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Electronegativity: A Force or Energy

P Ramakrishnan

Inspire Fellow (DST), NIT. Rourkela, Department of Chemical Engineering, Rourkela, Odisha, India

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ABSTRACT

Electronegativity as force or energy leads to new ansatz at critical point in binding (or bonding) state in between two similar atoms or dissimilar atoms. Electronegativity as a quantum-mechanical entity (energy) or non-quantum entity (force) is yet to be answered. The dual approach to electronegativity has been discussed in this paper. The aim of this paper is to prove that Electronegativity as Hellman-Feynman Force is more accurate and absolute. Electronegativity has been computed using the Hartree-Fock and Rothan-Hrtree-Fock energy equations and equivalent electrostatic force equation.

Key Words: *Electronegativity, Hellmann-Feynman Force, Hartree-Fock Force*

1. INTRODUCTION

Electronegativity is unique and useful concept in the science of chemistry, physics and biology. The historical background of this concept dates back from the beginning of 19th century. In the year 1811, J.J.Berzelius, a proponent of electrochemical dualism has first introduced the term electronegativity. In the year 1809, Amen do Avogadro has also introduced 'Oxygencity' a correlated topic of electronegativity. In the year 1836, Berzelius has proposed a correlation between evolution of heat and neutralization of charge in a chemical reaction on the basis of caloric theory of heat where caloric was proposed to consist of positive and negative electrical fluid.

He could not exploit the use of correlation to quantify the electronegativity scale by bringing a similar relationship between evolution of heat and difference of electronegativity. In the year1870 Baker had already inserted three atomic parameters like weight (quantity of matter), valence (quantity of an atom's combining power), and electronegativity (quality of an atom's combining power). The caloric theory of heat wasdiscarded completely in 1930s and the birth of thermo-chemistry from the laws of thermodynamics and kinetic molecular theory compelled the scientists to establish a correlation between the heat of a reaction and electronegativity. The probable correlation between electronegativity and heat of reaction was suggested by Van'tHoff[1,2], Caven & Lander[1,3] and Sackur[1,4]. Electronegativity was defined with help of terminologies such as hetrolytic/homolytic bond dissociation enthalpy data, electron affinity, ionization energy (adiabatic, ground state, ionization, ionization potential and vertical ionization), effective nuclear charge and covalent radius, average electron density, stretching force constants, compactness, configurational energy, dielectric properties, work function, number of valence electrons, pseudopotentials and power. The electronegativity is an intuitive-cum-qualitative construct[5]. This qualitative construct is very difficult to be quantified. The first quantification and assignment of numerical value to electronegativity was given by Linus Pauling[6]. From 1932, a number of qualitative and quantitative scales for electronegativity have been proposed by different researchers across the globe. The quest for new electronegativity scale study is still going on as this concept is confusing[7]. The concept of electronegativity has been used to sketch the distribution and rearrangement of electronic charge in a molecule[8,9]. The fundamental descriptors in chemical science like bond energies, bond polarity, dipole moments, and inductive effects are being conceptualized and modeled for evaluation The scope of this concept is so broad that ionic bond, atom-atom polarizability, equalization of electronegativity, apicophilicity, group electronegativity, principle of maximum hardness, electronic chemical potential, polar effect(inductive effect, effective charge ,pi-electron acceptor/donor group)field effect, conjugative mechanism, mesomeric effect could have been explained. The correlations between electronegativity and superconducting transition temperature for solid elements and high temperature superconductors[10,11], the chemical shift in NMR spectroscopy[12], isomer shift in Mossbauer spectroscopy[13] have already been explained. This concept has also been utilized for the design of materials for energy conversion and storage device[14]. The experimental determination of electronegativity of individual surface atoms using atomic force spectroscopy has already been reported[15]. In this article, various concepts of electronegativity are overviewed followed by introduction to a new concept based on Hellmann-Feynman theorem.

2. Energy model of electronegativity

2.1 Pauling's (1932) empirical electronegativity scale

A classical incarnation of electronegativity in terms of an atom's ability to attract electron towards itself was introduced by Linus Pauling in 1932[6]. In the first decade of 20th-century, the correlation between electronegativity and heat evolution was so explicit that Pauling's approach would seem almost self-evident. Pauling's intuition dictates electronegativity as a virtually constant atomic property irrespective of the valence states being different. Pauling proposed the difference in electronegativity as a square root of extra ionic resonance energy (Δ). Again, Pauling and Sherman[16] have reported that Δ was not always positive for which Pauling replaced [DE(A_2).DE(B_2)]/2 in place of [DE(A_2)+DE(B_2)]/2 for his electronegativity equation such as

$$\left| c_{A} - c_{B} \right| = 0.208 ´ \ D$$

Eq. 1

Where,

$$D = \begin{cases} D_{E\|AB} - 0.5(D_{E\|A_2} + D_{E\|B_2}) \text{ based on AM} \\ D_{E\|AB} - (D_{E\|A_2} ´ \ D_{E\|B_2})^{1/2} \text{ based on GM} \end{cases}$$

Eq. 2

The second term in eq. 2 represents energy of covalent bond A-B based on arithmetic mean and geometric mean respectively.

DE(AB) = Bond dissociation energy of AB (Actual bond energy)
DE(A_2) = Bond dissociation energy of A_2
DE(B_2) = Bond dissociation energy of B_2
Pauling's quantum mechanical approach also indicates the dipole moment due to the presence of significant ionic structure A^+B^-. The extra- ionic resonance energy(Δ) arises out of contribution of ionic canonical forms to bonding and it was experimentally verified[17,18]. Pauling proposed valence bond in terms of covalent part and ionic part. Pauling has established quantitative ionicity scale for molecules and crystals based on electronegativity difference, such as

$$i^{ionicity} = 1 - \exp\left(\frac{\left| \chi_A - \chi_B \right|^2}{4} \right)$$

Eq. 3

I (iconicity)= 1-exp[-1/4|X_A-X_B|^2] and i(iconicity)=1-(N/M)[exp-1/4|X_A-X_B|^2]

Pauling's thermochemical scale was viewed as the culmination of the 19th century concept of electronegativity. Pauling's empirical electronegativity values derived from bond energies have been used to correlate between chemical and physical properties of a large number of elements followed by theoretical justification[19–21]. In the year 1932, electronegativity values of ten non-metallic elements was proposed by Pauling[6] where χ(H)=2.1(arbitrary reference to construct a scale) latter changed to2.2, χ(F)=4. Furthermore, electronegativity values of 29 main group elements was proposed by Linus Pauling in 1939[19,22]. In 1946, Haissinsky reported electronegativity values for 73 elements[19,23]. In 1953, Huggins reported the re-evaluated electronegativity values for 17 elements where electronegativity number of hydrogen was assigned 2.2 in place of 2.1(Pauling's value)[19,24]. In 1960-61, A. L. Allred updated Pauling's original electronegativity values for 69 elements where electronegativity of hydrogen was taken as 2.2[19]. Pauling Electronegativity is not perfect because of the scientific objections like 1) To assign a single electronegativity value to each 'atom in a molecule at all enough' is not sufficient as reported by Haissinsky[17,23] and Walsh[17,25] inspite of confirmation of empirical usefulness through several investigations.

To obtain electronegativity is weak one as reported by Ferreira[17,26] because of the assignment of one number to an atom, non –consideration of changes of hybridization, total neglect of effects of atomic charges.3) Restriction on electronegativity as a fixed atomic character. Further, this scale has been criticized by Iczkowski and Margrrave[27],Pearson[28],Allen[29,30].The chemical validity of this scale is its continuity as standard for other scales. Pauling type electronegativity is an ambiguity for the elements with several oxidation states of different bond energies[31,32].

2.2 Mulliken's (1934 and 1935) absolute electronegativity

Mulliken[20,33] developed an alternative definition for the electronegativity shortly after Pauling's definition based on energy concept. He considered three structures (i)AB ,(ii)A+B-, (iii)A-B+ where the two ionic structures (ii) and (iii would be of equal weights in the wave function containing ii and iii and so that the complete covalent structure will be possible under the condition

$$IP_A - EA_B + V = IP_B - EA_A + V$$

Eq. 4

$$\Rightarrow IP_A + EA_A = IP_B + EA_B$$

Eq. 5

Mullikan suggested the term IP_A+A_A or IP_B+A_B is a measure of electronegativity of atom A or B respectively. V is coulomb potential. With I_A and I_B assumed to be I and A_A and A_B assumed to be A, Mullikan expressed electronegativity as

χ_M^A =(I_A+A_A)/2 or χ_M^B=(I_B+A_B)/2 Eq. 6

In general,

$$\chi Mk = (IP + EA)/2 \quad \text{eV} \qquad \text{Eq. 7}$$

Where, V=Coulomb Potential
IP – ionization potential (in eV or kcal/mol)
EA – electron affinity (in eV or kcal/mol)
The values of IP and EA can be computed for atoms in either of states such as ground, excited, or valence state. The scientific reports made by Stark[1,34], Martin[1,35], and Fajans[1,36] have concluded the co-relation between Electronegativity, ionization energy and electron affinity. The rigorous qualitative derivation has also been examined by Moffitt[37] and Mulliken[33] himself. The half factor included in eq. 7 represents electronegativity as the average binding energy of the electron in the vicinity of the concerned atom. Mulliken's electronegativity is an arithmetic average of ionization potential and electron affinity of an atom in the ground state.

