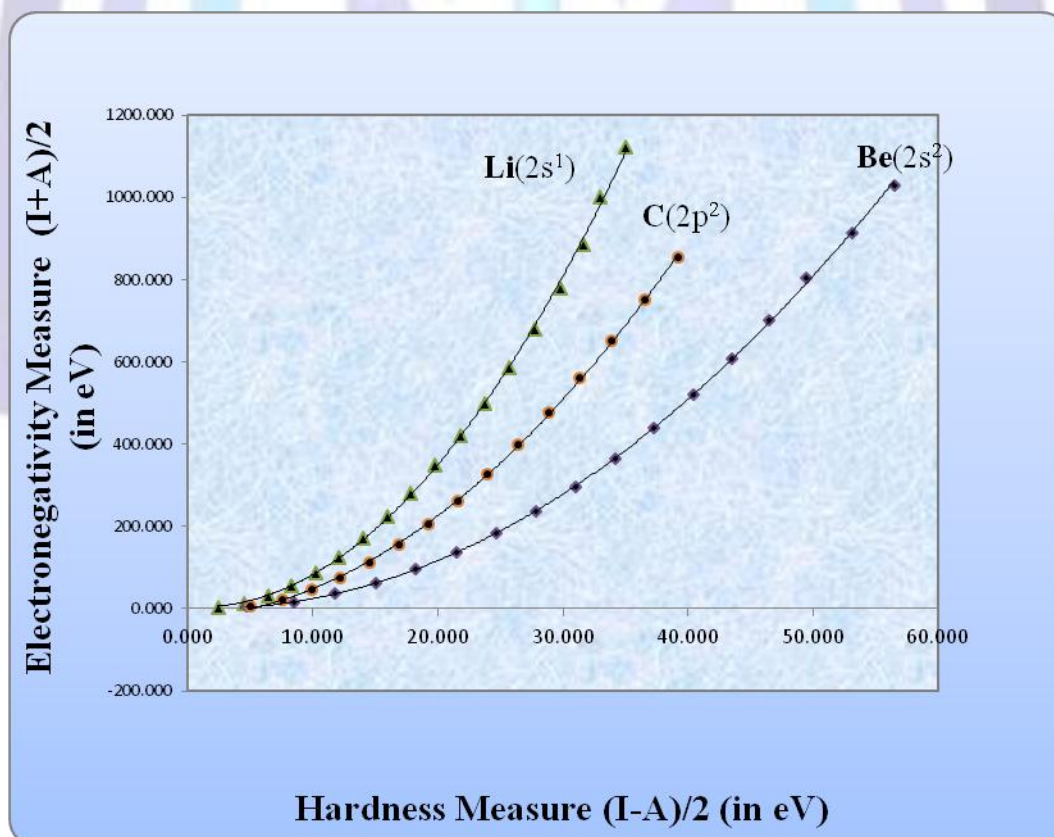


Fig. 6: Isoelectronic trend of the electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ for Li ($1s^2 2s^1$), Be ($1s^2 2s^2$) and C ($1s^2 2s^2 2p^2$) isoelectronic series. The solid curved lines are the least square curves. The $(I+A)/2$ and $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

