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RESEARCH ARTICLE

ELECTRONEGATIVITY: EXPECTATION VALUE OF POWER OF AN ATOM IN A MOLECULE.

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Abstract

Advancing theory of electronegativity, new approach is established by the study of binding (or bonding) state in between two homo- atoms or hetero- atoms. Electronegativity is a confused as it is sandwiched among three entities such as i) energy ii) force iii) Charge. This paper interprets that Electronegativity (χ) is the expectation value of attracting or holding power of electron an atom in either of homo-atomic or hetero-atomic system. This value has been described in terms of von Neuman -minimax theorem: $\chi(\max A, \min B) = \chi(\min A, \max B)$ where $\max A$ and $\max B$ stands for atom's maximum ability and $\min A$ and $\min B$ stands for atom's minimum ability. Three structures (i) AB (Covalent structure); mini-max theorem, (ii) A+B- (ionic structure); right-side of mini-max theorem, (iii) A-B+ (ionic structure); left-side of theorem for giving mathematical formulation electronegativity are established. Hellmann-Feynman force as an expectation value for electronegativity is established.

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Introduction:-

Electronegativity is as old as chemical science. This chemical property cannot be measured directly. This can be calculated from other atomic or molecular properties. This is not a property of atom alone but a property of atom in a molecule. Electronegativity of the concerned atom varies with environment. In the year 1811, J.J. Berzelius, classified atoms as electronegative or electropositive. In the year 1809, Amadeo Avogadro has also introduced 'Oxygenicity' a correlated topic of electronegativity. In the year 1870 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 complete death of caloric theory of heat and the birth of thermochemistry from the laws of thermodynamics and kinetic molecular theory led the scientific community to think of a correlation between the heat of a reaction and electronegativity. The probable correlation between electronegativity and heat of reaction was suggested by Van't Hoff^{1,2}, Caven & Lander^{1,3} and Sackur^{1,4}. Electronegativity was defined with help of terminologies such as heterolytic/homolytic bond dissociation, electron affinity, ionization energy (adiabatic, ground state, ionization, ionization potential and vertical ionization), and power. The electronegativity is an intuitive construct. This is being used to sketch the distribution and rearrangement of electronic charge in molecule. 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^{5,6}, the chemical shift in NMR spectroscopy⁷, isomer shift in Mossbauer spectroscopy⁸ have already been explained. This concept has also been utilized for the design of materials for energy conversion and storage device⁹. The quest for exact status of electronegativity is unending still to date. A vast number of qualitative and quantitative scales have been proposed intuitively by different researchers across the Globe.

Mathematical formulae of Electronegativity.

2.1 Pauling's electronegativity formula ;

Linus Pauling¹⁰ expressed mathematically the difference in electronegativity as a square root of extra ionic resonance energy (D). Again, Pauling et al. in 1937 paper have reported that (D) 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

$$|C_A - C_B| = 0.208' D$$

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

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(D) arises out of contribution of ionic canonical forms to bonding and it was experimentally verified^{11,12}.

2.2 Mulliken's (1934 and 1935) absolute electronegativity

Mulliken^{14,27} 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

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

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

Where IP_A+EA_A or IP_B+EA_B is a measure of electronegativity of atom A or B,

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

$$X(M) = -\mu(M)$$

Lang and Smith^{51,52} defined electronegativity as a simple function of

$$[\text{val} (Ia) + (1 - \text{val}(Ea))]$$

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.

Other electronegativity formulae

Malone³⁹ suggested in 1933 a rough proportionality between the dipole moment of the bond A-B and electronegativity difference as

$$\mu \propto |\chi_A - \chi_B|_{\text{Pauling}}$$

Gordy has reported various ways for calculation of electronegativity values^{41,42}. One of all the three ways considers the electronegativity in terms of electrostatic potential and covalent radius.

$$\chi_g = 0.62(Z'/r) + 0.5$$

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

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

Gordy⁴⁵ correlated the ionic character with electronegativity difference by the use of nuclear quadrupole couplings constants 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

$$|\chi_A - \chi_B| = 2 \text{ for } 2 \text{ and for } |\chi_A - \chi_B| \geq 2.$$

Wilmshurst, Polansky and Derflinger [J.A.Chem.Phys. 30, 561(1959)] have reported different ionic relation: $|\chi_A - \chi_B|/|\chi_A + \chi_B| = [\text{Ionic}(AB)]$ which is used to analyse quadrupole coupling constants.