Mulliken electronegativity can be also termed as negative of chemical potential by incorporating energetic definitions of IP and EA so that Mulliken Chemical Potential will be a finite difference approximation of electronic energy with no of electrons.

X(M)= -μ(M)= -(IP+EA)/2 Eq. 8

The empirical correlation reported by Mulliken[33] between $\chi_{Mulliken}$ and $\chi_{Paulling}$ as

$$\chi Pa = \frac{\chi Mk}{2.78} = \frac{(IP + EA)}{2.78}$$

Eq. 9

Where I, A in kcal/mol,1/2.78 is scale adjustment factor. Huheey[38] reported Mulliken electronegativity as

i. X=0.187(I+A)+0.17 with I and A in electron volts
ii. X=[{1.97X10-3.}(IP+EA)]+0.19 with IP and EA in kilojoules per mole

Pritchard and Skinner[39,40] have reported the correlation between $\chi_{Mulliken}$ and $\chi_{Paulling}$ as

$$\chi Mk = 3.15 \times \chi Pa$$ IP, EA in kcal/mol **Eq. 10**

3.15 is scale adjustment factor. And they have given an extensive set of Mulliken electronegativity values. REF

Ionization potential and electron affinity are associated with the atomic orbital forming the bond, valence state energies must be used in calculating IP are dependent on the nature of atomic orbital. Hence 'Orbital electronegativity' arises out of Mullikan's concept of electronegativity which can be generalized to all atomic orbitals to molecular orbitals because of close relation of I and A with respective removal of electron from highest occupied atomic orbital (HOAO) and addition of electron to lowest unoccupied atomic orbital(LUAO). Thus, conceptually orbital electronegativity is a measure of the power of bonded atom or molecule (an aggregate of atoms) to attract an electron to a particular atomic orbital or a molecular orbital. The scientific validity of this scale was justified by Pearson[41]. Mulliken electronegativity is absolute, reasonable and in principle dependent on chemical environment of an atom. This scale is independent of an arbitrary relative scale. A bond between two atoms is assumed as competition for a pair of electrons where each atom will lose one electron (i.e. resist to be a positive ion) and simultaneously gain the second electron (i.e. to be a negative ion). Thereby, the two processes can be seen as involving the ionization potential and electron affinity respectively. So, the average of the two values is a measure of the competition and in turn gives value of electronegativity. A series of papers appearing in early 1960s provides with an extensive studies of Mulliken's electronegativity values for non-transition atoms with various valence states[17,42,43].The main demerits of Mulliken electronegativity such as consideration of isolated atomic properties (IP and EA) ,non-inclusion of all valence electrons, unavailability of electron affinity data and even if for 57 elements upto 2006[17,26,37,44], incorrect determination of electronegativity values for transition metals.

2.2.1 Lang and Smith[45,46] defined electronegativity as a simple function of

[val (Ia)+(1- val(Ea)

where

val , Ia ,Ea stand for a fraction less than 1,ionization energy (ionization potential IP), electron affinity respectively

The ionization energy values (Ia) have been adjusted for pairing and exchange interaction. They have reported a set of electronegativity values for elements from hydrogen to Astatine except zero group elements.

2.3 Allen's absolute scale of Spectroscopic Electronegativity

Allen[29,30] defines Electronegativity as the average one-electron energy of valence shell electrons in ground-state free atom and proposed it as third dimension and also energy dimension of periodic table. So, this type of electronegativity is a Free- atom -ground –state quantity with a single defining number which gains its meaning as an extension of periodic table. Allen has introduced two terms Eenrgy index (in situ Xspec of free atom) and Bond polarity Index (projection operator being applied to a molecular orbital wave function to get in situ average one-electron energies for atoms in molecules i.e in situ Δx_{spec}).The fractional polarity defined from Bond polarity index is equivalent of Pauiling's dipole moment referenced 'ionic character percent' .Allen has reported a new chemical pattern by mounting a series funnel –shaped potential energy plots(E vs r) along a line of increasing Z i.e along a row of periodic table where a composite curve one-electron energy(vertical axis) vs a part row of periodic table is obtained. This composite curve shows a strong correlation between magnitude of X_{SPEC} and energy level spacing (large X_{Spec} with large spacing) like energy level like energy levels of Fermi-Thomas-Dirac atom and in case of other atoms.

Electronegativity for representative elements is independent of oxidation state because of the fact that the atomic charges carried by representative elements during the formation polar covalent bond are slightly close to their oxidation number there by negligible changes in electronegativity with change in molecular environmental system. For transition elements electronegativity is dependent on oxidation state because of closely spaced energy levels.

Electronegativity-for representative elements i.e. X spec= (a ∈s + b ∈p)/ a+ b equation (i) is occupation weighed average per electron ionization energy of an atom where a,b are occupation number and Is ,Ip are spherically ionization potentials which are determined through multiplet averaging. But for transition elements, I p is replaced by I d and a,b are the valence-shell occupancies of s-orbitals and d-orbitals in overlap region.

$$c_{spec} = \frac{a\hat{I}\ s + b\hat{I}\ d}{a + b}$$ Eq. 11

The main strength of this definition is that necessary spectroscopic energy data are available for many elements and electronegativity of Francium was estimated. The core question of this scale –

i. "How to determine the valence electrons for d-block and f -block elements'' is still an ambiguity in estimation of electronegativity because no such theory to determine the valency electron has been developed so far.
ii. Reason for electronegativity order such as Neon>Fluorine>Helium>Oxygen is yet to be given.

2.4 Jorgensen[47] introduced optical electronegativity scale (χ_{OP}) for rationalizing electron transfer spectra of transition metal complex (MX).In this scale a linear difference in χ_{OP} represent the photon energy(hγ) as per the following relation.

$$h\gamma = [\chi_{OP}(X) - \chi_{OP}(M)]\ 3 \times 10^4\ \mathrm{cm}^{-1} \qquad \text{Eq. 12}$$

A linear relationship of χ_{OP} to the difference in eigen values as introduced by Jorgensen is an idea which can be rationalized in terms of density functional approach to χ.

2.5 J.C.Slater et al.

J.C.Slater et. al.[48,49] defines Spin-Orbital electronegativity which is derived from the fact that the orbital energy eigen values in SCF-X∝(Self consistent field X∝ scattered wave) density functional approach to molecular orbital theory are equal to the first derivatives of total energy with respect to occupation number.

2.6

Simons[31,50] has reported a theoretical scale to determine atomic electronegativity values where bonds are described by Gaussian Type orbitals. These orbitals are assumed to float to a point of minimum energy between the atoms. The electronegativity values are obtained from Floating Spherical Gaussian Orbital (FSGO wave functions)[27]. Simmons and Frost defined an orbital multiplier ($f_{AB}= r_A/[r_A+r_B]$) where r_A and r_B label as atomic distances with respect to the orbital center. f_{AB} of 0.5 implies of equal attraction between the atoms . For $f_{AB}<0.5$, A attracts B to a large extent. For $f_{AB}>0.5$, B attracts A to large extent. Simmons defined the electronegativity difference as

$$|\chi_A - \chi_B| = k \times (f_{AB} - 0.5) \qquad \text{Eq. 13}$$

This scale is established with $\chi_{\text{Lithium}}=1$ and $\chi_{\text{Fluorine}}=4$. Also, this scale is quite consistent with Pauling scale and Allred-Rochow scale.

2.7

St. John and Bloch[51] have reported quantum-defect electronegativity scale using ''Pauli force'' model potential[52].This force model potential represents the pseudo potential of a one-valence-electron ion except in the vicinity of nucleus and is applied in studies of atoms, molecules and solids. Energy of the orbital is represented as

$$E(n,l) = -0.5Z^2\left[n + \hat{l}(l) - l\right]^{-2} \qquad \text{Eq. 14}$$

Where

Z=core charge

$\hat{l}(l)-l$=quantum defect

The orbital electronegativity for valence orbital is defined as

$$\chi_l^{JB} \equiv \frac{1}{r_l} \equiv \frac{1}{\hat{l}(\hat{l}+1)/Z} \qquad \text{Eq. 15}$$

where

l=0,1.2 represent s,p,d orbital respectively

χJB – orbital electronegativity for valence orbital

r – radius for valence orbital

l-orbital quantum number

Atomic electronegativity is represented as

$$\chi = 0.43 \times \sum_{l=0}^{2} \chi_l^{JB} + 0.24 \qquad \text{Eq. 16}$$

This theoretical scale like Gordy's is related to electrostatic potential idea, but in contrast to Gordy's it introduces the explicit idea of hybridization. They have suggested that this scale is sensitive indicator of chemical trends in the structures of solids and complex systems.