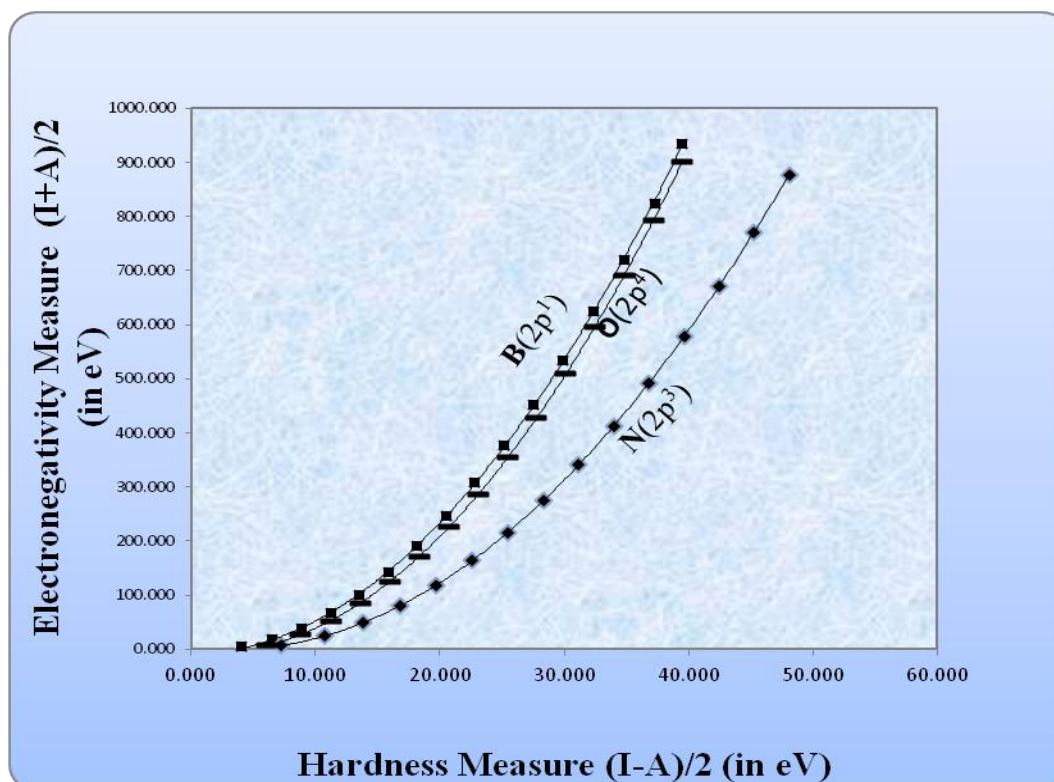


Fig. 7: Isoelectronic trend of the electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ for B ($1s^2 2s^2 2p^1$), N ($1s^2 2s^2 2p^3$) and O ($1s^2 2s^2 2p^4$) isoelectronic series. The solid curved lines are least square curves. The $(I+A)/2$ and $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.

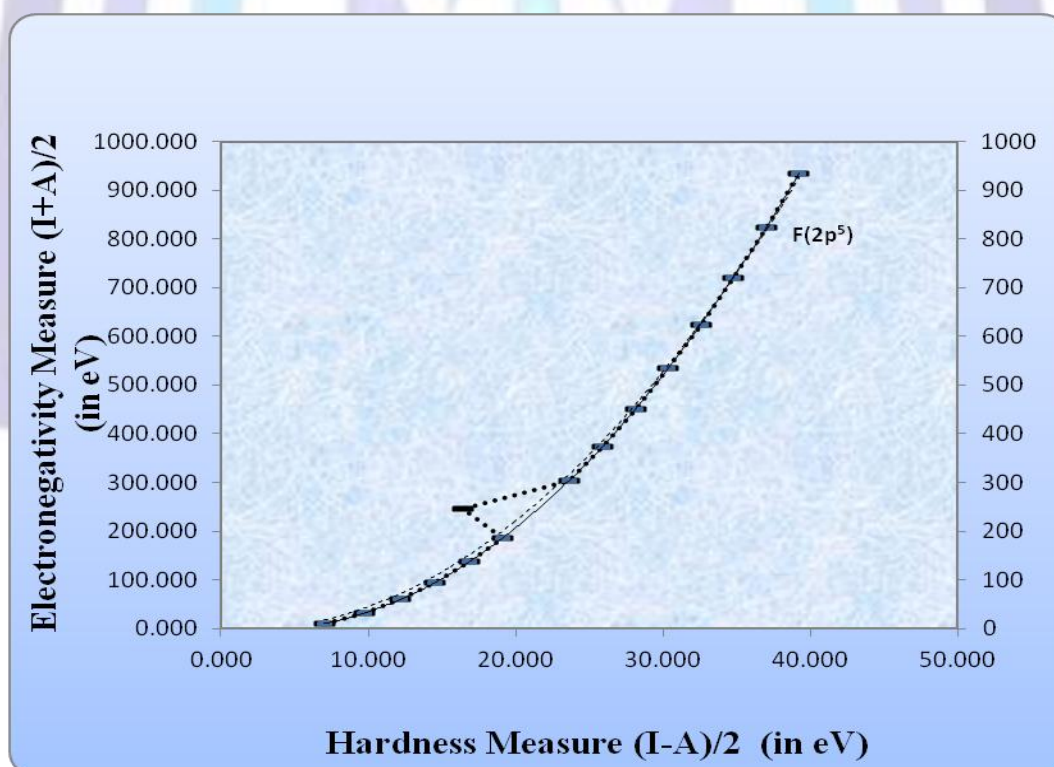


Fig. 8: Isoelectronic trend of the electronegativity measure, $(I+A)/2$ with the hardness measure, $(I-A)/2$ for Fluorine-like ($1s^2 2s^2 2p^5$) isoelectronic series. The abrupt irregularity corresponds to Phosphorous (see discussion). The curved lines through the data correspond to least square fitting. Dash and continuous curved lines are the least square curves including and excluding Phosphorous data, respectively. The abrupt thick dash-mark corresponds to the actual plot. The $(I+A)/2$ and $(I-A)/2$ values obtained using successive ionization potentials given in the reference 53.