2.3.4. Phillips⁴⁶ has suggested dielectric definition of electronegativity by proposing the static electronic dielectric equation

$$\epsilon_0 = 1 + \frac{(h\omega_p / 2\pi)^2}{\left[(E_{g0})^2 + (C_{AB})^2 \right] \times a}$$

Where

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

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.

Simons^{25,47} has reported a theoretical scale to determine atomic electronegativity values where bonds are described by Gaussian Type orbitals. Simmons defined the electronegativity difference as

$$|\chi_A - \chi_B| = k \times (f_{AB} - 0.5)$$

St. John and Bloch⁴⁸ have reported quantum-defect electronegativity formula using "Pauli force" model potential⁴⁹. 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

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

Where

Z=core charge

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

The orbital electronegativity for valence orbital is defined as

$$\chi_l^{JB} \equiv \frac{1}{r_l} \equiv \frac{1}{\hat{l}(\hat{l} + 1) / Z}$$

where

l=0,1,2 represent s,p,d orbital respectively

χ_l^{JB} – orbital electronegativity for valence orbital

r – radius for valence orbital

l-orbital quantum number

Atomic electronegativity is represented as

$$\chi = 0.43 \times \sum_{l=0}^2 \chi_l^{JB} + 0.24$$

Jorgensen⁵⁰ 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 ($h\nu$) as per the following relation.

$$h\nu = [c_{OP}(X) - c_{OP}(M)] \times 10^4 \text{ cm}^{-1}$$

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 .

Electronegativity formulae based on Energy and Charge

Iczkowski-Margrave²¹, Hinze-Whitehead-Jaffe³⁷, Huheey^{25,32,53,54}, Sanderson⁵⁵⁻⁶⁰, G Klopman^{33,61,62}, Ponc⁶³, Parr et al.⁶⁴⁻⁶⁶, Watson et al.⁶⁷ have reported about direct relation of the total energy of the system with the charges.

Iczkowski & Margrave approach

RP Iczkowski and JL Margrave²¹ 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

$$E = aN + bN^2 + cN^3 + dN^4$$

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. 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.

$$\chi = - \left(\frac{dE}{dN} \right)_{N=0}$$

$$= a + 2b = \frac{IP + EA}{2}$$

Hinze-Whitehead-Jaffe –formulation to Electronegativity

Hinze et al.⁵⁷ 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

$$\chi_{A,j}(\text{atomic orbital } j) = \delta E_A / \delta n_j \dots\dots(i)$$

$$C_{A,j}(\text{atomic orbital } j) = \frac{dE_A}{dn_j} \dots\dots(i)$$

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,

$$dn_A = dn_B$$

$$\frac{dE_A}{dn_A} = \frac{dE_B}{dn_B} \dots\dots(ii)$$

R T Sanderson approach to electronegativity

R T Sanderson⁵⁵⁻⁵⁸ 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 (ΔS) is obtained from the original electronegativity (SR) with the help of the following relation $\chi(\Delta S / \chi SR = 2.08$ and χSR value is expressed in terms value $[\sqrt{\chi P} - 0.77]/0.21$ where χP =Pauling's value⁵⁷. Sanderson⁵⁹ has also defined electronegativity in terms of electron density.

G Klopman's atomic electronegativity

G Klopman^{33,61,62} 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

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

Ry– Rydberg constant

n – Principal quantum number

σ – Screening constant

Z– atomic number

dn– Quantum defect

The screening constant (σ) is represented as

$$\sigma = \sum_{j \neq i} q_j \cdot \sigma_{ji}$$

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

$$dn = 3.687(Z^*) / IP$$

Where,

n – Principal quantum number

Z^* – effective nuclear charge

IP– Ionization potential

Total electronic energy of Valence shell,

$$E_{total} = \sum_i q_i \frac{13.6}{(n-d)^2} - \sum_{j,i} q_j s_{ji} = \sum_i q_i B_i + \frac{1}{2} \sum_i \sum_{j,i} q_j q_i A_{ij}^{\pm} + \sum_i q_i \sum_{j,i} \frac{e^2}{r_{ji}} C_{ji}$$

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

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

$$E_{total} = \sum_i q_i B_i + \frac{1}{2} \sum_i \sum_{j,i} q_j q_i A_{ij}^+ d_{ij} + \frac{1}{2} \sum_i \sum_{j,i} q_j q_i A_{ij}^- (1-d_{ij}) + \sum_i \sum_{j,i} \frac{e^2}{r_{ji}} C_{ji}$$