3. Energy Charge model of electronegativity

Iczkowski-Margrave[27], Hinze-Whitehead-Jaffe[43], Huheey[31,38,53,54], G Klopman[39,55,56], Ponec[57], Parr et al.[58–60], Mulliken-Jaffe[20,33,38,43], Watson et al.[61] have reported about direct relation of the total energy of the system with the charges.

3.1 Mulliken-Jaffe[20,33,38,43] electronegativity approach is based on the fact that the first ionization energy and the electron affinity are the simple sum of multiple ionization potential-electron affinity energies which fit a quadratic equation as follows.

$$E = a\,q + b\,q^2 \qquad \text{Eq. 17}$$

$$a = \frac{IE_V + EA_V}{2} \qquad \text{Eq. 18}$$

α –mulliken electronegativity

β – charge coefficient

E-Total energy in eV

q- ionic charge (+1 for cataion, -1 for anion)

IE is IP of sec 2.2

Based on this approach the electronegativity of a few elements of the periodic table can be computed.

3.2 Huheey's Idea of Group electronegativity

James E Huheey[53,54] in 1965 has reported a simple procedure to calculate electronegativity of 99 different groups by assuming variable electronegativity of the central atom in a group and equalization of electronegativity in all bonds. Huheey proposed that relatively low values of the charge coefficients cause the effect of promoting charge transfer. Huheey proposed the following set of equations

Eq. 19

$$[a_w + b_w\delta_w = a_x + b_x\delta_x]----Group-wx$$
$$[a_w + b_w\delta_w = a_x + b_x\delta_x = a_y + b_y\delta_y]---Group-wxy$$
$$[a_w + b_w\delta_w = x + b_x\delta_x = a_y + b_y\delta_y = a_z + b_z\delta_z]---Group-wxyz$$

which are coupled separately with relations like ∂G=0(Radical),1(cation), -1(anion) there giving the Huheey-relation between group electronegativity and partial charge in group i.e.

$$\chi_G = a + b\delta_G \qquad \text{Eq. 20}$$

Where δ_G represents partial charge due to gain/loss of one electron

a (normal group electronegativity/inherent electronegativity) = (IP-EA)/2
b (charge transfer coefficient) = IP+EA
S G Bratsch[17,62] has simplified Huheey's method by using Sanderson's principle of Electronegativity equalization.

$\chi=\chi A(1+\delta A)$, $X=(N+\delta g)/\sum(n)/\chi A)$ Eq. 21

$$c = c_A(1+d_A)$$

$$X =$$

Where χ represents electronegativity for the molecule or the group, n represents number of atoms of A, N=Σ(n) represents the total number of atoms, δ_G is the charge in the group. J Mullay[17] has reported the value of 'b' as 1.5 times of 'a'.

Weakness

Huheey's method speaks of total electronegativity equalization but this method has three major demerits i.e. inability to account for differences in isomers, treating groups with multiple bonding and overestimating of the effect of the atoms or groups linked to the bonding atom. In order to avoid the three major deficiencies Huheey[38,63] modified his method for 80% electronegativity equalization.

3.3 Hinze-Whitehead-Jaffe –contribution to Electronegativity

Hinze et al.[43] defined orbital electronegativity as the first derivative of energy of an atomic orbital (j) with respect to electron occupancy (n_j) of the orbital i.e

$\chi_{A.j(\text{atomic orbital j})}=\delta E_A/\delta n_j$ …….(i) Eq. 22

$$c_{A,j(\text{atomic orbital j})} = \frac{dE_A}{dn_j} \quad \text{……… (i)} \qquad \text{Eq. 23}$$

The justification for the said definition is obtained from the fact that atomic electronegativity is reasonably considered because of its reference to the atomic orbital which half-filled orbital(n_j=1) before the formation of bond. As energy of orbital is assumed to be be a quadratic function of n_j, then the definition of atomic electronegativity is reduced to Mullikan's electronegativity. The said definition of electronegativity appears to be valid for n_j=0(empty orbital), 1(half-filled orbital), 2(lone pair) and also leads to define 'bond electronegativity' for non-integral values of n_j. Again, the concept of bond electronegativity arises in the formation of a bond where electron paring occurs followed by electron transfer between two atoms A and B with energy changes ($\delta E_A/\delta n_A$) dq_A and ($\delta E_B/\delta n_B$) dq_B respectively. At equilibrium, there occurs no further change in energy. Hence, electronegativity values will be equalized during bond formation. Mathematically,

$$dn_A = dn_B \text{ ....(ii)} \qquad \text{Eq. 24}$$

$$\Rightarrow \frac{dE_A}{dn_A} = \frac{dE_B}{dn_B} \qquad \text{Eq. 25}$$

The electronegativity value acquired by an atom in bond formation is called 'bond electronegativity' which is not to be confused with Pauling electronegativity integral values of orbital occupation.

Strength

The Hinze et al. approach to the electronegativity theory is somewhat simple because it neglects resonance and electrostatic effects[17,53,54,64–66]. Pritchard[64] suggests the inequality of electronegativity by an order of 10% of the original electronegativity. Bartolotti et al. and Parr et al. have suggested the equality of electronegativity in their works[58,67]. Politzer et. al. have reported the non-importance of the idea of orbitals in electronegativity theory[68]. Mullay[17] and Watson et. al.[17,61] have reported the potential usefulness of group electronegativity which are obtained from the idea of orbital electronegativity in conjunction with electronegativity equalization.

Weakness

The Hinze et al.'s[42,43] work is simple still then it did not meet the criterion for electronegativity. Some authors[69] suggest that the orbital concept of electronegativity never solves the meaning -'Atom in Molecule'.

3.4 G Klopman's atomic electronegativity

G Klopman[39,55,56] used Rydberg formula for the calculation of the atomic spectra and proposed a modified formula for calculation of atomic electronegativity of the system in the valence state and also for quantitative determination of the diagonal matrix elements in self-consistent field calculation of a molecule .Modified Rydberg formula is represented as

$$E = \frac{Ry(Z-\sigma)^2}{(n-dn)^2} = \frac{13.5(Z-\sigma)^2}{(n-dn)^2} \text{ eV} \qquad \text{Eq. 26}$$

Ry– Rydberg constant
n – Principal quantum number
σ – Screening constant
Z– Atomic number
dn– Quantum defect

The screening constant (σ) is represented as

$$\sigma = \sum_{j\neq i} q_j \sigma_{ji} \qquad \text{Eq. 27}$$

Where
q_j is the occupation number of spin orbital j
σ_{ji} is the screening of the electron i by the electron j

The value of σ (core electron – valence cell electron) is considered to be 1 because core electrons are not considered. Quantum defect (dn) has been calculated from respective ionization potential i.e

$$dn = 3.687(Z^*)/IP \qquad \text{Eq. 28}$$

Where,
n – Principal quantum number
Z*– effective nuclear charge
IP– Ionization potential

Total electronic energy of Valence shell,

$$E_{total} = \sum_i q_i \frac{13.6}{(n-d)^2}\left[Z - \sum_{j\neq i} q_j \sigma_{ji}\right]^2 = \sum_i q_i B_i + \frac{1}{2}\sum_i \sum_{j\neq i} q_j q_i A_{ij}^{\pm} + \sum_i q_i \left(\sum_{j\neq i} q_j\right)^2 C_{ji}$$

Eq. 29

$$B_i = 13.6\frac{Z^2}{(n-d)^2}; \frac{1}{2}A_{ij}^{\pm} = -2[13.6/(n-d)2]\, Z\sigma_{ij}; C_{ji} = \frac{13.6}{(n-d)^2} \times \sigma_{ji}^2$$

Eq. 30

Further, Total electronic-energy equation of the diatomic system (AB) at barycenter is represented as,

$$E_{total} = \sum_i q_i B_i + \frac{1}{2}\sum_i \sum_{j\neq i} q_j q_i A^+ d_{ij} + \frac{1}{2}\sum_i \sum_{j\neq i} q_j q_i A^- (1-d_{ij}) + \sum_i \left[q_i \left(\sum_{j\neq i} q_j \right)^2 C \right] \quad \text{Eq. 31}$$

Klopman[39] defined atomic electronegativity as the derivative of total electronic energy of the valence cell with respect to the charge q_i as mentioned below.

$$\chi_{Atomic-\ Electronegativity.} = \frac{dE}{dq_i} = B_i + \sum_{j\neq i} q_j A^+ d_{ij} + \sum_{j\neq i} q_j A^- (1-d_{ij}) + 2\sum_{j\neq i}\left[q_i \sum_{r\neq j} q L r C \right] + \left(\sum_{j\neq i} q_j \right)^2 C \quad \text{Eq. 32}$$

And also neutral atomic electronegativity is obtained from the above equation when all the values of q_j (the occupation number of particular atomic spin orbital by an electron) will be equal to 1 except for participating electrons in the bonds where $q_j = 1/2$.

Strength

Kolpman's procedure helps in calculating Neutral Atomic Electronegativity. This procedure provides theoretical support and clarification for electronegativity suggested by Iczkowski and Margrave, Hinze, Whitehead and Jaffe.

