

A Critical Analysis on Electronegativity

P Ramakrishnan

^a Chemical Engineering Department, National Institute of Technology, Rourkela, Odisha – 769008, India

Abstract

Electronegativity is a mnemonic number for an atom in a molecule for expressing its ability to attract or hold the electron in diatomic or poly atomic system. This number is either used for energy (a quantum-mechanical entity) or for Force (non-quantum entity). In this article, a plethora of electronegativity models are revisited. A theoretical equation for Electronegativity in terms of Hellmann-Feynman Force or Ehrenfest Force is a special feature of this article. Electronegativity values are computed for various elements using numerical values of energy obtained through Hatree-Fock-Rothan calculation, effective nuclear charge and most probable radius.

Key Words: Electronegativity; Mnemonic Number, Coulomb Force, Hellmann-Feynman Force, Ehrenfest Force. Most Probable Radius.

Introduction

Electronegativity is unique and mnemonic number which is assigned to an atom through intuitive thought of researchers since the beginning of 19th century in the field of science. J.J.Berzelius, a proponent of the caloric theory of heat, has first introduced the term electronegativity. In the first decade of 19th century, Amen do Avogadro introduced 'Oxygency' a correlated topic of electronegativity. In the year 1870, Baker 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). By 1930s, the birth of thermo-chemistry from the laws of thermodynamics and kinetic molecular theory helps in establishing a correlation between the heat of a reaction and electronegativity. The 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 concept of electronegativity has been used to sketch the distribution and rearrangement of electronic charge in a molecule[5], [6]. 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[7], [8], the chemical shift in NMR spectroscopy[9], isomer shift in Mossbauer spectroscopy[10] have already been explained. This concept has also been utilized for the design of materials for energy conversion and storage device[11].

Electronegativity is also considered as an intuitive-cum-qualitative construct[12]. This qualitative construct is very difficult to be quantified. The first quantification and assignment of numerical value to electronegativity was assigned by Linus Pauling in 1932[13]. Following that landmark scale, a number of qualitative and quantitative scales for electronegativity have been proposed by different researchers across the globe to date. The quest for a new electronegativity scale is still going on as this concept remains confusing[14]. The experimental determination of electronegativity of individual surface atoms using atomic force spectroscopy has already been reported[15]. An intuitive linking map of electronegativity to three fundamental concepts is shown in Fig. 1. In this article, various concepts of electronegativity based on force, charge and energy are overviewed followed by introduction to a new concept based on Hellmann-Feynman theorem.

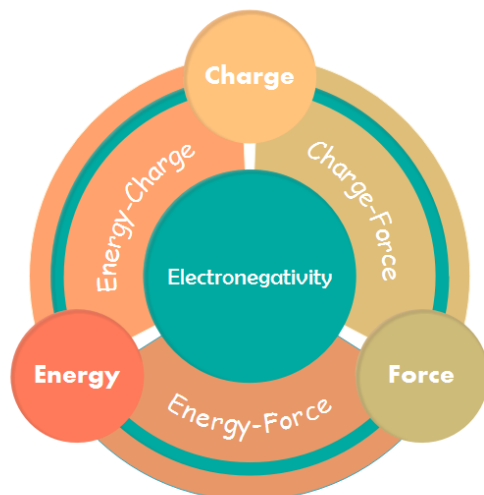


Figure 1. Intuitive linking of electronegativity with energy, force and charge

2.1 Pauling's 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[13]. 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 is not always positive. Following this, 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

$$\left| c_{Pa}^A - c_{Pa}^B \right| = 0.208 \sqrt{D} \quad (1)$$

Where,

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

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

$$i^{ionicity} = 1 - \exp\left\{-\frac{|C_{Pa}^A - C_{Pa}^B|^2}{4}\right\} \quad (3)$$

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[13] where $C_{Pa}^H = 2.1$ (arbitrary reference to construct a scale) latter changed to 2.2, $C_{Pa}^F = 4$. Furthermore, electronegativity values of 29 main group elements was proposed by Linus Pauling in 1939[19], [22]. In 1946, Haissinsky et.al. have 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 (i) 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. (ii) 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. Furthermore, this scale is criticized by Iczkowski and Marggrave[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 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, so that the complete covalent structure will be possible AB will be possible if and only if the eq. 5 is satisfied.

$$IP_A - EA_B + V = IP_B - EA_A + V \quad (4)$$

$$IP_A + EA_A = IP_B + EA_B \quad (5)$$

Mullikan suggested the term $IP_A + EA_A$ or $IP_B + EA_B$ is a measure of electronegativity of atom A or B respectively. V is coulomb potential. With IP_A and IP_B assumed to be IP and EA_A and EA_B assumed to be EA, Mullikan expressed electronegativity as

$$c_M^A = \frac{IP_A + EA_A}{2}; c_M^B = \frac{IP_B + EA_B}{2} \quad (6)$$

In general,

$$c_M^k = \frac{(IP_k + EA_k)}{2} \text{ eV} \quad (7)$$

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] concludes 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.

$$c_M = -m_M = -\frac{IP + EA}{2} \quad (8)$$

The empirical correlation reported by Mulliken[33] between χ_{Mulliken} and χ_{Pauling} as

$$c_{Pa} = \frac{c_M}{2.78} = \frac{(IP + EA)}{2.78} \quad (9)$$

1/2.78 is scale adjustment factor. Huheey[38] reported Mulliken electronegativity as

$$\text{For IP and EA in electron volts } c_M = 0.187(IP + EA) + 0.17 \quad (10)$$

$$\text{For IP and EA in kilojoules per mole } c_M = 1.97 \times 10^{-3}(IP + EA) + 0.19 \quad (11)$$

Pritchard and Skinner[39], [40] have reported the correlation between χ_M and χ_{Pa} as

$$c_M = 3.15' c_{Pa} \quad (12)$$

In eq. 12 IP, EA are expressed in kcal/mol. 3.15 is scale adjustment factor. They have given an extensive set of Mulliken electronegativity values. Ionization potential and electron affinity are associated with the atomic orbital forming the bond. The valence state energies must be used in calculating IP which 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 IP and EA with respective removal of electron from highest occupied atomic orbital (HOMO) and addition of electron to lowest unoccupied atomic orbital(LUMO). 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 provide with extensive studies of Mulliken's electronegativity values for non-transition atoms with various valence states[17], [42], [43]. Major disadvantages of Mulliken electronegativity include consideration of isolated atomic properties (IP and EA), non-inclusion of all valence electrons, unavailability of electron affinity data. The electron affinity is for 57 elements by 2006[17], [26], [37], [44], incorrect determination of electronegativity values for transition metals.