Table 4: The coefficients a, b, c and determination coefficient (r^2) of the electronegativity measure vs. the hardness measure quadratic isoelectronic trends of Fig. 5-8 and Eq. 10.

Isoelectronic Series		a	b	c	r^2
H-like($1s^1$)		0.180	+0.567	- 12.71	1
Li-like($1s^2 2s^1$)		0.949	- 1.669	+4.753	0.999
Be-like($1s^2 2s^2$)		0.344	- 1.070	+0.676	0.999
B-like($1s^2 2s^2 2p^1$)		0.601	+0.078	- 8.734	0.999
C-like($1s^2 2s^2 2p^2$)		0.524	+2.013	- 24.03	0.999
N-like($1s^2 2s^2 2p^3$)		0.435	- 2.764	+ 3.824	1
O-like($1s^2 2s^2 2p^4$)		0.628	- 1.894	- 5.279	1
F-like ($1s^2 2s^2 2p^5$) [*]	Set 1	0.651	- 1.901	- 1.357	0.990
	Set 2	0.708	-4.015	3.519	1

* Two sets of coefficients a, b and c, provided for Fluorine-like isoelectronic series. This is due to an abrupt irregularity in the curve (Fig. 8). The irregularity corresponds to atomic number 15 i.e Phosphorous value (6th ionization potential). Set 1 and 2 are including and excluding Phosphorous data, respectively. Set 2 is more appropriate. Change in the determination coefficient of the two sets to be noted.

In Table 5, the $(I+A)/2$ and $(I-A)/2$ values used in drawing plots of Fig. 1-8, and calculating the slopes, intercepts, coefficients of Table 1-4 are presented. All the successive ionization potential used to obtain $(I+A)/2$ and $(I-A)/2$ values are taken from the single reference source [53].

