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ELECTRONEGATIVITY: CORRELATION WITH ATOMIC NUMBER IN ISOELECTRONIC SERIES

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ABSTRACT

Mulliken's electronegativity measure, (I + A)/2, where I and A represent successive ionization potentials and electron affinity values, are correlated with atomic number Z in isoelectronic series. The isoelectronic series for which the correlations have been established are from $1s^1$ to $1s^2 2s^2 2p^6$ up to atomic number 20. A nonlinear variation is observed for all the ten series. These variations can satisfactorily be explained by an equation in the form $(I + A)/2 = \mathbf{a}Z^2 + \mathbf{b}Z + \mathbf{c}$. Finally, the coefficients a, b, and c are presented in tabulated form for all the ten isoelectronic series.

Key words: Electronegativity, Isoelectronic series, Atomic number.

INTRODUCTION

Originally defined by Pauling[1-2] as "the power of an atom in a molecule to attract electrons to itself," the concept of electronegativity has gained considerable interest and popularity. Besides chemistry it has also been used in physics, geology and biology. Its applications are also found in superconductors[3-6], photosensitive electrode properties[7], and nanochemistry[8] and several other areas of significant interest.

Electronegativity has been correlated with a variety of measurable atomic and molecular properties and several measures of electronegativity have been proposed. Pauling[1,2] scale, Mulliken[9,10] scale, Allred[11] scale, Gordy[12-15] scales are some of the pioneering and important measures of electronegativity. Among these special attention has been drawn for the Mulliken electronegativity. Coulson[16] has expressed the opinion that Mulliken's measure of electronegativity is better and more precise than that of Pauling. Further, a landmark contribution in favour of Mulliken electronegativity was provided by

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Iczkowski and Margrave[17]. They have established that the slope of E vs N curve, where E and N are total energy and number of electrons respectively, equals the average of ionization potential, I, and electron affinity, A, ie. (I + A)/2. The present scenario for electronegativity is based upon density–theories of many electron system. In the density functional theory (DFT) electronegativity (χ) is considered as negative of chemical potential ($-\mu$) and is defined as

$$\chi = -\mu = -(dE/dN) \approx (I+A)/2 = \chi_M$$

because of this fundamental relation, Mulliken electronegativity, χ_M, may reasonably be called the absolute electronegativity.

In this communication, we have correlated the Mulliken electronegativity measure, (I + A)/2, with the atomic number, Z. This has been done through systematic study of (I + A)/2 with atomic number in isoelectronic series.

Theoretical background

Isoelectronic series provide a very handy and versatile tool for the systematic study of a property. Isoelctronic species possess equal number of electrons, therefore, the variation in any property is mainly due to the atomic number of the species. Mulliken electronegativity measure, (I+A)/2, possess term due to ionization potential or electronaffinity, these two are likely to increase as the atomic numbers increase. Therefore, a positive relation is expected between two.

RESULTS AND DISCUSSION

We have explored the correlation of the Mulliken electronegativity measure, (I + A)/2 with the atomic number, Z. however, here A represents electronaffinity for a neutral species while for an ionic species it is the successive ionization potential. The results are presented in Figs. 1-3. It can be seen that for all the ten series a nonlinear relationship exists. They can be represented by (1).

$$(I + A)/2\ (ev) = \mathbf{a}Z^2 + \mathbf{b}Z + \mathbf{c} \qquad \ldots(1)$$

In Table 1 the coefficients a, b, and c are listed for the curves drawn through the data of Figs. 1-3.

Table 1: Coefficients a, b and c for the correlations of (I + A)/2 with atomic number Z (See Eq. 1)

Isoelectronic series	a	b	c
$1s^1$	13.725 ± 0.009	-9.910 ± 0.190	5.203 ± 0.867
$1s^2$	8.563 ± 0.004	-14.649 ± 0.074	7.612 ± 0.312
$1s^22s^1$	3.483 ± 0.002	-13.288 ± 0.055	12.082 ± 0.280
$1s^22s^2$	3.447 ± 0.003	-18.629 ± 0.063	23.949 ± 0.344
$1s^22s^22p^1$	3.447 ± 0.001	-24.141 ± 0.031	38.722 ± 0.178
$1s^22s^22p^2$	3.429 ± 0.001	-28.445 ± 0.037	53.280 ± 0.221
$1s^22s^22p^3$	3.425 ± 0.004	-33.636 ± 0.112	74.456 ± 0.711
$1s^22s^22p^4$	3.432 ± 0.005	-39.061 ± 0.145	99.934 ± 0.970
$1s^22s^22p^5$	3.397 ± 0.043	-42.673 ± 1.244	118.445 ± 8.684
$1s^22s^22p^6$	2.484 ± 0.046	-35.032 ± 1.386	112.883 ± 10.083