2.3 Lang-Smith definition of electronegativity

Lang and Smith[45], [46] defined electronegativity as a simple function of ionization potential and electron affinity.

$$c_{LS} = val(IP) + 1 - val(EA) \quad (13)$$

The quantity 'val' is taken as a fraction less than 1. The ionization potential or energy values 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.

2.4 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. He projected it as third dimension or energy dimension of periodic table. According to this definition, 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 Energy index (in situ C_{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 ∇C_{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 of funnel shaped potential energy plots (E vs r) along a line of increasing atomic number (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 C_{spec} and energy level spacing (large C_{spec} with large spacing). This is similar to energy level of Fermi-Thomas-Dirac 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 resulting 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.

Spectroscopic electronegativity for s and p orbital elements is represented as,

$$c_{spec(s,p)} = \frac{a' IP_s + b' IP_p}{a + b} \quad (14)$$

Eq. 14 represents occupation weighed average per electron ionization energy of an atom where a,b are occupation number and IP_s , IP_p are spherically ionization potentials determined through multiplet averaging. However, IP_p is replaced by IP_d and a,b are the valence-shell occupancies of s-orbitals and d-orbitals in overlap region for transition elements.

$$c_{spec(d)} = \frac{a' IP_s + b' IP_d}{a + b} \quad (15)$$

Major advantage of this definition is that, necessary spectroscopic energy data are available for many elements. Electronegativity of Francium was estimated using this definition. The drawbacks of this scale are (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 valence electron has been developed so far. (ii) Reason for electronegativity order such as Neon>Fluorine>Helium>Oxygen is yet to be given.

Optical electronegativity scale

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

$$hn = [c_{OP}(X) - c_{OP}(M)] \cdot 3 \cdot 10^4 \text{ cm}^{-1} \quad (16)$$

A linear relationship of c_{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 electronegativity.

2.6 Spin-Orbital electronegativity

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

2.7. Simons scale of atomic electronegativity

Simons[31], [50] 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 ($f_{AB} = r_A(r_A + r_B)^{-1}$) 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

$$|\chi_A - \chi_B| = k \times (f_{AB} - 0.5) \quad (17)$$

This scale is established with $C_{Lithium} = 1$ and $C_{Fluorine} = 4$. This scale is quite consistent with Pauling scale and Allred-Rochow scale.

2.8. Quantum-defect electronegativity scale

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

$$E(n,l) = -0.5Z^2 \frac{1}{n^2} + \hat{l}(l) - l \frac{\tilde{\nu}}{a}^2 \quad (18)$$

$\hat{l}(l) - l$ represents quantum defect.

The orbital electronegativity for valence orbital is defined as

$$C_l^{JB} = \frac{1}{r_l} \frac{1}{\hat{l}(\hat{l} + 1) / Z} \quad (19)$$

l takes the value 0,1,2 represent s,p,d orbital respectively. Atomic electronegativity is represented as

$$\chi = 0.43 \times \sum_{l=0}^2 \chi_l^{JB} + 0.24 \quad (20)$$

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[53]. They have suggested that this scale is sensitive indicator of chemical trends in the structures of solids and complex systems.

2.9. Size Dependent Electronegativity

D C Ghosh[54] defined electronegativity on the basis of environment independent absolute radii of atoms. He treated electronegativity as an intrinsic free-atom property and quantum mechanically viable. He has suggested the following quantitative general formula.

$$c = c_1(1/r_{absolute}) + c_2 \quad (21)$$

The constants C_1, C_2 are determined by least square fitting method. This empirical formulation is based on the fact that, the computation of one atomic property is made from other atomic properties[55], [56]. Furthermore, this derives the theoretical support from mathematical relationship between chemical potential and radius as derived by Dmitrieva and Plindov on the basis of statistical Fermi-Amaldi model[57].

2.10. Energy-Charge model of electronegativity

Iczkowski-Margrave[27], Hinze-Whitehead-Jaffe[43], Huheey[31], [38], [58], [59], G Klopman[39], [60], [61], Ponc[62], Parr et al.[63]–[65], Mulliken-Jaffe[20], [33], [38], [43] and Watson et al.[66] have reported possible relation of the total energy of the system with the charges.

2.11 Mulliken-Jaffe electronegativity approach

Mulliken-Jaffe[20], [33], [38], [43] electronegativity approach is based first ionization energy and the electron affinity. It can be expressed as sum of multiple ionization potential and electron affinity energies. A fitted quadratic equation is given in eq. 22.

$$E = c_M q + q q^2 \quad (22)$$

$$c_M = \frac{IE_V + EA_V}{2} \quad (23)$$

E stands for total energy in eV. Based on this approach the electronegativity of a few elements of the periodic table can be computed.

2.12. Huheey's Idea of Group electronegativity

James E Huheey[58], [59] in 1965 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.

$$[a'_w + b'_w d_w = a'_x + b'_x d_x] - - - \text{Group} - wx \quad (24)$$

$$[a'_w + b'_w d_w = a'_x + b'_x d_x = a'_y + b'_y d_y] - - - \text{Group} - wxy \quad (25)$$

$$[a'_w + b'_w d_w = a'_x + b'_x d_x = a'_y + b'_y d_y = a'_z + b'_z d_z] - - - \text{Group} - wxyz \quad (26)$$

Eq. 24-26 are coupled separately with relations like d_G of value 0(Radical),1(cation), -1(anion). The Huheey-relation between group electronegativity and partial charge in group is given in eq. 27.

$$c_G = a\phi + b\phi_G, \quad a' = \frac{IP - EA}{2}, b' = IP + EA \quad (27)$$

J Mullay[17] has reported the value of ' b' ' as 1.5 times of ' a' '. S G Bratsch[17], [67] simplified Huheey's scheme by using Sanderson's principle of electronegativity equalization. The followings simplified relations was derived.

$$c = \frac{(N + d_G)}{\bar{a} (n) / c_A} \quad (28)$$

In eq. 28 χ represents equalized electronegativity for the molecule or the group, n represents number of A atoms, $N = \sum(n)$ represents the total number of atoms, δ_G is the charge in the group.