Weakness :Kolpman's work has been modified and extended to provide a simple procedure for calculation of atomic or orbital electronegativity and also for group electronegativity[17]

3.5 Ponec 's idea of Global electronegativity

R Ponec[17,57] has reported a generalization of the orbital electronegativity concept of Hinze et al.[43] and it is based on the semi empirical Complete Neglect of Differential Overlap (CNDO) approximation. Ponec's basic equation is written as,

$$\chi_{Aj} = -E_j^A - (\rho_A - 1/2)\gamma_A \quad \text{Eq. 33}$$

Where

χ_{Aj} – orbital electronegativity

E_j^A – one electron energy of orbital j

γ_A – electron repulsion integral

p_A – total electron density associated with atom A

For neutral atoms the orbital electronegativity is reduced to Mulliken-Jaffe values for isolated atom but in a molecule global electronegativity term can be defined as

$$\chi_{G(A)} = \frac{\sum P_j \chi_{Aj}}{\sum P_j} \quad \text{Eq. 34}$$

Where

$\chi_{G(A)}$ – Global electronegativity in a molecule

P_j – charge density on atomic orbital j on A

χ_{Aj} – Orbital electronegativity

Global electronegativity values for some molecules have been correlated to X-ray Photoelectron Spectroscopy (ESCA) chemical shifts with good results. Ponec's extension[56] of the ideas based on Intermediate Neglect of Differential Overlap (INDO) approximation gives better results than those obtained by H O Pritchard[64].

3.6 Iczkowski & Margrave approach

RP Iczkowski and JL Margrave[27] introduced the energy equation of atoms in terms of net-charge(number of electrons minus nuclear charge) on an atom relative to neutral atom. The energy is termed as valence state energy.The expression is represented as

$$E = aN + bN^2 + cN^3 + dN^4 \quad \text{Eq. 35}$$

In above equation, N is the net-charge on the atom and the charge coefficients a,b,c,d are the constants that depend atom including its valence state and these constants can be calculated by comparing the values of E(for different N) with experimental ionization potential values. Electronegativity of the atom is defined in terms of the first derivative of E with N and this derivative represents the potential around the atom for a given atomic charge. This derivative measures the power of atom to attract electrons. In equation below, The quantity $-(dE/dN)_{N=0}$ (for neutral atom) represents electronegativity.

$$\chi = -\left(\frac{dE}{dN} \right)_{N=0} \quad \text{Eq. 36}$$

This also represents (i) the tendency of an atom in a molecule to attract electrons for small charge dislocation during interaction of atoms and (ii) the decrease of energy of moreelectronegative atom than the increase in energy for less electronegative atom. Hence, the energy of molecule is decreased simply by transfer of charge from one tom to another. The energy change in this case is not at all accrued from the electrostatic attraction between ions. Thus, electronegativity characterizes both the internal constitution of atom and the ions which can be formed from it. Again, the electronegativity represents an intensity factor in charge transfer from one atom to the other atom.

Strength

This concept of electronegativity in terms of energy-charge derivative have also been justified through ingenious and laudable efforts of various authors[70–73].The scope of this definition is described as i) dE/dN have been calculated for various 1st row and 2nd row elements and are in close agreement with Mulliken's electronegativity. ii)The calculations were extended to many elements along with metals by C K Jorgensen[39,74] who used similar equations up to three first terms. iii) The above equation up to first two terms using N=1 leads to the Mulliken's definition of electronegativity i.e.

$$\left(\frac{dE}{dN} \right)_{n=0} = a + 2b = \frac{IP + EA}{2} \quad \text{Eq. 37}$$

With this approximation Jaffe et al. were able to calculate the group orbital electronegativity (i.e. electronegativity of free orbital of an atom bound to other atom). iv)The principle of electronegativity equalization of Sanderson[75] helped in initiating the calculation of charge distribution. V) The above general principle has been used by Ferreira[76] for calculation of bond energy and charge distribution in many binuclear molecules.

Weakness
The expression of energy in terms net-charge is not a continuous function as net-charge takes only integral values. The assumption of envisioning 'atom in molecule to have an average fractional number of electrons so as to make energy-charge expression continuous and differentiable' has already been criticized by various authors[77–80].

3.7 Parr's density functional electronegativity;

Parr et. al[58] defines Density functional electronegativity with the help of Density Functional Theory (DFT) which is based on the theorems of Hohenbrg and Kohn[81] such as

$$\text{Theorem I}: E[\rho] = \int \rho(1)v(1)d\tau_1 + F[\rho] \qquad \text{Eq. 38}$$

$$\text{Theorem II}: E_v\left[\rho'\right] = \int \rho'(1)v(1)d\tau_1 + F\left[\rho'\right]$$

Eq. 39

However, theorem I implies that the ground state electronic energy is a functional of the density. Whereas, theorem II considers inequality with equality holding for ρ'=ρ, $E_v[\rho'] \geq E_v[\rho]$. The density ρ and energy E are determined from the stationary principle. The true energy   is obtained by minimizing the function with the constraint so that the density integrates to the total number of electrons. This constraint is Lagrange multiplier **μ**= -[**δ**E/**δρ**]$_v$=constant external potential and Parr et al.[58] identified electronegativity as the negative of Lagrange multiplier which is also considered as chemical potential. **μ**= -[**δ**E/**δρ**]$_v$=external potential. These authors have replaced [dE/d**ρ**]$_v$ by the first derivative of energy with respect to N such as [**δ**E/δN]$_v$ on the basis work of Einhorn etal [124].where v stands for fixed potential due to set of nuclei and external field,**ρ** represents for electronic density. Parr et. al.[58] defined electronegativity as,

$$\chi = -\mu = -\left(\frac{dE}{dN}\right)_V \qquad \text{Eq. 40}$$

by considering the similarity between the above expression for **μ** and electronegativity expression of Iczwoscki and Margrave . The concept of chemical potential has also kept Electronegativity as a Global index to characterize the chemical structure. The geometric mean electronegativity equalization principle holds only when each chemical potential is exponential in the number of electrons and the fall-off parameter γ is same for chemical potentials of neutral atoms. Again from density functional theory studies, it is suggested that for a nearly neutral atom, energy is an exponentially decaying function of the number of electrons but the classical suggestion states that the energy is a quadratic function of number of electrons and the classical suggestion leads to the Mulliken formula of electronegativity in equation number μ = -χ = (IP+EA)/2. Parr and Bartolotti[59] proposed the formula for **μ** as

$$\mu = \gamma \frac{IP \times EA}{IP - EA} \qquad \text{Eq. 41}$$

Where, they have proposed the approximate constancy of γ (i.e. a fall-off parameter) in the following electron loss and gain process such as

$$A^+ \xrightarrow{+(e)} A \xrightarrow{+(e)} A^-.$$

The geometric mean law constitutes a prediction on how molecular electronegativity are related to atomic electronegativity and does not trivially extend to a prediction of molecular electronegativity from functional group electronegativity because the primary sites for electron attraction in a molecule are nuclei of atoms. Parr and Bartolotti[59] have justified that electronegativity is constant throughout an atom or a molecule and also remains constant from orbital to orbital within an atom or a molecule .Again, it is shown how valence state electronegativity differences drive charge transfer on molecule formation. Parr and Pearson[60] have established an Global Electrophilicity Power index

(w) = μ 2/2η Eq. 42

where η=chemical hardness.
This index is a measure of lowering energy of the chemical entity during the transfer of electron. This density functional electronegativity encounters with severe differentiability problem[70,71] where a discontinuous function is put forcibly to differentiation by violating the basic definition of derivative. This above problem was solved partially by ingenious efforts of the proponents[72,73,82,83].The strength for this concept comes from electronegativity equalization principle. This electronegativity is defined in terms of ground-state energy of a free atom or a free molecule. The conversion of Parr et. al.[58] electronegativity into Mulliken electronegativity was made possible by considering dE/dN as average of $\Delta E/\Delta N$ for the loss or gain of electron. The constancy of external potential in electronegativity formula needs no importance for free atom but bears energy of 3 eV or more for a molecule. The adiabatic IP and EA values should be mentioned in the formula. Allen[29,30], Pearson[28] ,Komorowski[84] ,Datta et. al.[85] have pointed out that Parr et. al.[58] formula implies the transfer of electron between free-atom or free-molecule and external surroundings whereas initial concept of electronegativity is always referred to redistribution of electrons within a molecule.