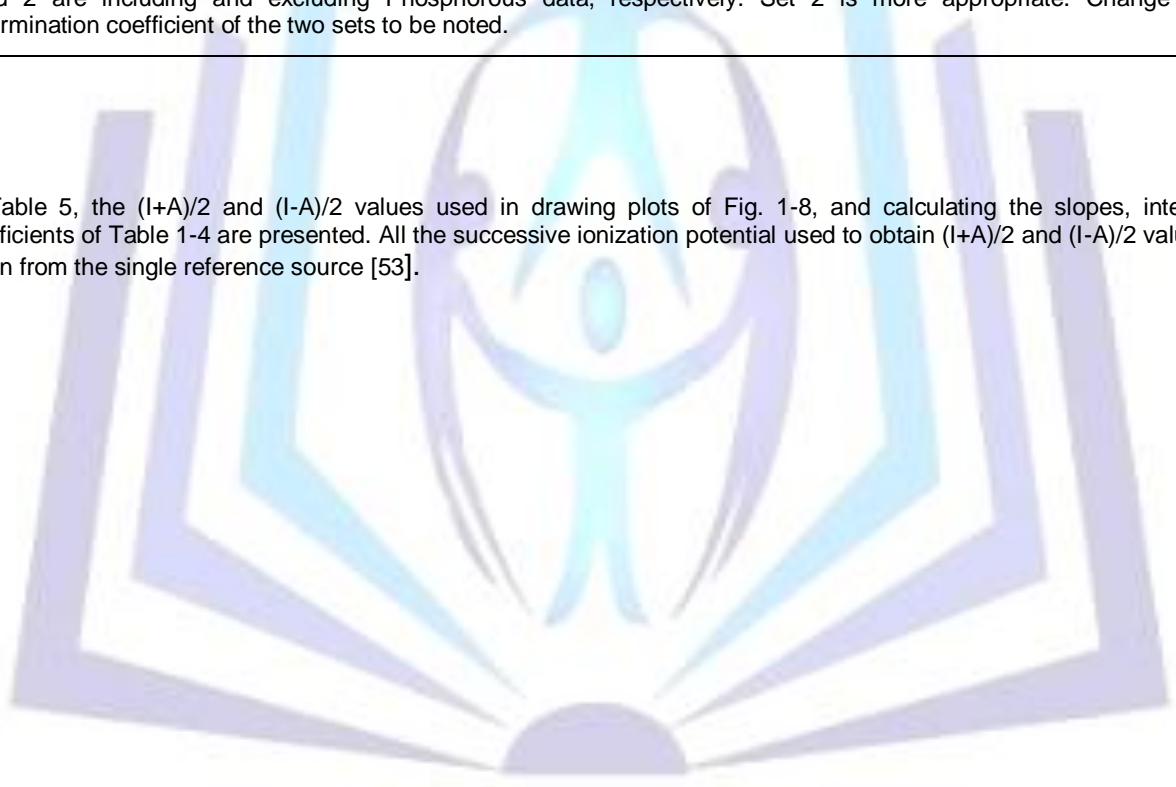




Table 5: The values $(I+A)/2$ and $(I-A)/2$ used in isoelectronic plots of Fig. 1-8 and calculating the slope, intercept and the coefficients of table 1-4. All the successive ionization potentials are from reference [53] and are in electron volts.

S.N.	At. No.	Isoelectronic Series									
		$(1s^1)$		$(1s^2)$		$(1s^2 2s^1)$		$(1s^2 2s^2)$		$(1s^2 2s^2 2p^1)$	
		$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$
1	1	6.4219	7.1761								
2	2	14.9145	39.5015	12.2935	12.2935						
3	3	23.4065	99.0445	35.123	40.515	2.387	3.005				
4	4	31.91	185.803	67.841	86.052	4.4445	13.7665	4.661	4.661		
5	5	40.4245	299.793	110.719	148.649	6.388	31.542	8.428	16.726	4.0105	4.2875
6	6	48.952	441.029	163.793	228.2845	8.3025	56.1895	11.752	36.135	6.5615	17.8215
7	7	57.486	609.543	227.085	324.9725	10.208	87.68	15.012	62.46	8.9235	38.5245
8	8	66.036	805.351	300.6	438.7155	12.11	126.006	18.244	95.654	11.239	66.173
9	9	74.6015	1028.49	384.352	569.534	14.0105	171.172	21.4605	135.701	13.551	100.686
10	10	83.1835	1278.98	478.354	717.4435	15.91	223.18	24.67	182.6	15.86	142.07
11	11	91.784	1556.88	582.611	882.4805	17.845	282.025	27.855	236.325	18.16	190.31
12	12	100.406	1862.21	697.136	1064.1264	19.79	347.74	31.025	296.925	20.48	245.42
13	13	109.049	2195.03	821.957	1264.0277	21.75	420.32	34.18	364.39	22.81	307.4
14	14	117.716	2555.39	957.088	1480.588	23.72	499.78	37.315	438.745	25.165	376.265
15	15	126.41	2943.35	1102.55	1714.397	25.72	586.78	40.42	519.99	27.535	452.035
16	16	135.132	3358.97	1258.35	1965.488	27.755	679.385	43.49	608.14	29.935	534.715
17	17	143.884	3802.31	1424.52	2233.908	29.825	779.565	46.525	703.215	32.36	624.33
18	18	152.668	4237.45	1601.39	2519.389	31.625	886.375	49.51	805.24	34.82	720.91
19	19	161.488	4772.44	1788.48	2822.478	33	1001	53.115	914.885	37.32	824.45
20	20	170.347	5299.39	1986.02	3144.023	35	1122	56.5	1030.5	39.44	934.56