Huheey's method expresses total electronegativity equalization[38], [68]. However, this method has three major shortcomings i.e. inability to account for differences in isomers, treating groups with multiple bonding and overestimating the effect of the atoms or groups linked to the bonding atom.

2.13 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

$$c_{A,j(\text{atomic orbital } j)} = \frac{dE_j^A}{dn_j} \quad (29)$$

(30)

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.

The Hinze et al. approach to the electronegativity theory is somewhat simple because it neglects resonance and electrostatic effects[17], [58], [59], [69]–[71]. Pritchard[69] 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[63], [72]. Politzer et. al. have reported the non-importance of the idea of orbitals in electronegativity theory[73]. Mullay[17] and Watson et. al.[17], [66] have reported the potential usefulness of group electronegativity which are obtained from the idea of orbital electronegativity in conjunction with electronegativity equalization. The Hinze et al.'s[42], [43] work is simple still then it did not meet the criterion for electronegativity. Some authors[74] suggest that the orbital concept of electronegativity never solves the meaning 'Atom in Molecule'.

2.14 G Klopman's atomic electronegativity

G Klopman[39], [60], [61] 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

$$E = \frac{Ry(Z - s)^2}{(n - dn)^2} = \frac{13.5(Z - s)^2}{(n - dn)^2} \text{ eV} \quad (31)$$

The screening constant (σ) is represented as

$$s = \sum_{j \neq i} q_j s_{ji} \quad (32)$$

The value of σ (core electron–valence cell electron) is considered to be 1 because core electrons are not

considered. Quantum defect (dn) is calculated from respective ionization potential i.e. $dn = 3.687(Z^*) / IP$

$$(33)$$

Total electronic energy of Valence shell,

$$E_{total} = \sum_i q_i \frac{13.6}{(n - dn)^2} - \sum_{j \neq i} q_j s_{ji} = \sum_i q_i B_i + \frac{1}{2} \sum_i \sum_{j \neq i} q_j q_i A_{ij}^{\pm} + \sum_i \sum_{j \neq i} q_i q_j C_{ji} \quad (34)$$

$$B_i = 13.6 \frac{Z^2}{(n - dn)^2}; \frac{1}{2} A_{ij}^{\pm} = -2[13.6 / (n - dn)^2] Z s_{ij}; C_{ji} = \frac{13.6}{(n - dn)^2} s_{ji}^2 \quad (35)$$

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

$$E_{total} = \sum_i q_i B_i + \frac{1}{2} \sum_i \sum_{j \neq i} q_j q_i A^+ s_{ij} + \frac{1}{2} \sum_i \sum_{j \neq i} q_j q_i A^- (1 - s_{ij}) + \sum_i \sum_{j \neq i} \frac{q_i q_j}{\epsilon_{ij}} C_{ij} \quad (36)$$

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

$$C_{Atomic- Electronegativity} = \frac{dE_{total}}{dq_i} = B_i + \sum_{j \neq i} q_j A^+ d_{ij} + \sum_{j \neq i} q_j A^- (1 - d_{ij}) + 2 \sum_{j \neq i} \frac{q_i q_j}{\epsilon_{ij}} C_{ij} + \sum_{j \neq i} \frac{q_j^2}{\epsilon_{ij}} C_{ij} \quad (37)$$

Furthermore, the 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 $q_j = 1/2$.

Kolpman's procedure helps in calculating neutral atomic electronegativity. This procedure provides theoretical support and clarification for electronegativity formulated by Iczkowski and Margrave[27]. 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].

2.16 Ponec 's idea of Global electronegativity

R Ponec[17], [62] has reported a generalization of the orbital electronegativity concept of Hinze et al.[43]. It is based on the semi empirical Complete Neglect of Differential Overlap (CNDO) approximation. Ponec's basic equation is written as,

$$c_{Aj}^{JB} = - E_j^A - (r_A - 1/2)g_A \quad (38)$$

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

$$c_{G(A)} = \frac{\sum_j P_j c_{Aj}^{JB}}{\sum_j P_j} \quad (39)$$

Global electronegativity values for some molecules have been correlated to X-ray Photoelectron Spectroscopy (ESCA) chemical shifts with good results. Ponec's extension⁵⁶ of the ideas based on Intermediate Neglect of Differential Overlap (INDO) approximation gives better results than those obtained by H O Pritchard[69].

2.17 Iczkowski & Margrave approach to Electronegativity.

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

$$E = a_1N + a_2N^2 + a_3N^3 + a_4N^4 \quad (40)$$

In eq. 41, N is the net-charge on the atom and the charge coefficients a_1, a_2, a_3, a_4 are the constants that depend atom including its valence state. 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 w.r.t. N.

$$c = - \left. \frac{dE}{dN} \right|_{N=0} \quad (41)$$

This derivative represents the potential around the atom for a given atomic charge. Furthermore, it measures the power of atom to attract electrons. In eq. 42, The quantity $-(dE/dN)_{N=0}$ (for neutral atom) represents electronegativity. This also represents (i) the tendency of an atom in a molecule to attract electrons for small charge dislocation during interaction of atoms, (ii) the decrease of energy of more electronegative atom than the increase in energy for less electronegative atom. Hence, the energy of molecule is decreased simply by transfer of charge from one atom to another. The energy change in this case is not at all accrued from the electrostatic attraction between ions. Therefore, electronegativity characterizes both the internal constitution of atom and the ions which can be formed from it. Moreover, the electronegativity represents an intensity factor in charge transfer from one atom to the other atom.