Klopman³³ defined atomic electronegativity as the derivative of total electronic energy of the valence cell with respect to the charge q_i as mentioned below.

$$C_{Atomic-Electronegativity} = \frac{dE}{dq_i} = B_i + \sum_{j,i} q_j A_{ij}^+ d_{ij} + \sum_{j,i} q_j A_{ij}^- (1-d_{ij}) + 2 \sum_{j,i} \sum_{r,j} \frac{e^2}{r_{ji}} C_{ji} + \sum_{j,i} q_j \frac{e^2}{r_{ji}} C_{ji}$$

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 $q_j=1/2$.

Ponec 's idea of Global electronegativity

R Ponec^{11,63} has reported a generalization of the orbital electronegativity concept of Hinze et al.³⁷ and it is based on the semi empirical Complete Neglect of Differential Overlap (CNDO) approximation. Ponec's basic equation is written as,

$$\chi_{Aj} = -U_j^A - (P_A - 1/2) \gamma_A$$

Where

χ_{Aj} – orbital electronegativity

U_j^A – one electron energy of orbital j

γ_A – electron repulsion integ

Parr's density functional electronegativity;

Parr et. al⁶⁴ defines Density functional electronegativity with the help of Density Functional Theory (DFT) which is based on the theorems of Hohenbrg and Kohn⁸⁶ such as

$$\text{Theorem I : } E[r] = \int r(1) v(1) dt_1 + F[r]$$

$$\text{Theorem II : } E_v[r] = \int r(1) v(1) dt_1 + F[r]$$

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 $\rho'=\rho$, $E_v[\rho'] \geq E_v[\rho]$. 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 $\mu = -[dE/d\rho]_v = \text{constant}$ external potential and Parr et al.⁶⁴ identified electronegativity as the negative of Lagrange multiplier which is also considered as chemical potential. $\mu = -[dE/d\rho]_v = \text{external potential}$. These authors have replaced $[dE/d\rho]_v$ by the

first derivative of energy with respect to N such as $[\delta E/\delta N]_v$ on the basis work of Einhorn et al [124]. where v stands for fixed potential due to set of nuclei and external field, ρ represents for electronic density. Parr et. al.⁶⁴ defined electronegativity as,

$$c = -m = -\frac{\partial E}{\partial N} \bigg|_v$$

Parr and Bartolotti⁶⁵ proposed the formula for μ as

$$m = g \frac{IP' - EA}{IP + EA}$$

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



The geometric mean law constitutes a prediction on how molecular electronegativity are related to atom. Parr and Pearson⁶⁶ have established an Global Electrophilicity Power index

$$(w) = \mu / 2\eta$$

where η =chemical hardness

Allen's formula of Spectroscopic Electronegativity

Allen^{23,24} 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 Eenergy index (in situ X_{spec} 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 Δ_{spec}). The fractional polarity defined from Bond polarity index is equivalent of Pauling'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.

$$\text{Electronegativity-for representative elements i.e. } X_{spec} = (a \epsilon_s + b \epsilon_p) / (a + b) \quad \text{Eq-}, \quad c_{spec} = \frac{a \hat{I}_s + b \hat{I}_d}{a + b}$$

Eq- for transition elements

Implies occupation weighed average per electron ionization energy of an atom where a, b are occupation number and ϵ_p, ϵ_s are spherically ionization potentials which are determined through multiplet averaging. But for transition elements, ϵ_d, ϵ_s are spherically ionization potentials and b, a are the valence-shell occupancies of d-orbitals and s-orbitals in overlap region.

$$c_{spec} = \frac{a \hat{I}_s + b \hat{I}_d}{a + b}$$

Mulliken-Jaffe Formula of Electronegativity

Mulliken-Jaffe^{14,27,32,37} 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.

$$E = aq + bq^2$$

$$a = \frac{IE_V + EA_V}{2}$$

α –mulliken electronegativity

β – charge coefficient

E-Total energy in eV

q- ionic charge (+1 for cation, -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.