3.8 Politzer[68] has reported the reaffirmation of the principle of electronegativity equalization as the dependence of the direction of migration of electronic charge on electronegativity difference. This new approach to the electronegativity like Hellmann-Feynman theorem[33,86,87] has been deduced in terms two physical models where in one model, total energy of molecular system AB is a function of associated electrons with each atom (n_a and n_b) , corresponding atomic numbers (Z_a and Z_b) and inter-nuclear distance (R).

$$E = f\left(n_a, n_b, Z_a, Z_b, R\right) \qquad \text{Eq. 43}$$

For a molecule ab in the ground state under equilibrium,

$R=R_E$; $dE=0$; $dn=-dn_a=dn_b$, Eq. 44

Where R_E – equilibrium inter nuclear separation between a and b

dn – Infinitesimal electronic charge under transfer from a to b

Here Eectronegativity of A and B

$$-\left(\partial E/\partial N_a\right)_{R_E,n_b}=\chi_A \text{ ,-}\left(\partial E/\partial N_b\right)_{R_{E,}n_a}=\chi_B$$

Eq. 45

In another model, total energy of the molecular system AB, $E=f\left(n_a,n_b,Z_a,Z_b,n_x,R\right)$ is either a function of i.atomic numbers Z_a, Z_b,atoms n_a,n_b and delocalized atoms inter-nuclear separation or a function of atomic number Z_a, Z_b atoms n_1,n_2,n_3……..Inter-nuclear separation

$E=f\left(Z_a,Z_b,n_1,n_2......,R\right)$ is either a function of i.atomic numbers Z_a, $Z_b$atoms n_a,n_b , the electronegativity values (or the chemical potential) are expressed[58,70,88–90]. This idea of electronegativity is not bound within a particular theory like Density Functional Theory, wave functions under quantum mechanics.

4. Charge model of electronegativity

4.1 R T Sanderson approach to electronegativity

R T Sanderson[75,88,91,92] considered electronegativity is an explanation of chemical reaction where charge transfer takes place . The driving force for reaction comes from electronegativity equalization. The charge transfer occurs from atom with lower electronegativity (higher chemical potential) to atom with higher electronegativity (lower chemical potential) and Sanderson reported equalization of different atomic electronegativity values during the formation of a molecule or a radical. The final value is obtained by considering the geometric mean of all atomic electronegativity values for estimating the atomic charge. He introduced the ratio of electronegativity change in forming the compound to the change in acquisition of a unit positive or negative charge. The unit change in electronegativity (ΔSR) is obtained from the original electronegativity (SR) with the help of the following relation

χ(ΔS/√χSR =2.08 and χSR value is expressed in terms value[√χP - 0.77]/0.21 where χP=Pauiling's value[91]. Sanderson[93] has also defined electronegativity in terms of electron density.

4.2 Gordy has reported various ways for calculation of electronegativity values[94,95]. One of all the three ways considers the electronegativity in terms of electrostatic potential and covalent radius.

Xg= 0.62(Z'/r)+ 0.5 Eq. 46

Z' – screen charge by Gordy's technique.

The screening factor for close shell electrons and valence electrons in Gordy's technique are 1 and 0.5 respectively. For the atom with n valence electrons, Z'=0.5(n+1) the above expression is modified as

$$\chi^G=0.31\times\frac{(\nu+1)}{r}+0.5$$

Eq. 47

Weakness:

The Gordy's electronegativity can not be correlated with Pauling because of severe difficulty in estimation of screen nuclear charge.

Utility:

This scale is very useful because of introducing the idea of the electrostatic potential into electronegativity along with bringing the equivalence of electronegativity with Allred-Rochow force scale[96] inspite of the basis of two different parameters. Politzer and Parr[97] reported some merit in the Gordy scale which gains theoretical support to some extent from Iczkowksi[27]

4.3 Gordy[98] correlated the ionic character with electronegativity difference by the use of nuclear quadrupole couplings const ants for halide molecules. Gordy has assumed the use of p-orbitals by halogen atoms in formation of single bonds and has established the ionic character equation

|χA-Xb|= 2 for 2 and for | χA- χB |≥2.

Wilmshurst[99] have reported different ionic relation: |χA-χB|/|χA+ χB|=[Ionic(AB)] which is used to analyse quadrupole coupling constants.

4.4 Boyd and Edgecombe[100] defines electronegativity quite different from that of Pauling and Allred –Rochow by determining electronegativity from computed electron density distributions for hydrides of representative elements where atomic radii are determined by a point of minimum charge density along non-metallic hydride bond. Electronegativity is supposed to be direct function of charge density (ρ)at minimum no of valence electrons, non-metal hydride separation(d) and an inverse function of atomic radii(r).

4.5 Malone[101] suggested in 1933 a rough proportionality between the dipole moment of the bond A-B and electronegativity difference as

$$\mu \square \left|\chi_A-\chi_B\right|_{Pauling}$$ Eq. 48

Where μ is dipole moment in debye (CGS unit of electric dipole moment).

The Malone's measure of electronegativity was rejected because of the reports of Coulson[102]

4.6 Phillips[103] has suggested dielectric definition of electronegativity by proposing a simple model for the static electronic dielectric constants of zinc-blende and wurtzite crystal. The dielectric constants have been correlated with that of diamond crystal which is a sp^3 hybridized net-work. Phillip has extended two dimensional homo-polar model Hamiltonian to a four dimensional space which yields a relation between energy gap (E_{g0}) and the hetropolar static dielectric constant (ε_0) such as

$$\varepsilon_0 = 1 + \frac{\left(h\omega_p / 2\pi\right)^2}{\left[\left(E_{g0}\right)^2 + \left(C_{AB}\right)^2\right] \times a} \qquad \text{Eq. 49}$$

Where

$$C_{AB} = 0.9e^2 \left(\frac{Z_A}{r_{A0}} - \frac{Z_B}{r_{B0}}\right) \exp\left(-k_s r_{A0}\right) \qquad \text{Eq. 50}$$

C_{AB} – semi-classical charge transfer constant which represents dielectric electronegativity.
a – a number of order unity
$h\omega_p / 2\pi$ – plasma energy
k_s – Thomas Fermi screening radius for a free electron gas
This scale is exclusively used for calculation of electronegativity values for tetravalent elements like Carbon, Silicon, Germanium and Tin.

5. Force Model OF Electronegativity:
5.1 Allred and Rochow absolute scale

AL Allred and EG Rochow[96] defined the electronegativity of an atom with electrostatic field and presented an equation for its evaluation and electronegativity will be equal to Coulomb force of attraction between the nucleus and an electron at the covalent radius.

X (AR) ≡ Z*e^2 / r^2 ……………..(i) Eq. 51

Where, Z^*= effective nuclear charge, Z*=Z – σ (slater constant=shielding constant), r =mean radius of the orbital i.e. covalent radius for the atom(considering smaller value as well as outer radial maxima).The Coulomb force is a measure of power of an atom in a molecule with which is electron is dragged towards an atom. Thus electronegativity will be absolute one. X (AR) dimension is not straight –forward as it is evaluated through expression (i). The quantity Z^*/r^2 was calculated through Pauling's work and Slater rules for determining the effective nuclear charge[96,104,105] . The Pauling's Scale and Allred-Rochow scale can be made to coincide by expressing the electronegativity from the electrostatic approach as the linear function of Z^*/r^2. mean radius is expressed in picometer[106].

$$\chi_{AR} = 3590 \times \left(Z^* / r^2\right) + 0.744 \text{ ………….. (ii)} \qquad \text{Eq. 52}$$

Where 3590 and 0.744 are arbitrary numerical constants. The expression (ii) does not compute any force in the real world.

Strength of this scale is two-fold such as
Introducing the idea of force into electronegativity theory so that it seems quite consistent with Pauling's definition. Emphasizing the idea for simple calculation, because r and Z^* are readily available quantities for many elements. The modification and extension of the above ideas were reported by different authors.

Weakness of this scale is also three fold such as
- independent of electron affinities, bond dissociation energies
- Slater rules for finding effective nuclear charge are empirical
- Covalent radii are known for few elements

5.2. The first extension of Allred-Rochow scale by Huheey[17,31] is based on two assumptions, r ~ (1/Z*) and Z*~δ.
δ – Partial atomic charge
r – Covalent radius

$$\chi^H = 0.36 \times \frac{\left(Z^* - 3\delta\right)}{r^2} + 0.74 \qquad \text{Eq. 53}$$

5.3. The second extension of Allred-Rochow scale

The second extension of Allred-Rochow scale by Boyd and Markus[17,107] is based on non -empirical approach where empirical covalent radius is replaced by relative covalent radius which is obtained from the free- atom wave function by density contour technique. The effective nuclear charge is obtained through integration of radial density function from nucleus to relative-distance. Electrostatic-electronegativity is expressed as,

$$\chi = Z / r^2 \left[1 - \int_0^r \rho(r)\,dr\right] \qquad \text{Eq. 54}$$

Where
Z – Atomic number
r – Relative covalent radius
ρ(r) - radial charge density

The radial charge density ρ(r) can be obtained from the Hartree Fock atomic orbitals data[108,109]. The computed electronegativity values follow the general pattern of Mulliken ground state electronegativity values with an exception for groups 2 and 3 of periodic table because D(r) decreases as expectation of (IP. r) where IP=ionization potential,r->infinity

5.4. The third extension of the scale was made Mande et al. [17,110] where the value of effective nuclear (Z^*) charge was obtained spectroscopic analysis. So the values are less arbitrary than Slater's. This electronegativity scale is more fundamental and reliable. The correlation of the scale is excellent with that of Pauling's scale. The electronegativity values obtained for 1st transition metals are more reasonable than Allred-Rochow scale.

5.5. The fourth extension of this scale was made by Yonghe Zhang[17,111] where electronegativity has been calculated on the basis of electrostatic force [F = n*√(IPz/R) /r^2]in terms of ultimate ionization potential for outer electron (Iz=R.Z*^2/n*^2). This type of scale is based on the concept of different electron-attracting power of an element in different valence. Therefore, ectronegativity is termed as a function of oxidation number.