This concept of electronegativity in terms of energy-charge derivative have also been justified through ingenious and laudable efforts of various authors[75]–[78]. 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], [79] 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.

$$\frac{\partial E}{\partial N} = a_1 + 2a_2 = \frac{IP + EA}{2} \quad (42)$$

With this approximation, Jaffe et al.[80] 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[81] helped in initiating the calculation of charge distribution. V) The above general principle was used by Ferreira[82] for calculation of bond energy and charge distribution in many binuclear molecules. Despite above advantages, 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 as continuous and differentiable’ is already criticized by various authors[83]–[86].

2.18 Parr’s density functional electronegativity;

Parr et. al[63] defines Density functional electronegativity with the help of Density Functional Theory (DFT) which is based on the theorems of Hohenberg and Kohn[87] such as

$$\text{Theorem I : } E[r] = \int r(1)v(1)dt_1 + F[r] \quad (43)$$

$$\text{Theorem II : } E_v[r] = \int r(1)v(1)dt_1 + F[r] \quad (44)$$

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 $r = r'$, $E_v[r'] \leq E_v[r]$. 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 $m = - (dE/dr)_v$, being constant external potential, Parr et al.[63] identified electronegativity as the negative of Lagrange multiplier which is also considered as chemical potential m equivalent to external potential. These authors have replaced $(dE/dr)_v$ by the first derivative of energy with respect to N such as $(dE/dN)_v$ on the basis of work by Einhorn et. al.[63], [76].where v stands for fixed potential due to set of nuclei and external field, r represents for electronic density. Parr et. al.[63] defined electronegativity as,

$$\chi = -m = - \frac{\partial E}{\partial N} \quad (45)$$

by considering the similarity between the above expression for μ and electronegativity expression of Iczwoski and Margrave in eq. 42. 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. The fall-off parameter γ is same for chemical potentials of neutral atoms. Again from density functional theory studies, for a nearly neutral atom, energy is an exponentially decaying function of the number of electrons. However, the classical suggestion states that, the energy is a quadratic function of number of electrons. The classical suggestion leads to the Mulliken formula of electronegativity in eq. 8. Parr and Bartolotti[64] proposed the formula for m as

$$m = g \frac{IP' - EA}{IP - EA} \quad (46)$$

They proposed the approximate constancy of γ (i.e. a fall-off parameter) in the following electron loss and gain process such as $A^+ \rightarrow A + e^+$ and $A^- \rightarrow A + e^-$. The geometric mean law constitutes a prediction on how molecular electronegativity is related to atomic electronegativity. It 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[64] 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[65] established an Global Electrophilicity Power index term such as in this case

$$(w) = \frac{m^2}{2h} \quad (47)$$

This index is a measure of lowering energy of the chemical entity during the transfer of electron. The density functional electronegativity encounters with severe differentiability problem[75], [76] where a discontinuous function is put forcibly to differentiation by violating the basic definition of derivative. This problem was solved partially by ingenious efforts of the proponents[77], [78], [88], [89]. The strength for this concept comes from electronegativity equalization principle. In this instance, electronegativity is defined in terms of ground-state energy of a free atom or a free molecule. The conversion of Parr et. al.[63] electronegativity into Mulliken electronegativity was made possible by considering dE/dN as average of DE/DN 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[90] and Datta et. al.[91] pointed out that, Parr et. al.[63] 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.

2.19 Politzer's endorsement to electronegativity equalization

Politzer[73] 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], [92], [93] is deduced in terms of two physical models. In one model, total energy of molecular system AB is taken as a function of associated electrons with each atom (n_A and n_B), corresponding atomic numbers (Z_A and Z_B) and inter-nuclear separation (R). Total energy of molecular system AB is

$$E = f(n_A, n_B, Z_A, Z_B, R) \quad (48)$$

For a molecule AB in the ground state under equilibrium,

$$R = R_E; dE = 0; dq = -dn_A = dn_B \quad (49)$$

In eq. 50 the term dq is the Infinitesimal electronic charge under transfer from A to B. The electronegativity of A and B is expressed as,

$$-\left(\frac{\partial E}{\partial N_A}\right)_{R_E, n_B} = c_A, -\left(\frac{\partial E}{\partial N_B}\right)_{R_E, n_A} = c_B \quad (50)$$

In another model, total energy of the molecular system AB, $E = f(n_A, n_B, Z_A, Z_B, n_x, R)$ is a function of atomic numbers Z_A, Z_B , atoms n_A, n_B , delocalized atoms n_x and inter nuclear separation R . The electronegativity values (or the chemical potential) have been reported by authors[63], [75], [94]–[96]. This idea of electronegativity is not bound within a particular theory like Density Functional Theory or wave functions under quantum mechanics.

R T Sanderson approach to electronegativity

R T Sanderson[81], [94], [97], [98] considered electronegativity as 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). 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 is obtained from the original electronegativity with the help of the relation in eq. 52[97]. Sanderson[99] has also defined electronegativity in terms of electron density.

$$V_{c_{sr}} = 2.08' \sqrt{c_{sr}} \quad (51)$$

Where

$$c_{sr} = 4.76(\sqrt{c_{Pa}} - 0.77) \quad (52)$$

2.21 Gordy's electronegativity scales

Gordy has reported various ways for calculation of electronegativity values[53], [100]. One of them considers the electronegativity in terms of electrostatic potential and covalent radius.

$$c_g = 0.62 \frac{Z'}{r} + 0.5 \quad (53)$$

The screening factor for close shell electrons and valence electrons in Gordy's technique are 1 and 0.5 respectively.

For the atom with p number of valence electrons $Z = 0.5(p + 1)$. Eq. 54 is modified as,

$$c^G = 0.31' \frac{(p + 1)}{r} + 0.5 \quad (54)$$

This scale is very useful because of introducing the idea of the electrostatic potential into electronegativity. It brings the equivalence of electronegativity with Allred-Rochow force scale[101] in spite of the basis of two different parameters. Politzer and Parr[102] reported some merit in the Gordy scale which gains theoretical support to some extent from Iczkowski[27]. However, Gordy's electronegativity can not be correlated with Pauling because of severe difficulty in estimation of screen nuclear charge.