S.N.	At. No.	Isoelectronic Series									
		$(1s^2 2s^2 2p^2)$		$(1s^2 2s^2 2p^3)$		$(1s^2 2s^2 2p^4)$		$(1s^2 2s^2 2p^5)$		$(1s^2 2s^2 2p^6)$	
		$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$	$(I-A)/2$	$(I+A)/2$
1	6	4.99855	6.26145								
2	7	7.5335	22.0675	7.267	7.267						
3	8	9.909	45.025	10.749	24.367	6.078445	7.539555				
4	9	12.2155	74.9225	13.8685	48.8385	8.774	26.196	7.010405	10.4116		
5	10	14.55	111.66	16.83	80.28	11.244	52.206	9.699	31.263	10.782	10.782
6	11	16.88	155.27	19.74	118.65	13.635	85.275	12.177	59.463	21.0735	26.2125
7	12	19.22	205.72	22.62	163.88	16.01	125.25	14.5485	94.6915	32.554	47.589
8	13	21.58	263.01	25.48	215.95	18.38	172.09	16.86	136.85	45.7715	74.2185
9	14	23.965	327.135	28.325	274.845	20.735	225.785	19.14	185.91	60.8145	105.9555
10	15	26.385	398.115	31.16	340.57	23.095	286.315	16.395	246.825	82.7035	147.7265
11	16	28.845	475.935	33.995	413.095	25.435	353.665	23.65	304.58	96.4405	184.4895
12	17	31.355	560.615	36.82	492.44	27.785	427.835	25.885	374.165	117.0435	231.2365
13	18	33.925	652.165	39.645	578.595	30.135	508.815	28.12	450.56	139.492	282.948
14	19	36.555	750.575	42.465	671.555	32.48	596.61	30.345	533.785	163.813	339.627
15	20	39.255	855.865	45.29	771.32	34.82	691.21	32.57	623.82	189.99	401.26



4. DISCUSSION

4.1 Hardness versus Atomic number

For the first time, a relationship between hardness and fundamental property-atomic number has been approached via novel isoelectronic series methodology. The methodology is very simple and involves some statistics, and does not require rigorous computation.

It can be seen that the plots of Fig. 1 and Fig. 2, which include **H** ($1s^1$), **Li** ($1s^2 2s^1$), **Be** ($1s^2 2s^2$), **B** ($1s^2 2s^2 2p^1$), **C** ($1s^2 2s^2 2p^2$), **N** ($1s^2 2s^2 2p^3$), **O** ($1s^2 2s^2 2p^4$) and **F** ($1s^2 2s^2 2p^5$) like non-inert gas configuration isoelectronic series, exhibit linear relationship. It reveals from the determination coefficients, listed in Table 1, that the plots are excellently linear. The plots of Fig. 3 which include **He** and **Ne** inert gas configuration ($1s^2$ and $1s^2 2s^2 2p^6$ respectively) isoelectronic series are nonlinear. Within the purview of the present study, eight out of the first ten isoelectronic series exhibit excellent linear variation, while the other two isoelectronic series with inert gas configuration have nonlinear relationship. The exact expression of the linear variation is Eq. (7) expressed through Table 1. Therefore, it is clear that as neutral atom is also a part of the isoelectronic series, for Hydrogen, Lithium, Beryllium, Boron, Carbon, Nitrogen, Oxygen and Fluorine atoms, the hardness is a linear function of Z and might be considered as proportional to Z ($\eta \propto Z$). Similarly, in the other two cases i.e. Helium and Neon the hardness is a quadratic function of atomic number and might be considered as proportional to square of atomic number ($\eta \propto Z^2$). *The study unfolds a significant fact that the nature of relationship between the hardness and atomic number depends on the isoelectronic series to which the neutral atom belongs. The findings are in discord with the suggestion made by Islam et al [38], who have sketched direct proportionality between hardness and effective nuclear charge without making any distinction regarding electronic configuration of the species.* Here, it is being opined that for inert gas configuration species the hardness is proportional to Z^2 and not Z .

A potential use of the $(I-A)/2$ versus Z plots (and relations), irrespective of the fact whether $(I-A)/2$ serves as the hardness measure or not, should be pointed out. These plots can be used to predict the accuracy or the evaluation of the much needed ionization potentials. As $(I-A)/2$ two successive ionization potentials are being compared, and the $(I-A)/2$ values are generally expected to be lower than I or A values (though not always). Therefore, if there is any ambiguity in reported or listed I or A value, it will reflect as a significant deviation in $(I-A)/2$ versus Z plots. In fact, any single anomaly of I or A value will be seen as deviation in plots of two different isoelectronic series, and these two deviations will be opposite in sense. A striking example is 6th ionization potential of Phosphorous (atomic number 15).