Zhang electronegativity is given by,

$$\chi_Z = 0.241[F] + 0.775 \qquad \text{Eq. 55}$$

where
r= pauling's covalent radius

IPz= ultimate ionization potential for outer electron

Yonghe Zhang has reported dual parameter equation[111].

$$Z = \frac{Z}{r_i^2} - 7.7c_Z + 8.0 \qquad \text{Eq. 56}$$

where Z=Nuclear Charge,
r (i)=ionic radius

This equation is used as a scale for the strength of Lewis acid.

6. Quantum model of Electronegativity

Putz M.V[112–115] defined electronegativity by a specialized affinity-ionization wave function within Fock Space having fermions(electrons) where quantum mechanical description of electronegativity was made through field perturbation on a valence state for chemical system. Putz electronegativity is termed as quantum electronegativity which is considered as viable quantum concept with observable character. The mathematical expression is represented as[115],

$$\chi_{Putz} = -\frac{E_0}{\rho_0} = -\mu_0 = \begin{cases} \infty & ,\ \rho_0 \to 0(E_0 < 0) \\ -E_0 = -\langle \psi_0 | H | \psi_0 \rangle, & \rho_0 \to 1 \end{cases} \qquad \text{Eq. 57}$$

This idea of quantum electronegativity helps in applying affinity-ionization wave function on the valence state of a chemical system to recover the Eigen energy value of that state within density functional chemical potential formulation .The density functional electronegativity of Parr et.al[58] was confirmed with Putz's fundamental quantum mechanical arguments which helped in identifying the flaws made by Bergmann and Hinze[116].

7. Ionocovalency model of Electronegativity

Yonghe Zhang[111,117,118] has reported ionocovalency model which is correlated with quantum –mechanical potential. This model describes quantitatively the properties of effective ionic potential, charge density, charge distribution, effective polarizing power and bond strengths. Ionocovalency (IC) was defined as a product of the ionic function I(Z*) and the covalent function C(1/r).The Bohr energy expression(E=-R.(Z)2/(n)2) was modified by replacing energy by ultimate Ionization energy(IPz) , Nuclear charge(Z) by effective nuclear charge(Z*), principal quantum number (n)by effective principal quantum number(n*) . The expression, so obtained, Z*=n*[(IPz)/R] was used to correlate the bond properties to the quantum mechanics and IC model is represented as

$$I(IPz) \times C(n^*/r) = \left(\frac{IPz}{R}\right)^{1/2} \times \frac{n^*}{r} \qquad \text{Eq. 58}$$

The electronegativity defined in terms of Ionocovalency is correlated with Pauling's electronegativity values and it is mathematically expressed as

$$c_{ic} = 0.412\frac{n^*(Iz/R)}{r} + 0.387 \qquad \text{Eq. 59}$$

where
n*=effective principal quantum number
IPz = ultimate ionization energy
1/r=linear covalency or **σ**-covalency
R=Rydberg Constant. The electronegativity values of elements from Hydrogen to Lawrencium in different cationic states have been calculated by Y Zhang on the basis of Ionocovalency model.

8. Other models

8.1 Huggins (1953) model represents another alternative thermochemical procedure for electronegativity.
8.2 Walsh (1951)model brings relationship between electronegativity and stretching force constants of the bonds of an atom to hydrogen atom.
8.3 Michaelson (1978) model relates atomic electronegativity to the work function.
8.4 Martynov & Batsanov(1980) model gives electronegativity values through the average of successive ionization energies of the valence electrons of an element.

9. New model of electronegativity

In the presented work the force expression based on Hellmann-Feynman theorem has been proposed as electronegativity. This force must be equivalent to the primary definition of electronegativity such as ability of an atom to attract electron towards itself. We propose a modified primary definition of electronegativity as the inherent ability of an atom to attract and hold electron. The electronegativity in terms of this force is also equal to B-O force for an atom in diatomic system and also equal to Hartree-Fock force of an atom in poly-atomic system.

Born-Oppenheimer Force and Hartree-Fock Force:-

This force concept arises out of Born-Oppenheimer energy approximation as well as Hartree-Fock energy approximation. M Born and J R Oppenheimer[119,120] have contributed a celebrated paper to science that brings the systematic correspondence of the energy of electronic motion, nuclear vibration and rotation to the terms of power series in the fourth root of electron –nucleus mass ratio. Born and Oppenheimer have suggested that total wave function (**ψ**) can be written as the product of the nuclear wave function (**ψ**$_n$) and electronic wave function (**ψ**$_e$). This approximation simplifies complicated Schrödinger equation into electronic equation ($He\psi_e = E\psi_e$) and nuclear equation ($Hn\psi_n = E_e\psi_e$). The equation devised by them for the rotation represents a generalization of the treatment of Kramer and Pauli. This approximation also justifies Frank-Condon principle[121,122] used in explaining the intensity of band lines. In the last several decades, rigorous –mathematical work haS been reported on the validity of the B-O approximation. Quite a more no of papers[66,70–81] contain the study of B-O and also have reported that a reduced Hamiltonian is an appreciable approximation to true molecular Hamiltonian but a few is closely related to works[112,113,135] on semi- classical Schrodinger matrix operators. B-O approximation is based on "assumption of ignoring motions of nearly stationary nuclei with much larger mass and smaller velocity with respect to motion of electron with much smaller mass and larger velocity". The approximation holds good for the ground state of molecule and breaks down for the excited state. Complete Hamiltonian is represented as

$$H = H_n + H_e = T_n + T_e + V_{nn} + V_{en} + V_{ee} \qquad \text{Eq. 60}$$

$$H = -\frac{1}{2}\sum_A \nabla_A^2 - \frac{1}{2}\sum_i \nabla_i^2 + \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|} - \sum_{A,i} \frac{Z_A}{|r_i - R_A|} + \sum_{i,j} \frac{1}{|r_i - r_j|}$$

Eq. 61

Again, Molecular Hamiltonian[136] (H^{mol})

$$H^{mol} = -\frac{1}{2}\sum_{A}\nabla_A^2 - \frac{1}{2}\sum_{i}\nabla_i^2 + \sum_{B,A}\frac{\lambda^2 Z_A Z_B}{|R_B - R_A|} - \sum_{A,i}\frac{\lambda Z_A}{|r_i - R_A|} + \sum_{i,j}\frac{1}{|r_i - r_j|}$$

Eq. 62

Where λ is treated as parameter and it may vary between 0 and 1.

The exact solution to the electronic Schrodinger equation, obtained from B-O approximation can be reachable for one electron systems. For multi-electronic systems, Hartree-Fock approximation is a good enough to approximate the energies and wave function. The electronic Hamiltonian(i) and energy(ii) based on Hartree-Fock approximation can be written as follows[137] .

(i)

$$H_e = \sum_{i} z(A) + \sum_{A<B} h(A,B) + V_{nn}(R) \qquad \text{Eq. 63}$$

The first term represents a one-electron operator, the second term represents a two electron operator and third term is a constant for the fixed set of nuclei coordinates R.

(ii)

$$E_{Hrtree-Fork} = \langle \Psi_0(\lambda)|H(\lambda)|\Psi_0(\lambda)\rangle = \sum_{A}\langle A|z|A\rangle + \frac{1}{2}\sum_{AB}([AA|BB] - [AB|BA])$$

Eq. 64

Where the first term represents one-electron integral, the second as two-electron Coulomb integral, the third term as exchange integral and all the integrals can be computed by existing computer algorithms. The energy difference between non-relativistic energy of the system and Hartree-Fock limit energy is considered as both static and dynamic electronic correlation energy. The derivative (-∂He/∂R) of electronic Hamiltonian operator with respect to distance of nucleus of atom from electron can also be defined in quantum mechanics. Further, within simple Born-Oppenheimer approximation or (Hartree-Fock approximation) Energy (E) plays the role of potential energy for actual motion and also -∂E/ ∂R replaces the above derivative and it is equal to the B-O force (also Hartree-Fock force) because nuclear co-ordinates are simply treated as external parameters. The term - (∂He/∂R ≡ F) is the operator which represents the force on atom A due to electrons and other atom B. This force is better to be termed as B-O force in the steady state. The electronegativity will be equal to B-O force (also Hartree-Fock force).