In another attempt, Gordy[103] correlated the ionic character with electronegativity difference by the use of nuclear quadrupole couplings constants for halide molecules. Gordy assumed the use of p-orbitals by halogen atoms in formation of single bonds and established the ionic character equation.

$$\left| c_g^A - c_g^B \right|^3 \quad 2 \quad (55)$$

Wilmshurst[104] have reported different ionic relation, $\left| c_A - c_B \right| / \left| c_A + c_B \right| = \text{Ionic}(AB)$ which is used to analyze quadrupole coupling constants.

2.22 Boyd and Edgecombe([105]Boyd and Edgecombe, 1988)(Boyd and Edgecombe 1988)(Boyd & Edgecombe, 1988)(Boyd and Edgecombe 1988)(Boyd and Edgecombe 1988)¹⁰⁵[105]¹⁰⁵ approach to electronegativity

Boyd and Edgecombe[105] have defined electronegativity quite differently from that of Pauling and Allred & Rochow. The electronegativity was computed from 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. According to this definition, electronegativity is supposed to be direct function of charge density at minimum no of valence electrons, non-metal hydride separation and an inverse function of atomic radii.

2.24 Electronegativity and dipole moment

Malone[106] suggested a rough proportionality between the dipole moment of the bond A-B and electronegativity difference as

$$\left| c_A - c_B \right|_{Pa} = m_{dipole} \quad (56)$$

Where m_{dipole} is dipole moment in debye (CGS unit of electric dipole moment). Malone's measure of electronegativity was rejected because of the reports made Coulson[107].

2.25 Dielectric definition of electronegativity

Phillips[108] 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 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

$$e_0 = 1 + \frac{(hw_p / 2p)^2}{\epsilon_0 (E_{g0})^2 + (C_{AB})^2 \frac{u}{u}} a_0 \quad (57)$$

Where,

$$C_{AB} = 0.9e^2 \left(\frac{Z_A}{r_{A0}} - \frac{Z_B}{r_{B0}} \right) \exp(-k_s r_{A0}) \quad (58)$$

a_0 is a number of order unity. C_{AB} is the semi-classical charge transfer constant which represents dielectric electronegativity. This scale is exclusively used for calculation of electronegativity values for tetravalent elements like Carbon, Silicon, Germanium and Tin.

2.26 Allred and Rochow absolute scale

AL Allred and EG Rochow[101] defined the electronegativity of an atom with help of electrostatic field. According to this definition, electronegativity is equal to Coulomb force of attraction between the nucleus and an electron at the covalent radius.

$$c_{AR} \propto Z^* \frac{e^2}{r^2} \quad (59)$$

The term $Z^* = Z - \sigma$. In eq. 60, r is 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 that drags electron towards nucleus. Therefore, electronegativity is an absolute one. c_{AR} dimension is not straight forward as it is evaluated through eq. 60. The quantity Z^*/r^2 was calculated through Pauling's work and Slater rules for determining the effective nuclear charge[101], [109], [110]. 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 [111]. Here mean radius is expressed in picometer.

$$c_{AR} = 3590' (Z^* / r^2) + 0.744 \quad (60)$$

The numbers 3590 and 0.744 are arbitrary numerical constants. Eq.61 does not compute any force in the real world.

Introduction of the idea of force into electronegativity theory makes this scale seem quite consistent with Pauling's definition. It also emphasizes the idea for simple calculation, because r and Z^* are readily available quantities for many elements. It is to be noted that, this scale independent of electron affinities and bond dissociation energies. Slater rules for finding effective nuclear charge are empirical.

Four extension of the Allred and Rochow's idea were reported by different authors. The first extension of Allred-Rochow scale by Huheey[17], [31] is based on two assumptions, r of order $(1/Z^*)$ and Z^* of order σ .

$$c_H = 0.36' \frac{(Z^* - 3s)}{r^2} + 0.74 \quad (61)$$

The second extension of Allred-Rochow scale by Boyd and Markus[17], [112] is based on non empirical approach. The empirical covalent radius is replaced by relative covalent radius 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,

$$c = \frac{Z}{r^2} \int_0^r \rho(r) dr \quad (62)$$

The radial charge density $\rho(r)$ can be obtained from the Hartree Fock atomic orbitals data[113], [114]. 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 $\rho(r)$ decreases as per the expectation rule i.e. $\langle IP' r \rangle > \text{¥}$.

The third extension of the scale was made Mande et al. [17], [115] where the value of effective nuclear (Z^*) charge was obtained spectroscopic analysis. Therefore, the values become less arbitrary than that of 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[17], [116] where electronegativity was calculated on the basis of electrostatic force given by,

$$F = n^* \frac{\sqrt{IP_z / Ry}}{r^2} \quad (63)$$

$$\text{Where } IP_z = Ry \frac{Z^* \sigma^2}{n^* \sigma} \quad (64)$$

IP_Z is ultimate ionization potential for outer electron. This type of scale is based on the concept of different electron attracting power of an element in different valence state. Therefore, electronegativity is termed as a function of oxidation number. Zhang has also reported dual parameter equation[116]. Zhang electronegativity is given by,

$$c_z = 0.241F + 0.775 \quad (65)$$

$$Z = \frac{Z}{r_i^2} - 7.7c_z + 8.0 \quad (66)$$

2.27 Quantum model of Electronegativity

Putz M.V[117]–[120] defined electronegativity by a specialized affinity ionization wave function within Fock Space having fermions(electrons). The quantum mechanical description of electronegativity was made through field perturbation on a valence state for chemical system. Putz electronegativity is also termed as quantum electronegativity. It is considered as viable quantum concept with observable character. The mathematical expression is represented as[120],

$$c_{\text{Putz}} = - \frac{E_0}{r_0} = - m_0 \frac{\int \psi^* H \psi}{\int \psi^* \psi} - E_0 = - \langle y_0 | H | y_0 \rangle, r_0 \approx 1 \quad (67)$$

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[63] was confirmed with Putz's fundamental quantum mechanical arguments. It helped in identifying the flaws made by Bergmann and Hinze[121].