In $(I-A)/2$ versus Z plot of Fig. 2, a large deviation is observed at atomic number 15 in Fluorine ($1s^2 2s^2 2p^5$) isoelectronic series (below the straight line). A close look of Fig. 3, reveals that in Neon ($1s^2 2s^2 2p^6$) isoelectronic series also, there is one deviation at atomic No.15 (above the curve). Obviously, this deviation is opposite in nature to the Fluorine isoelectronic series. These two deviations are sufficiently unique, to make us question the reliability of the listed reference [53] value of 6th ionization potential of Phosphorous (atomic No. 15). Considering these two deviations we estimate a value around 220.7 eV, and assuming a printing error suggest a value 220.43 eV for the 6th ionization potential of phosphorous, in place of listed reference [53] value of 230.43 eV. Our estimated and suggested value agrees well with the value 21267 J/mol = 220.417 eV listed elsewhere [54]. This signifies the potential use of $(I-A)/2$ versus Z plots and relations in pointing incorrect (reported or listed) ionization potentials and their evaluation as well. For the same reason, phosphorous has not been included while performing least square fit (captions Table-1, and Fig. 2-3).

The $(I-A)/2$ versus atomic number plots provide us a new way for the evaluation of hardness values of anionic or cationic atomic species, if $(I-A)/2$ is considered as the hardness measure. For example, the hardness of hydrogen neutral atom is governed as per the $1s^1$ isoelectronic series (Eq.7 Table 1). However, for H^- and H^+ anions the hardness will be governed as per the $1s^2$ and $2s^1$ isoelectronic series (Eq. 8 and Table 2 ; Eq. 7 and Table 1) respectively, as these are part of these series now. One can estimate the hardness by substituting atomic number in the corresponding equations along with the coefficients, slopes intercepts etc. For example the hardness value for H^- anion would be 0.374 (Eq. 8 and Table 2). In the same way, the hardness for other anions or cations can be calculated. A negative hardness value may indicate non-existence of the species.

Within the purview of nonlinear quadratic variation of the electronegativity measure with atomic number [52], the present variation of the hardness measure with atomic number can be ascribed to mutual cancellation of Z^2 terms. Unlike non-inert gas configuration species, the cancellation of Z^2 terms is not possible in inert gas configuration series species as the electron addition and removal involves different shells. For example, in **He** series the electron is removed from the $1s$ orbital, while the electron is added in $2s$ orbital. Similarly, in **Ne** series electron is removed from the $2p$ orbital but the electron is added in $3p$ orbital. Slopes of the linear isoelectronic trends appear to be very sensitive indicator of electron spin pairing and orbital change. Unusual slopes of Li-like ($1s^2 2s^1$), Be-like ($1s^2 2s^2$) and N-like ($1s^2 2s^2 2p^3$) isoelectronic series can be explained on these grounds. Excluding hydrogen which involve different shell, others series have slopes between 2.3 to 2.42.

4.2 Electronegativity versus Hardness

For the first time, the novel isoelectronic series methodology has been used to explore nature of relationship between $(I+A)/2$ and $(I-A)/2$, the DFT measures of electronegativity and hardness, respectively. It is to be noted that the $(I+A)/2$ vs. $(I-A)/2$ plots of Fig. 4, which are for **He** and **Ne** like isoelectronic series, are linear. From the value of the determination coefficient (r^2) listed in Table 3, which are nearly one, it is evident that the plots are remarkably linear. It is worth mentioning that these plots or lines belong to the isoelectronic series which have inert gas configurations viz. $1s^2$ and $1s^2 2s^2 2p^6$, respectively. It can be seen that the plots of Fig. 5-8, which includes **H**, **Li**, **Be**, **B**, **C**, **N**, **O** and **F** like non-inert



gas configuration isoelectronic series exhibit nonlinear relationship. From the determination coefficient listed in Table 4, it is clear that there is high degree of correlation among the $(I+A)/2$ and $(I-A)/2$ data. Fig. 5-8 further justifies this finding; the curves are smooth and data are reasonably un-scattered, except one abrupt irregularity in Fig. 8.