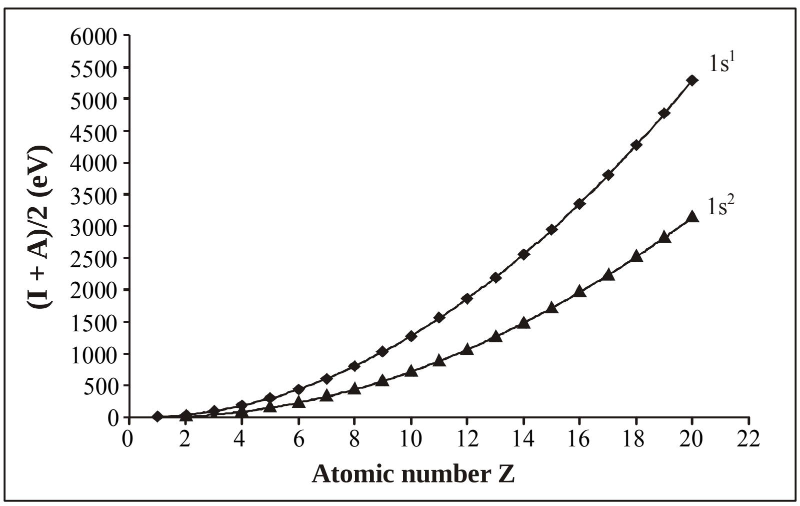

Fig. 1: Relation between Z and (I + A)/2 for $1s^1$ and $1s^2$ series

Perhaps for the first time a relationship has been approached between Mulliken electronegativity measure and atomic number. For this, inherent characteristics of isoelectronic series have been used as a new approach. Isoelectronic series may be treated just like a fundamental property. A close look of the Figs. 1-3 reveals that a positive, nonlinear relationship exists between (I + A)/2 and Z. Very smooth nature of the curves

(Figs. 1-3) is quite appealing. Therefore, these curves can reasonably be used to check and evaluate (I + A)/2 values. (I + A)/2 can also be extrapolated for higher atomic numbers.