4.2. Politzer⁸² 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^{27,91,92} 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).

$$E = f(n_a, n_b, Z_a, Z_b, R)$$

For a molecule ab in the ground state under equilibrium,

$R = R_E$

$dE = 0$

$dn = -dn_a = dn_b$,

Where R_E – equilibrium inter nuclear separation between a and b

dn – Infinitesimal electronic charge under transfer from a to b

Here Electronegativity of A and B

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

In another model, total energy of the molecular system AB, $E = f(n_a, n_b, Z_a, Z_b, n_x, R)$ 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, \dots . Inter-nuclear separation $E = f(Z_a, Z_b, n_1, n_2, \dots, R)$ 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^{56,60,64,68,93}. This idea of electronegativity is not bound within a particular theory like Density Functional Theory, wave functions under quantum mechanics.

A. Therefore, electronegativity is termed as a function of oxidation number.

Zhang electronegativity is given by,

$$c_Z = 0.241[F] + 0.775$$

where

r = pauling's covalent radius

I_z = ultimate ionization potential for outer electron

Yonghe Zhang has reported dual parameter equation¹⁰¹.

$$Z = \frac{Z}{r_i^2} - 7.7c_Z + 8.0$$

where Z = Nuclear Charge,

$r(i)$ = ionic radius

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

Quantum-Mechanical formula of electronegativity;

Putz M.V.¹⁰²⁻¹⁰⁵ 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 as¹⁰⁵,

$$\chi_{Putz} = -\frac{E_0}{\rho_0} = -\mu_0$$

$$= \begin{cases} \infty & , \rho_0 \rightarrow 0 (E_0 < 0) \\ -E_0 = -\langle \psi_0 | H | \psi_0 \rangle, \rho_0 \rightarrow 1 \end{cases}$$

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.al⁶⁴ was confirmed with Putz's fundamental quantum mechanical arguments which helped in identifying the flaws made by Bergmann and Hinze¹⁰⁶.

Ionocovalency formula of electronegativity

Yonghe Zhang^{101,107,108} 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 ($E = -R.(Z)/(n)^2$) was modified by replacing energy by ultimate Ionization energy (I_z), Nuclear charge (Z) by effective nuclear charge (Z^*), principal quantum number (n) by effective principal quantum number (n^*). The expression, so obtained, $Z^* = n^*[(I_z)/R]$ was used to correlate the bond properties to the quantum mechanics and IC model is represented as

$$I(I_z) \cdot C(n^* / r) = \frac{I_z}{R} \cdot \frac{n^*}{r}$$

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

$$(X_{ic}) = 0.412[n^*(I_z/R)]/r + 0.387$$

$$c_{ic} = 0.412 \frac{n^*(I_z/R)}{r} + 0.387$$

where

n^* = effective principal quantum number

I_z = 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.

Allred and Rochow electronegativity formula

AL Allred and EG Rochow⁴³ 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.

$$X(AR) \equiv Z^*e^2 / r^2$$

Where, Z^* = effective nuclear charge, $Z^* = Z - \sigma$ (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^{43,94,95}. 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 picometer⁹⁶.

$$\dots\dots\dots (ii) \quad \chi_{AR} = 3590 \times \left(Z^* / r^2 \right) + 0.744$$

Huheey^{11,25} formula for electronegativity is based on two assumptions, $r \sim (1/Z^*)$ and $Z^* \sim \delta$.

δ – Partial atomic charge

r – Covalent radius

$$c^H = 0.36' \frac{(Z^* - 3d)}{r^2} + 0.74$$

B. 9.3. Boyd and Markus^{11,97} has reported non-empirical formula 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,

$$c = Z / r^2 - \int_0^r \rho(r) dr$$

Where

Z – Atomic number

r – Relative covalent radius

$\rho(r)$ - radial charge density where IP=ionization potential, $r \rightarrow \infty$

The radial charge density $\rho(r)$ can be obtained from the Hartree Fock atomic orbitals data^{98,99}.

Mande et al.^{11,100} has used the value of effective nuclear (Z^*) charge from 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.

The fourth extension of this scale was made by Yonghe Zhang^{11,101} where electronegativity has been calculated on the basis of electrostatic force [$F = n^* \sqrt{(Iz/R)} / r^2$] in terms of ultimate ionization potential for outer electron ($Iz = R \cdot Z^{*2} / n^{*2}$). This type of scale is based on the concept of different electron-attracting power of an element in different valence. Therefore, electronegativity is termed as a function of oxidation number.