2.28 Ionocovalency model of Electronegativity

Yonghe Zhang[116], [122], [123] has reported the Ionocovalency model of electronegativity well correlated with quantum mechanical potential. This model describes the properties of effective ionic potential, charge density, charge distribution, effective polarizing power and bond strengths quantitatively. Ionocovalency (IC) was defined as a product of the ionic function $I(Z^*)$ and the covalent function $C(1/r)$. The Bohr energy expression $E = - Ry(Z/n)^2$ was modified by replacing energy by ultimate Ionization energy(IP_Z), Nuclear charge(Z) by effective nuclear charge(Z^*) and principal quantum number (n) by effective principal quantum number(n^*). The

expression, so obtained, $Z^* = n^*(IP_Z / Ry)$ was used to correlate the bond properties to the quantum mechanics. Ionocovalency model is represented as,

$$I(IP_Z) \cdot C(n^* / r) = \frac{IP_Z}{Ry} \cdot \frac{n^*}{r} \quad (68)$$

The electronegativity defined in terms of Ionocovalency is correlated with Pauling's electronegativity values. It is mathematically expressed as,

$$c_{ic} = 0.412[n^*(IP_Z / Ry)(1/r)] + 0.387 \quad (69)$$

The term $1/r$ represents linear covalency or sigma covalency. 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[123].

2.29 Other models

Huggins model represents another alternative thermochemical procedure for electronegativity[124]. Walsh model brings relationship between electronegativity and stretching force constants of the bonds of an atom to hydrogen atom[125]. Michaelson model relates atomic electronegativity to the work function[126]. Martynov and Batsanov model gives electronegativity values through the average of successive ionization energies of the valence electrons of an element[127], [128].

3. New model of electronegativity

The above presented models of electronegativity are theorized by individual's intuition. The qualitative understanding of electronegativity is not up to the mark. Universal acceptance on the common agreement of the above models seems impossible. In this section an independent approach to define electronegativity is presented. The force expression based on Hellmann-Feynman theorem is proposed as electronegativity. Moreover, this force must be equivalent to the primary definition of electronegativity such as ability of an atom to attract electron towards itself. Following the proposition, the definition of electronegativity becomes 'inherent ability of an atom to attract and hold electron'. The electronegativity in terms of Hellmann Feynman force is equal to Born Oppenheimer force for an atom in diatomic system and Hartree Fock force of an atom in poly atomic system. Prior to the force based definition of electronegativity and relevant correlations, the four relevant force concepts are briefly discussed.

3.1 Born-Oppenheimer Force

This force concept arises out of Born Oppenheimer(BO) energy approximation. M Born and J R Oppenheimer[129], [130] have contributed a celebrated paper to science. It 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 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 ($H_e\psi_e = E_e\psi_e$) 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 theorem and Pauli exclusion principle[131], [132]. This approximation also justifies Frank-Condon principle[133], [134] used in explaining the intensity of band lines. In the last several decades, rigorous mathematical work has been reported on the validity of the BO approximation. Quite a few number of papers 66,70–81 contain the study of BO have reported that, a reduced Hamiltonian is an appreciable approximation to true molecular Hamiltonian. However, a few of those are closely related to works on semi classical Schrodinger matrix operators[117], [118], [147]. BO 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

$$H = H_n + H_e = T_n + T_e + V_{nn} + V_{en} + V_{ee} \quad (70)$$

$$H = -\frac{1}{2} \nabla_A^2 - \frac{1}{2} \nabla_i^2 + \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|} - \sum_{A,i} \frac{Z_A}{|r_i - R_A|} + \sum_{i,j} \frac{1}{|r_i - r_j|} \quad (71)$$

Again, Molecular Hamiltonian[148] (H^{mol})

$$H^{mol} = -\frac{1}{2} \nabla_A^2 - \frac{1}{2} \nabla_i^2 + \sum_{B,A} \frac{l^2 Z_A Z_B}{|R_B - R_A|} - \sum_{A,i} \frac{l Z_A}{|r_i - R_A|} + \sum_{i,j} \frac{1}{|r_i - r_j|} \quad (72)$$

λ is treated as parameter and it may vary between 0 and 1. The exact solution to the electronic Schrodinger equation, obtained from BO approximation can be reachable for one electron systems.

3.2 Hartree-Fock Force

This force concept arises out of Hartree-Fock energy approximation for multi electronic systems. The Hartree-Fock approximation is a good enough to approximate the energies and wave function. The electronic Hamiltonian and energy based on Hartree-Fock approximation can be written as follows[149].

$$H_e = \sum_i \hat{a}_i z(a) + \sum_{a<b} \hat{a}_{ab} h(a,b) + V_{nn} \quad (73)$$

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 nuclear coordinates

$$E_{hf} = \sum_a \hat{a}_a \langle a|z|b \rangle + \frac{1}{2} \sum_{ab} \hat{a}_{ab} ([aa|bb] - [ab|ba]) \quad (74)$$

Where the first term represents one electron integral, the second term represents two electron Coulomb integral, the third term represents exchange integral. 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 ($-\partial H_e / \partial V$) of electronic Hamiltonian operator w.r.t. distance of nucleus of an atom from electron can also be defined in quantum mechanics. Furthermore, within simple Born-Oppenheimer approximation and Hartree-Fock approximation, Energy (E) plays the role of potential energy for actual motion. Moreover, $\partial E / \partial V$ replaces the above derivative and it is equal to the BO force (also Hartree Fock force) because nuclear coordinates are simply treated as external parameters. The term ($-\partial H_e / \partial V^0 = F$) 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 BO force in the steady state. The electronegativity will be equal to B-O force (also Hartree Fock force)[150].