Within the purview of present study, eight out of the first ten isoelectronic series exhibit nonlinear relation of $(I+A)/2$ with $(I-A)/2$, while the other two with inert gas configuration, show linear relationship. The exact nature of these variation is represented by Eq. (9) and Eq. (10), expressed through slopes, intercepts and coefficients listed in Table 3 and Table 4. On this basis, for neutral atomic species belonging to **H, Li, Be, B, C, N, O** and **F** like isoelectronic series *viz.* Hydrogen, Lithium, Beryllium, Boron, Carbon, Nitrogen, Oxygen and Fluorine atoms respectively, the electronegativity $(I+A)/2$ is a quadratic function of the hardness, $(I-A)/2$, and electronegativity might be considered as proportional to square of hardness ($\chi \propto \eta^2$). In the other two cases *viz.* the neutral atomic species belonging to **He** and **Ne** like isoelectronic series, the electronegativity, $(I+A)/2$ is a linear function of the hardness, $(I-A)/2$, and electronegativity might be considered as proportional to hardness ($\chi \propto \eta$). Within the purview, the study unveils a significant fact that if $(I+A)/2$ and $(I-A)/2$ are the electronegativity and hardness measures respectively, the mutual relation between electronegativity and hardness would depend on the electronic configuration of the neutral species. Moreover, in most of the cases the electronegativity might be considered as proportional to square of the hardness measure. Furthermore, the previously suggested connection(s) between electronegativity and hardness has been of the proportionality type. Here, proportionality between electronegativity and square of the hardness is inferred and suggested; barring the species with inert gas configuration(s) where, direct proportionality between electronegativity and hardness is being suggested. *This is in discord with the suggestion made by Ayer [32], and Putz and co-workers [37] that electronegativity and hardness are proportional to each other. Philosophically, electronegativity and hardness might be having same origin- the screened nuclear charge [38], their mathematical relation will depend on the electronic configuration of the species.* Hence it is being opined here that in most of the cases the electronegativity is proportional to square of hardness rather than the hardness.

The $(I+A)/2$ versus $(I-A)/2$ plots can be very useful in pointing the accuracy of ionization potentials. These plots can also be used to extrapolate and evaluate $(I+A)/2$ or $(I-A)/2$ values. An abrupt irregularity is observed in Fig. 8. This irregularity, which corresponds to Phosphorous, is sufficiently unique to make us question the reliability of $(I+A)/2$ and $(I-A)/2$ data obtained using listed ionization potentials [53]. This inconsistency might be associated with either **I**, or **A**, or both. Here, the irregularity can be accounted to the sixth ionization potential of phosphorous, as discussed in hardness vs. atomic number section.

Electronegativity and hardness are the gateway or the approximate solution to many problems and the novel isoelectronic series methodology provides a simpler strategic tool to deal with them rather than any rigorous computation.

CONCLUSION

A potential use of isoelectronic series in exploring relationships has been suggested. The novel isoelectronic series methodology is very simple and does not involve any rigorous computation. It requires some statistics and is based on the fact that every atomic species is also a part of some isoelectronic series and from the isoelectronic trend one can infer about the relationship.

The novel isoelectronic methodology reveals electronic configuration dependent relationship between the hardness and atomic number, and electronegativity and hardness. In majority of the cases, the hardness measure $(I-A)/2$ is a linear function of atomic number and the hardness might be considered as proportional to it ($\eta \propto Z$). Similarly, in majority of the cases, the electronegativity measure $(I+A)/2$ is a quadratic function of the hardness measure, $(I-A)/2$ and electronegativity might be considered as proportional to square of the hardness ($\chi \propto \eta^2$). In both the cases, the inert gas series species are the exceptions where, hardness and electronegativity might be considered as proportional to square of atomic number ($\eta \propto Z^2$) and proportional to hardness ($\chi \propto \eta$), respectively.

The $(I-A)/2$ vs. Z plots, irrespective of the fact whether $(I-A)/2$ serves as a measure of hardness or not, can be a very powerful tool in pointing the accuracy and evaluation of much needed ionization potentials. A striking example is **VI** ionization potential of phosphorous where a value 220.43eV in place of listed 230.43eV value⁵³ is being suggested and this value agrees well with the value listed elsewhere. It is suggested that the linear $(I-A)/2$ vs. Z variations arise as a result of cancellation of Z^2 terms. Due to involvement of different shells, the mutual cancellation of Z^2 terms is not possible in the inert gas configuration isoelectronic series resulting in the nonlinear plots. Slopes of the linear isoelectronic trends appear to be very sensitive indicator of electron spin pairing and orbital changes. The $(I-A)/2$ and atomic number relationships can also be potentially used to obtain hardness values of cationic and anionic atomic species.

Like the $(I-A)/2$ vs. Z plots, $(I+A)/2$ vs. $(I-A)/2$ plots can also be used in pointing the incorrect **I** or **A** values. Again, the data corresponding with phosphorous has been put under question and it can be associated with the **VI** ionization potential.

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