Zhang electronegativity is given by,

$$c_Z = 0.241[F] + 0.775$$

where

r = pauling's covalent radius

Iz = ultimate ionization potential for outer electron

The concept of B-O force for electronegativity arises from Born-Oppenheimer energy approximation^{109,110} which 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-Oppenheimer has 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 Schrodinger equation into electronic equation ($H_e \Psi_e = E \Psi_e$) and nuclear equation ($H_n \Psi_n = E_n \Psi_n$). The equation devised by them for the rotation represents a generalization of the treatment of Kramers and Pauli. This approximation also justifies Frank-Condon principle^{111,112} used in explaining the intensity of band lines. In the last several decades, rigorous –mathematical works have 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^{102,103,125} 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

$$\begin{aligned}
 H &= H_n + H_e \\
 &= T_n + T_e + V_{nn} + V_{en} + V_{ee} \\
 &= -\frac{1}{2} \sum_A \tilde{N}_A^2 - \frac{1}{2} \sum_i \tilde{N}_i^2 + \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|} - \sum_{A,i} \frac{Z_A}{|r_i - R_A|} + \sum_{i,j} \frac{1}{|r_i - r_j|}
 \end{aligned}$$

Again, Molecular Hamiltonian¹²⁶ (H^{mol})

$$H^{\text{mol}} = -\frac{1}{2} \sum_A \tilde{N}_A^2 - \frac{1}{2} \sum_i \tilde{N}_i^2 + \sum_{B,A} \frac{l^2 Z_A Z_B}{|R_B - R_A|} - \sum_{A,i} \frac{l Z_A}{|r_i - R_A|} + \sum_{i,j} \frac{1}{|r_i - r_j|}$$

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

The exact solution to electronic 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) can be written as follows¹²⁷.

(i)

$$\hat{H}_e = \sum_i \hat{a}_i^\dagger z(A) + \sum_{A < B} \hat{a}_i^\dagger h(A, B) + V_{nn}(R)$$

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)

$$\begin{aligned}
 E_{\text{Hrtree-Fork}} &= \langle Y_0(l) | H(l) | Y_0(l) \rangle \\
 &= \sum_A \langle A | z | A \rangle + \frac{1}{2} \sum_{AB} \langle [AA | BB] - [AB | BA] \rangle
 \end{aligned}$$

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 ($-\partial H_e / \partial R$) 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, (Hartree-Fock approximation), Energy (E) plays the role of potential energy for actual motion and also $-\partial E / \partial R$ replaces the above derivative and it is equal to the B-O(also Hartree-Fock) force because nuclear co-ordinates are simply treated as external parameters. This term - ($\partial H / \partial R \equiv F$) 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).

Electronegativity in terms of Hellmann-Feynman Force

Hellmann - Feynman^{91,128-130} theorem is an intuitive topic. This theorem have already been reported by different authors¹³⁰⁻¹³⁴. 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 states 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.Hurley¹³⁵⁻¹³⁸ 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.Bader¹³⁹⁻¹⁴³ for interpreting chemical binding, (ii) by Koga T and H.Nakatsuji¹⁴⁴⁻¹⁴⁶ for force modelling of molecular geometry, (iii) by P.Politzer and K.C.Daiker^{147,148} for models of Chemical Reactivity, (iv) by A.J.Coleman¹⁴⁹⁻¹⁵¹ for calculation of first and second order reduced density matrices and also withstand the critical examination of theoretical physicists 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 Berlin⁹² gave clear interpretation of this electrostatic force arising out of Hellmann and 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 $Z_B \gg Z_A$ 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^{91,126,152}.

Hellman-Feynman force for steady state and non- steady state,

$$F_\lambda = -\partial E / \partial \lambda \text{ and } F'_\lambda = -\partial \bar{E} / \partial \lambda \text{ where average energy } \bar{E} = \int \psi^* H \psi d\tau$$

Generalized form of Hellman-Feynman force is represented as ,

$$F_\lambda = F'_\lambda = -\partial E / \partial \lambda = - \int \psi^* \left(\frac{\partial H}{\partial \lambda} \right) \psi d\tau \dots\dots\dots 1$$

$$\text{Where } H_e = T + V, \frac{\partial H_e}{\partial \lambda} = \frac{\partial V}{\partial \lambda} \text{ and } \int \psi^* \left(\frac{\partial V}{\partial \lambda} \right) \psi d\tau; \int \psi^* V \psi d\tau$$

$$F(R_A) = - \frac{\partial E}{\partial R_A} = - \frac{Z_A Z_B}{R_{B,A}^2} + \int \frac{Z_A}{|r_i - R_A|^2} r(r) dr \dots\dots\dots 2$$