3.3 Hellman-Feynman Force

The force concept is the consequence of Hellmann Feynman[92], [151]–[153] theorem. The expression for this theorem have already been reported by different authors[153]–[157]. 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 and chemical reaction. Energy concept is not proved to be satisfactory always because they lack the simplicity and elegant nature. A.C.Hurley[158]–[161] 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. The Hellmann Feynman force concept have been used (i) by R.F.W.Bader[162]–[166] for interpreting chemical binding, (ii) by Koga T and H.Nakatsuji[167]–[169] for force modelling of molecular geometry,(iii) by P.Politzer and K.C.Daiker[170], [171] for models of Chemical Reactivity, (iv) by A.J.Coleman[172]–[174] for calculation of first and second order reduced density matrices. It also withstands 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. The 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. It is more sensitive to any change in wave functions than energy. T Berlin[93] gave clear interpretation of this electrostatic force arising out of Hellmann Feynman theorem. This force is 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[92], [148], [175]. See eq. 76-86 for reference.

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

$$F_V = - \left(\frac{\partial E}{\partial V} \right) \quad (75)$$

$$F_V = - \langle E / \langle V \rangle \quad (76)$$

$$\text{where average energy } \bar{E} = \int \psi^* H \psi \, dv \quad (77)$$

Generalized form of Hellman Feynman force is represented as ,

$$F_V = F_V = - \langle E / \langle V \rangle = - \int \psi^* \nabla H_e / \langle V \rangle \psi \, dv \quad (78)$$

$$\text{Where } H_e = T + V, \quad \frac{\langle H_e \rangle}{\langle V \rangle} = \frac{\langle V \rangle}{\langle V \rangle} \quad \text{and} \quad \int \psi^* \nabla \left(\frac{\langle V \rangle}{\langle V \rangle} \right) \psi \, dv; \quad \int \psi^* \nabla V \psi \, dv \quad (79)$$

$$F(R_A) = - \frac{\langle E \rangle}{\langle V_A \rangle} = - \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|^2} + \int \frac{Z_A}{|r_i - R_A|^2} r(r) \, dr \quad (80)$$

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

$$F(R_A) = - \frac{\langle E \rangle}{\langle V_A \rangle} = - 2l \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|^2} + \sum_A Z_A \int \frac{r(r, l)}{|r_i - R_A|^2} \, dr \quad (81)$$

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

$$F(R_A) = \frac{Z_A}{R_A^2} \sum_B Z_B - \sum_i f_i(R_A) \quad (82)$$

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

$$F(R_A) = F(R_B) = \frac{1}{2} [F(R_A) + F(R_B)] = - \frac{1}{2} \int f(r) r(r) \, dr \quad (83)$$

The term $f(r)$ is called berlin quantity[176]. And also the electronic contribution $F(R_A)$ in terms of the quantum mechanical average of the electric field operator is also mathematically represented as,

$$F(R_A) = Z_A \int \psi^* \sum_{i=1}^n \nabla \left(\frac{1}{|r_i - R_A|} \right) \psi \, dr_n \quad (84)$$

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.

$$F(R_A) = Z_A \int \tilde{N}_A (|r - R_A|)^{-1} \rho(r) dr \tag{85}$$

where

$$\rho(r) = n \int ds_1 \int dx_2 \dots \int y_{(x_1, x_2, \dots, x_n)}^* y_{(x_1, x_2, \dots, x_n)} dx_n \tag{86}$$

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 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 $\rho(r)dr$.

3.4 Ehrenfest Force:: The Ehrenfest force theorem, a primal force theorem involves fluxes of corresponding current density through the surface bounding the system whether this be a surface of zero-flux for an atom in a molecule or the surface bounding an infinitesimal volume element, the properties of which are described in the local form of the theorem. The atomic statement for Ehrenfest force is given as,

$$m \int_{(A)} dr \partial j(r) / \partial t = \int_A dr \int dr' \psi^* (-\nabla \hat{V}) \psi + \iint dS(r_s) \cdot \sigma_s(r) \tag{88}$$

Where the left side integral in the above expression represents the rate of change of the total momentum of electron density in atomic-basin. The first term in the right side integral not only comes from averaging of the commutator $\langle i / (h / 2\pi) \rangle [H.P]$ but also represents the Ehrenfest force, $F(r, t) = N \int dr' \psi^* \langle -\nabla V' \rangle \psi$ 89

where $\nabla \hat{V}$ is the gradient with respect to coordinates of electron located at r of total potential energy operator \hat{V} which speaks of all interactions within the system and $-\nabla \hat{V}$ is the **force exerted on the electron at position r** by all of remaining electrons and nuclei in the system. And also the net force exerted on the electron density distribution $\rho(r)$ in a molecule at point r , i.e. the sum of the attraction forces by all the nuclei and repulsion forces by the average electron density, is the Ehrenfest force.

4. Equation and Computation for Electronegativity

Electronegativity ≡ Hellmann-Feynman Force = Ehrenfest Force χ

$$= F(R_A) = \frac{Z_A}{R_A^2} \frac{\partial}{\partial R_A} \langle \psi | Z_B - \sum_i \frac{1}{|r_i - R_A|} | \psi \rangle = F(r, t) = N \int dr' \psi^* \langle -\nabla V' \rangle \psi \dots\dots\dots 90^{**}$$

The Hellmann Feynman electrostatic force leads two opposing terms, 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. This follows from the energy approximations postulated by Born Oppenheimer for di atomic system and Hartree Fock for poly atomic systems. This is true as, 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 the possibility of mysterious quantum mechanical force in mono atomic, di atomic as well as poly atomic systems.

Electronegativity of an atom (A) in a molecule AB may be defined as Hellmann Feynman force. This is also equivalent to Hartree Fock force in steady and non-steady states. In steady state, $r(r)$ may be interpreted as a number or charge density and $r(r)dr$ as amount of electronic charge in the volume element. Based on above explanation, Electronegativity=Hellmann-Feynman Force=Hartree-Fock Force.

$$c = F_{VA} = - \frac{\int E}{\int V_A} \tag{91}$$

Based on the BO approximation

$$F_{VA} = - \frac{\int E}{\int V_A} = - \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|^2} + \sum_i \frac{Z_A}{|r_i - R_A|^2} r(r)dr \tag{92}$$

Based on the basis of Hartree-Fock approximation

$$F_{VA} = - \frac{\int E}{\int V_A} = - 2l \sum_{B,A} \frac{Z_A Z_B}{|R_B - R_A|^2} + \sum_A Z_A \sum_i \frac{r(r, l)}{|r_i - R_A|^2} dr \tag{93}$$

First terms in eq. 90 and 91 represent classical nuclear contribution. Second terms in eq. 90 and 91 above represent electronic contribution.