Hellman-Feynman Force:

The force concept is the consequence of Hellmann - Feynman[86,138–140] theorem .The expression for this theorem have already been reported by different authors[140–144]. This concept dictates that the actual force on any nucleus can be interpreted in terms of classical electrostatics if three dimensional charge distribution in a system of electrons and nuclei were known from quantum mechanical procedure. The force on a nucleus will be equal to charge on that nucleus times the electric field due to all electrons and other nuclei. R Feynman further stated that a three dimensional electron cloud in a molecule is restricted from collapsing as it obeys Schrödinger equation. The force concept explains the nature of chemical bonding, the change in molecular shape on excitation, chemical reaction. Energy concept is not proved to be satisfactory always because they lack the simplicity and elegant nature. A.C.Hurley[145–148] has given the theoretical justification of the actual use of such electrostatic approach and shown that the force calculations are valid even for approximate wave functions. H-F force concept have been used (i) by R.F.W.Bader[149–153] for interpreting chemical binding, (ii)by Koga T and H.Nakatsuji[154–156] for force modelling of molecular geometry,(iii)by P.Politzer and K.C.Daiker[157,158] for models of Chemical Reactivity, (iv) by A.J.Coleman[159–161] for calculation of first and second order reduced density matrices and also withstand the critical examination of theoretical physists and chemists as well. This force concept has certain advantage over the concept of total energy even though the calculation of force always involves an approximate charge density function. The advantage of calculating charge density is possible through molecular orbital method and total force on a nucleus is simple sum of orbital contributions but total energy is not sum of orbital energies. The second advantage is that force is an expectation value of one-electron, momentum independent operator which is more sensitive to any change in wave functions than energy. T Berlin[87] gave clear interpretation of this electrostatic force arising out of Hellmann-Feynman theorem. This force will be equivalent to infinitesimal change in energy per change in distance (parameter). Classical physics states that a force is the negative gradient of energy. He proposed a term binding (related force acting on the nucleus) in place of bonding (related to changes in energy) in the picture of chemical bonding. He has proposed the physical partitioning of three dimensional space of electrons of diatomic system into a binding region($f_i > 1$), anti-binding region($f_i < 1$) and the nonbinding region($f_i = 1$) . The charge density is positive everywhere and thus the sign of contribution to force to the charge in each volume element depends on the sign of f_i. The net value of f_i around 1 helps to assign the electronegativity to the concerned atom in molecule for the diatomic system with $Z_B > Z_A$, the anti-binding region for A is closed while anti-binding region for B in the limit $Z_B >> Z_A$ approaches a plane perpendicular to inter-nuclear axis. The idea of closing of anti-binding region is used to justify to assign more electronegativity value to B. Hellmann-Feynman force equation can be written in various forms[86,136,162]. See below 1234

Generalized form of Hellman-Feynnman force is represented as ,

$$F_\lambda = F_\lambda' = -\partial E/\partial\lambda = -\int \psi\psi^*(\partial H_e/\partial\lambda)dv \qquad \text{Eq. 65}$$

Where $H_e = T + V$, $\frac{\partial H_e}{\partial\lambda} = \frac{\partial V}{\partial\lambda}$ and

$$\int \psi^*\psi\left(\frac{\partial V}{\partial\lambda}\right)dv \; ; \; \int \psi^*\psi V dv \qquad \text{Eq. 66}$$

$$F(R_A) = -\frac{\partial E}{\partial X_A} = -\sum_{B,A}\frac{Z_A Z_B}{|R_B - R_A|^2} + \int \frac{Z_A}{|r_i - R_A|^2}\rho(r)dr \qquad \text{Eq. 67}$$

Where the first term is independent of the electronic coordinates and is constant during integration over the coordinates. This term gives ordinary columbic force of repulsion between the nuclei. The second term represents charge density distribution due to ith electron.

$$F(R_A) = -\frac{\partial E^*}{\partial X_A} = -2\lambda \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|} + \sum_{A} Z_A \int \frac{\rho(r,\lambda)}{|r_i - R_A|} dr$$

Eq. 68

Where the λ is a parameter which solves two problems. Firstly, it helps to apply simultaneously to all nuclei. Secondly it is a continuous function between 0 and 1 so that differentiation of energy w.r.t. nuclear coordinates is made possible.

The other form of Hellmann-Feynman force equation can be written as

$$F_A(R_A) = \frac{Z_A}{R^2}\left[Z_B - \sum_i f_i(R_A) \right] \ldots \qquad \text{Eq.69.}$$

the electronic contribution to the force on either nucleus can be written as

$$F_A(R) = F_B(R) = \frac{1}{2}\left[F_A(R) + F_B(R)\right] = -\frac{1}{2}\int f(r)\rho(r)dr$$

Eq. 70

And also the electronic contribution $F_A(R)$ in terms of the quantum mechanical average of the electric field operator is also mathematically represented as,

$$F_A(R) = Z_A \int dr \ldots \int \psi^* \left[\sum_{i=1}^{N} \nabla_A \left(|r_i - R_A| \right)^{-1} \right] \psi dr_N$$

Eq. 71

The equivalence of the electron in the above equation is equivalent to N times the average force exerted on an atom by one electron so the above equation can be written in the form of electronic charge density.

$$F_A(R) = Z_A \int \nabla_A \left(|r - R_A| \right)^{-1} \rho(r) dr$$

Eq. 72

where

$$\rho(r) = N \int ds_1 \int dx_2 \ldots \int \psi^*_{(x_1,x_2,\ldots,x_N)} \psi_{(x_1,x_2,\ldots,x_N)} dx_N$$

Eq. 73

Where ρ(r) denotes electronic charge density in a stationary state, ρ(r) dr stands for amount of electronic charge in a volume element dv and x_i denotes the product of space co-ordinate (r_i)and spin co-ordinate (s_i) of the ith electron. The interpretation of ρ(r) as a physical model of the electrons in line with the HF theorem includes the possibility of ascribing a value to the electrostatic force exerted at atom A by each and every element ρ(r)dr.

9.1 Corelation among Electronegativity , Hellman-Feynman and Hartree –Fock Force

This electrostatic force leads two opposing terms such as one from nuclear-nuclear repulsions and other from electron-nuclear attractions. The electron-nuclear attractive force is expressed in terms of three dimensional electron density. This force can be termed as charge-equivalent force and this follows from the energy (Born-Oppenheimer approximation (in turn Hartree-Fock approximation) because the fast motion of electron allows electronic wave function and probability density for immediate adjustment to changes in nuclear configuration. The fast motion of electron causes the sluggish nuclei to see electrons as charge cloud rather than discrete particles. This fact affirms the force as electrostatic by nature thereby ruling out mysterious quantum mechanical force in mono-atomic, di-atomic as well as poly-atomic systems.

Electronegativity of an atom (A) in a molecule A-B may be defined as HF (Hellmann-Feynman) force which is also Hartree-Fock force in steady state and also in non-steady state. In steady state, p(r) may be interpreted as a number or charge density and p(r)dr as amount of electronic charge in the volume element. ability of an atom to attract electron. **We propose this new model i.e Electronegativity=Hellmann-Feynman Force=Hartree-Fock Force**

$$\chi = \langle F_A \rangle = -\frac{\partial E}{\partial R_A} \qquad \text{Eq.74}$$

ON THE BO approximation

$$\langle F_A \rangle = F(R_A) = -\frac{\partial E}{\partial X_A} = -\sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|^2} + \int \frac{Z_A}{|r_i - R_A|^2} \rho(r) dr$$

Eq. 75

Based on the basis of Hartree-Fock approximation

$$\langle F_A \rangle = F(R_A) = -\frac{\partial E^*}{\partial X_A} = -2\lambda \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|} + \sum_{A} Z_A \int \frac{\rho(r,\lambda)}{|r_i - R_A|} dr$$

Eq.76

Where

First terms in Eq 75 AND 76 above represent classical nuclear contribution

Second terms in Eq 75 AND 76 above represent electronic contribution

χ=Electronegativity

<F_A>= Hellman-Feynman force is a sum of classical contribution due to classical nuclear contribution and electronic contribution

F_A=one electron, momentum-independent operator

ρ(r)=electronic charge density (always positive)

x_i =product of space coordinate r_i and spin coordinate s_i of the ith electron

R_A=Distance of nucleus of atom A form electron

R_B= Distance of nucleus of atom B from electron

9.2 Computation of Electronegativity

In this paper, energy was computed by using Hartree-Fock procedure for most of the elements of the periodic table. The following equations for computation of electronegativity in terms of energy gradient (au/pm unit) considered as Hellman-Feynman Force.

(i)Xe=E(hf)/r(absolute radius) $\chi_e = \dfrac{E(hf)}{r_{absolute}}$ Eq. 77

And also, the computational equations for electronegativity have also been considered in terms Coulombic force (au) ii)X_F=Z*/r^2(absolute radius)

$$\chi_f = \frac{Z^*}{r^2_{absolute\ radius}}$$

Eq. 78

In this case, 1 a.u of force=e^2/a^2 where e=charge of electron(in coulomb) and a=Bohr radius(pm).

Electronegativity values based on energy and force from Hydrogen to Lawrencium have been computed through the above equations and are mentioned as follows.