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.

$$F(R_A) = - \frac{\partial E^*}{\partial R_A} = - 2l \frac{Z_A Z_B}{R_{B,A}^2} + \frac{Z_A}{R_A} \int \frac{r(r, l)}{|r_i - R_A|} dr \dots\dots\dots 3$$

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

$$F_A(R_A) = \frac{Z_A}{R^2} \sum_B \dot{Z}_B - \sum_i \dot{f}_i(R_A) \dots\dots\dots 4$$

Where

$$f_i(R_A) = R^2 \frac{\partial}{\partial r_i} (\cos q_{(vA)} / r_{(vA)}^2) dt$$

In the limiting condition $\cos \theta_{vA} \rightarrow 1, r(vA) \rightarrow R$ and

$$f_i^A(R \rightarrow \infty) = \int \rho_i(B) d\tau = N_i B$$

In the above force equation, the electronic contribution to the force on either nucleus can be written as

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

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

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

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.

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

where

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

Where $\rho(r)$ denotes electronic charge density in a stationary state, $\rho(r) dr$ 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 i th electron. The charge density difference distribution being combined with electrostatic HF theorem gives rise to a novel physical model to the chemical binding. The interpretation of $\rho(r)$ 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 $\rho(r)dr$. By identifying λ as real parameter in H, ψ as a normalizable Eigen function, E as Eigen value,

This force arises out of 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. H-F force concept follows from the Born-Oppenheimer energy approximation (in turn Hartree-Fock) since the rapid motion of electron allows electronic wave function and probability density will be adjusted immediately to changes in nuclear configuration. The fast motion of electron causes the sluggish nuclei to see electrons as charge cloud rather than discrete particles. The fact that “effective force on nuclei are electrostatic” affirms that there is no 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.

$$\chi = \langle F_A \rangle = -\frac{\partial E}{\partial R_A}$$

$$\langle F_A \rangle = -Z_A \int \rho(r) \frac{R_A - r_s}{|R_A - r_s|^3} dr(i) + Z_A \sum_{B \neq A} Z_B \frac{R_A - R_B}{|R_A - R_B|^3} (ii)$$

Where

(i) and (ii) represents nuclear state and bound-state respectively.

χ =Electronegativity

$\langle F_A \rangle$ = Hellman-Feynman force is

a sum of classical contribution due to electronic charge density (i) and ii) classical nuclear contribution

F_A =one electron, momentum-independent operator

$\rho(r)$ =electronic charge density (always positive)

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

R_A =Distance of nucleus of atom A from electron

R_B = Distance of nucleus of atom B from electron

Computation of Electronegativity

Electronegativity values of some elements (Table-1) have been calculated from the force equation for diatomic AB molecule such as,

$$F_A = \frac{e^2 Z_A}{R^2} - \sum_i \frac{\partial}{\partial R} (Z_B - f_i) \quad \text{-----Eq-1}$$

where 'i' is subset of AB ($i \in AB$) and electronegativity can be expressed as follows

$$C = \sum_i f_i = \sum_i f_i^{AA} + \sum_i f_i^{BB} + \sum_i f_i^{AB} \quad \text{-----Eq-2}$$

Table 1:-

Elements/Z	$\sum f_i^{AA}$ Atomic force	$\sum f_i^{BB}$ Screening force	$\sum f_i^{AB}$ Overlap force	χ Electronegativity
Fluorine/ 9	-1.949	8.381	2.505	8.937
Oxygen /8	-2.284	6.788	3.486	7.990
Nitrogen/ 7	-1.943	5.136	3.853	7.046
Carbon/ 6	-0.735	4.523	2.198	5.987
Boron /5	-0.644	3.887	1.708	4.951
Lithium /3	-0.563	2.591	0.927	2.955

Conclusion:-

Electronegativity is a confused in spite of a vast no of papers published by the various authors. Mathematical formulation is required for reification of this concept. Till today, there exists no unique- mathematical formulation for which there had been scope of many scales of measurement. This attempt to define electronegativity is characterized by specific physical meaning and reliable theoretical basis since it is derived from Hellmann-Feynman theorem and Born-Oppenheimer (in turn conventional Hartree-Fock) approximation and min-max theorem. This various definitions of electronegativity such as in terms of energy or force or intrinsic strategy are logical ones 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.

N.B:Symbol For Electronegativity; C and X

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