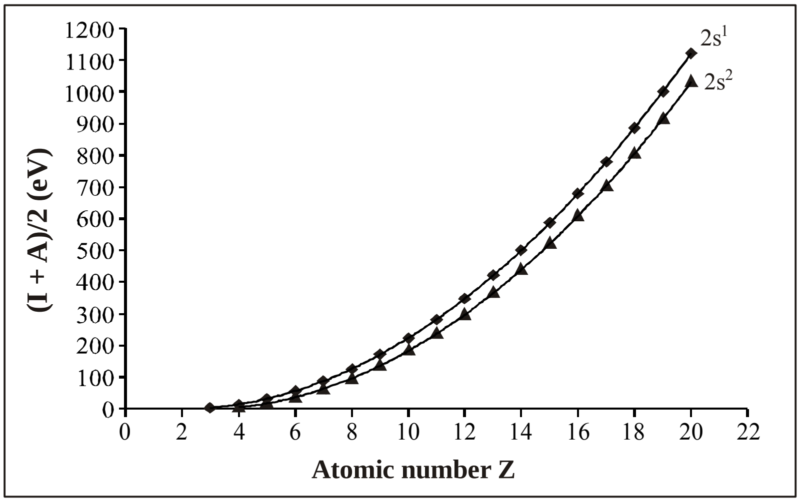

Fig. 2: Relation between Z and (I + A)/2 for $2s^1$ and $2s^2$ series

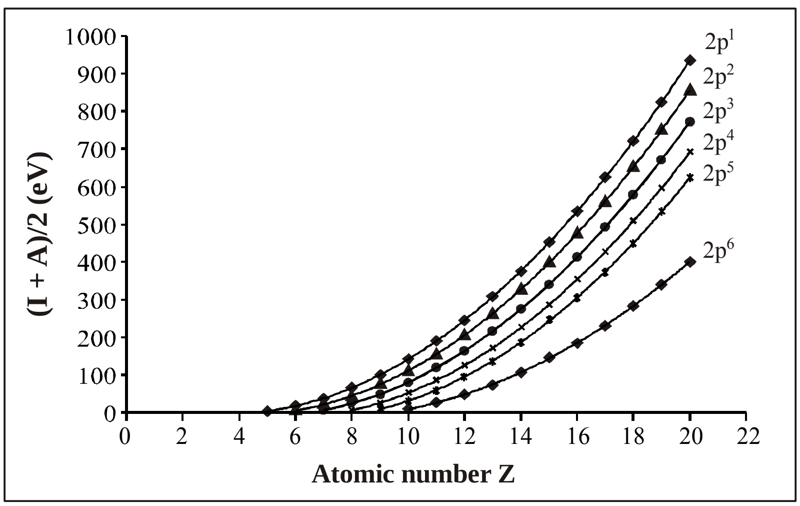

Fig. 3: Relation between Z and (I + A)/2 for $2p^1$; $2p^2$; $2p^3$; $2p^4$; $2p^5$; $2p^6$ series

An investigation of Table 1 reveals that the values of coefficient a from $1s^2\ 2s^1$ to $1s^2\ 2s^2\ 2p^5$ isoelectronic series is almost the same. Therefore, for the same atomic number, (I + A)/2 values for the isoelectronic species of these series mainly will be governed by the coefficients **b** and c. If we carefully observe the values of coefficients **b** and **c** from $1s^2\ 2s^1$ to

$1s^2\,2s^2\,2p^5$ series, then a correlation of these coefficients is observed with the number of electrons possessed by the isoelectronic series. These variations are presented in figure 4 and 5. It is seen that the variation of **b** with the electron number is almost linear, while **c** has a nonlinear variation.

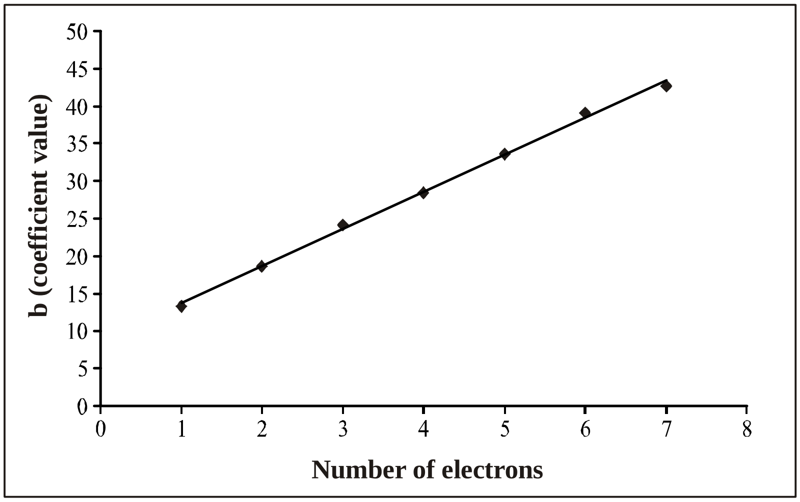

Fig. 4: Variation of coefficient b with the number of electrons possessed by the isoelectronic series

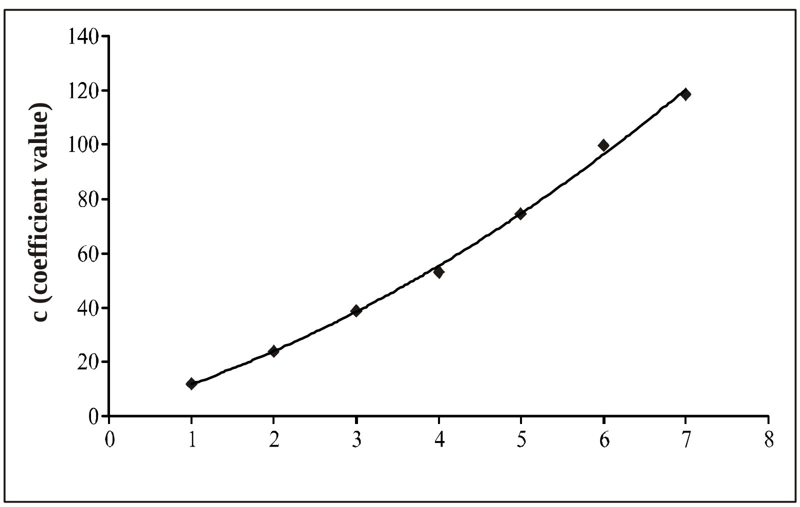

Fig. 5: Variation of coefficient c with the number of electrons possessed by the isoelectronic series

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