Hartree-Fock Energy (au).[163]
Z* Slater effective neucler charge[164]
Gaussian-Energy (au) [163,165]
Slater Radius (pm)[166] emprical
Clementi Radius (pm) calculated[167,168]
Density metric Radius(pm){Boyd-1977}{Bader-1967 [169]Absolute radi Radii(pm) [170]
Z*(Clementi) [167,168]

Table1. Energy Based Electronegativity Data

ELEMENTS	Hartree-Fock Energy(HFE) (au).	Absolute Radii(pm)	X(hf)-2/AbR(pm)
H	0.499	52.92	0.01
He	2.861	31.13	0.09
Li	7.432	162.83	0.05
Be	14.572	108.55	0.13
B	24.414	81.41	0.3
C	37.531	65.13	0.58
N	54.404	54.28	1
O	74.619	46.52	1.6
F	99.163	40.71	2.44
Ne	128.546	36.71	3.5
Na	161.858	216.5	0.75
Mg	199.614	167.11	1.19
Al	241.802	136.08	1.78
Si	288.757	114.77	2.52
P	340.718	99.22	3.43
S	397.384	87.39	4.55
Cl	459.338	78.08	5.88
Ar	526.816	70.56	7.47
K	599.164	329.3	1.82
Ca	676.757	254.19	2.66
Sc	759.553	241.49	3.15
Ti	848.054	329.98	2.57
V	942.482	219.53	4.29
Cr	1043.36	210	4.97
Mn	1149.87	201.24	5.71
Fe	1262.18	193.19	6.53
Co	1380.93	185.75	7.43
Ni	1506.33	178.88	8.42
Cu	1638.96	172.5	9.5
Zn	1777.85	166.54	10.68
Ga	1923.19	144.89	13.27
Ge	2075.27	128.23	16.18
As	2234.24	114.5	19.51
Se	2399.76	104.24	23.02
Br	2572.32	95.32	26.99
Kr	2752.05	87.82	31.34
Rb	2938.36	384.87	7.63
Sr	3131.55	297.09	10.54
Y	3331.56	282.44	11.8
Zr	3538.75	268.8	13.16
Nb	3753.44	256.58	14.63
Mo	3975.55	254.43	15.63
Tc	4204.79	235.2	17.88
Ru	4441.23	225.79	19.67
Rh	4685.54	217.11	21.58
Pd	4937.92	209.07	23.62
Ag	5197.7	201.6	25.78
Cd	5465.13	194.65	28.08
In	5740.1	169.34	33.9
Sn	6022.85	149.86	40.19
Sb	6313.49	134.4	46.98
Te	6611.69	121.83	54.27
I	6917.88	111.41	62.09

Xe	7232.14	102.63	70.47
Cs	7553.93	424.33	17.8
Ba	7883.54	327.53	24.07
La	8220.95	266.73	30.82
Ce	8566.37	224.94	38.08
Pr	8920.39	194.47	45.87
Nd	9283.04	171.29	54.19
Pm	9654.39	153.03	63.09
Sm	10034.5	138.3	72.56
Eu	10423.5	126.15	82.63
Gd	10820.5	115.96	93.31
Tb	11225.8	107.3	104.62
Dy	11640.5	99.84	116.59
Ho	12064.3	93.35	129.24
Er	12497.3	87.65	142.58
Tm	12939.7	82.61	156.64
Yb	13391.5	78.12	171.42
Lu	13851.7	74.09	186.96
Hf	14321	70.56	202.96
Ta	14799.6	67.16	220.36
W	15287.4	64.16	238.27
Re	15784.5	61.41	257.04
Os	16290.5	58.9	276.58
Ir	16805.8	56.57	297.08
Pt	17330.9	54.43	318.41
Au	17865.4	52.44	340.68
Hg	18409	50.6	363.81
Tl	18961.8	186.7	101.56
Pb	19523.9	165.23	118.16
Bi	20095.6	148.18	135.62
Po	20676.4	134.31	153.95
At	21266.8	122.83	173.14
Rn	21866.8	131.15	166.73
Fr	22475.9	444.79	50.53
Ra	23094.3	343.32	67.27
Ac	23722.1	326.15	72.73
Th	24359.4	310.61	78.42
Pa	25006.5	227.56	109.89
U	25663.6	197.67	129.83
Np	26330.7	174.73	150.69
Pu	27008.4	144.96	186.32
Am	27695.9	129.15	214.45
Cm	28392.7	129.6	219.08
Bk	29099.5	112.47	
Cf	29816.7	104.65	
Es	30544.2	97.85	
Fm	31282.1	91.88	
Md	32030.6	86.59	
No	32789.5	81.88	
Lr	33557.6	80.86	

Table2. Force Based Electronegativity data

ELEMENTS	Absolute Radii(pm)	Z*(Clementi)	X Z*(Clementi)/Absolute Radii(pm) (force unit)Di-atomic System
H	52.92	1	0.357
He	31.13	1.688	1.742
Li	162.83	1.279	0.048
Be	108.55	1.912	0.162
B	81.41	2.421	0.365
C	65.13	3.136	0.739
N	54.28	3.834	1.301
O	46.52	4.453	2.058
F	40.71	5.1	3.077
Ne	36.71	5.758	4.273
Na	216.5	2.507	0.053
Mg	167.11	3.308	0.118

Al	136.08	8.963	0.484
Si	114.77	4.117	0.313
P	99.22	4.903	0.498
S	87.39	5.642	0.739
Cl	78.08	6.367	1.044
Ar	70.56	7.068	1.42
K	329.3	3.495	0.032
Ca	254.19	4.398	0.068
Sc	241.49	4.632	0.079
Ti	329.98	4.871	0.045
V	219.53	4.981	0.103
Cr	210	5.133	0.116
Mn	201.24	5.283	0.13
Fe	193.19	5.434	0.146
Co	185.75	5.576	0.162
Ni	178.88	5.716	0.179
Cu	172.5	5.842	0.196
Zn	166.54	5.965	0.215
Ga	144.89	6.222	0.296
Ge	128.23	6.78	0.412
As	114.5	7.499	0.572
Se	104.24	8.2867	0.763
Br	95.32	9.028	0.994
Kr	87.82	9.338	1.211
Rb	384.87	4.985	0.034
Sr	297.09	6.071	0.069
Y	282.44	6.256	0.078
Zr	268.8	6.446	0.089
Nb	256.58	5.921	0.09
Mo	254.43	6.106	0.094
Tc	235.2	7.227	0.131
Ru	225.79	6.485	0.127
Rh	217.11	6.64	0.141
Pd	209.07	6.766	0.155
Ag	201.6	6.756	0.166
Cd	194.65	8.192	0.216
In	169.34	8.413	0.293
Sn	149.86	10.629	0.473
Sb	134.4	11.617	0.643
Te	121.83	12.538	0.845
I	111.41	11.612	0.936
Xe	102.63	12.425	1.18
Cs	424.33	2.2	0.012
Ba	327.53	2.85	0.027
La	266.73	3.5	0.049
Ce	224.94	4.15	0.082
Pr	194.47	4.8	0.127
Nd	171.29	5.45	0.186
Pm	153.03	6.1	0.26
Sm	138.3	6.75	0.353
Eu	126.15	7.4	0.465
Gd	115.96	8.05	0.599
Tb	107.3	8.7	0.756
Dy	99.84	9.35	0.938
Ho	93.35	10	1.148
Er	87.65	10.65	1.386
Tm	82.61	11.3	1.656
Yb	78.12	11.95	1.958
Lu	74.09	12.6	2.295
Hf	70.56	12.6	2.531
Ta	67.16	13.25	2.938
W	64.16	13.9	3.377
Re	61.41	14.55	3.858
Os	58.9	15.2	4.381
Ir	56.57	15.85	4.953
Pt	54.43	16.5	5.569

Au	52.44	17.15	6.236
Hg	50.6	17.8	6.952
Tl	186.7	18.45	0.529
Pb	165.23	5	0.183
Bi	148.18	5.65	0.257
Po	134.31	6.75	0.374
At	122.83	7.6	0.504
Rn	131.15	8.25	0.48
Fr	444.79	2.2	0.011
Ra	343.32	2.85	0.024
Ac	326.15	3	0.028
Th	310.61	3.15	0.033
Pa	227.56	4.3	0.083
U	197.67	4.95	0.127
Np	174.73	5.6	0.183
Pu	144.96	5.6	0.266
Am	129.15	7.4	0.444
Cm	129.6	7.55	0.45
Bk	112.47	8.51	0.673
Cf	104.65	9.35	0.854
Es	97.85	10	1.044
Fm	91.88	10.65	1.262
Md	86.59	11.3	1.507
No	81.88	11.95	1.782
Lr	80.86	12.1	1.851

10. Conclusion

The exact status of electronegativity might be attributed as dual concept of force and energy. The attempt to measure electronegativity needs reification of this concept for which mathematical formulation is required. Till today, there exists no unique- mathematical formulation of this reified noumenon for which there had been scope of many scales o measurement. The new attempt to define electronegativity is characterized by specific physical meaning and reliable theoretical basis since it is derived from two famous mathematical formulation i.e Hellmann-Feynman theorem and Born-Oppenheimer (in turn conventional Hartree-Fock) approximation. This definition will be acting like a bridge in between two parallel definitions of electronegativity (either in energy or force) and also it will be logical to consider electronegativity equalization in a diatomic as well as polyatomic system. This new approach will be helpful to assign the more accurate electronegativity values to various elements of the periodic table and also more valuable in different areas of chemical science for example to predict the structure and property of materials and also to design efficiently new electrode materials, electrocatalysts with novel properties for energy conversion devices like Fuel cell, Solar cell etc.

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