The Hartree Fock energy for most of the elements of the periodic table have been used for computation of electronegativity in terms of energy gradient in au/picometer unit.

$$(i) \quad C_{e- slater} = \frac{E_{hf}}{r_{slater}} \quad (94)$$

$$ii) \quad C_{e- clementi} = \frac{E_{hf}}{r_{clementi}} \quad (95)$$

$$(iii) \quad C_{e- absolute} = \frac{E_{hf}}{r_{absolute}} \quad (96)$$

The computational equations for electronegativity is also considered in terms Coulomb force.

$$(iv) \quad C_{f- slater} = \frac{Z_{slater}^*}{r_{slater}^2} \cdot 1000 \quad (97)$$

$$(v) \quad C_{f- clementi} = \frac{Z_{clementi}^*}{r_{clementi}^2} \cdot 1000 \quad (98)$$

$$(vi) \quad C_{f- absolute} = \frac{Z_{clementi}^*}{r_{absolute}^2} \cdot 1000 \quad (99)$$

For reference, 1 au of force = $\frac{e^2}{4\pi\epsilon_0 a_0^2}$

In eq. 95-97, 1000 is multiplied to make the data more convincible . Electronegativity values based on force from Hydrogen to Lawrencium have been computed through the above equations and are mentioned in table 1 and 2. In case of unavailability of data the spaces are ‘*’ marked. The necessary data for Hartree-Fock Energy[177], Z* Slater effective nuclear charge[178], Z* Clementi effective nuclear charge[179], [180], Empirical Slater Radius[181], Absolute Radius[182] and calculated Clementi Radius[179], [180] and are taken from cited references.

Table 1. Electronegativity in terms of Hellmann-Feynman Force

Element Symbol	E_{hf} (au)	$r_{clementi}$ (pm)	$r_{absolute}$ (pm)	$C_{e- slater}$	$C_{e- clementi}$	$C_{e- absolute}$

H	0.49994557	53	52.92	0.019998	0.009433	0.009447195	
He	2.86115334	31.13	0.023843	0.092295	0.091909841		
Li	7.43271968	145	167	162.83	0.05126	0.044507	0.045647115
Be	14.5729681	105	112	108.55	0.13879	0.130116	0.134251203
B	24.4144654	85	87	81.41	0.287229	0.280626	0.299895165
C	37.5310547	70	67	65.13	0.536158	0.560165	0.576248345
N	54.4042654	65	56	54.28	0.836989	0.971505	1.00228934
O	74.6191049	60	48	46.52	1.243652	1.554565	1.604022031
F	99.1639672	50	42	40.71	1.983279	2.361047	2.435862619
Ne	128.546472	160	38	36.71	0.803415	3.382802	3.50167453
Na	161.8586	180	190	216.5	0.899214	0.851887	0.747614781
Mg	199.614215	150	145	167.11	1.330761	1.37665	1.194507899
Al	241.802199	125	118	136.08	1.934418	2.049171	1.776912103
Si	288.757442	110	111	114.77	2.625068	2.601418	2.515966211
P	340.718822	100	98	99.22	3.407188	3.476723	3.433973211
S	397.384664	100	88	87.39	3.973847	4.515735	4.547255567
Cl	459.338687	100	79	78.08	4.593387	5.814414	5.882923758
Ar	526.816781	71	71	70.56	7.419955	7.419955	7.466224221
K	599.164348	220	243	329.3	2.723474	2.465697	1.819509104
Ca	676.757668	180	194	254.19	3.759765	3.488442	2.662408702
Sc	759.553865	160	184	241.49	4.747212	4.12801	3.145280819
Ti	848.05445	140	176	329.98	6.057532	4.818491	2.570017728
V	942.482641	135	171	219.53	6.981353	5.511594	4.293183806
Cr	1043.35589	140	166	210	7.452542	6.285276	4.968361381
Mn	1149.86888	140	161	201.24	8.213349	7.142043	5.713918108
Fe	1262.18252	140	156	193.19	9.015589	8.090914	6.533373984
Co	1380.93099	135	152	185.75	10.22912	9.085072	7.434352571
Ni	1506.33054	135	149	178.88	11.158	10.1096	8.420899709
Cu	1638.96277	135	145	172.5	12.14046	11.30319	9.501233449
Zn	1777.84664	135	142	166.54	13.16923	12.52005	10.67519299
Ga	1923.18595	130	136	144.89	14.79374	14.14107	13.27342087
Ge	2075.26686	125	125	128.23	16.60213	16.60213	16.18394182
As	2234.23911	115	114	114.5	19.42817	19.59859	19.51300533

Se	2399.75947	115	103	104.24	20.86747	23.29864	23.02148379
Br	2572.31642	115	94	95.32	22.36797	27.36507	26.98611435
Kr	2752.05419	*	88	87.82	*	31.27334	31.33744238
Rb	2938.35681	235	265	384.87	12.50365	11.08814	7.634673552
Sr	3131.545	200	219	297.09	15.65773	14.29929	10.5407284
Y	3331.55545	180	212	282.44	18.50864	15.71488	11.7956219
Zr	3538.75135	155	206	268.8	22.83065	17.1784	13.16499758
Nb	3753.43518	145	198	256.58	25.88576	18.95674	14.62871299
Mo	3975.55206	145	190	254.43	27.4176	20.92396	15.62532744
Tc	4204.79397	135	183	235.2	31.14662	22.97702	17.87752538
Ru	4441.23215	130	178	225.79	34.16332	24.95074	19.66974689
Rh	4685.53924	135	173	217.11	34.7077	27.08404	21.58140684
Pd	4937.9198	140	169	209.07	35.27086	29.21846	23.61850002
Ag	5197.69786	160	165	201.6	32.48561	31.5012	25.78223145
Cd	5465.1321	155	161	194.65	35.25892	33.94492	28.07671256
In	5740.10075	155	156	169.34	37.03291	36.79552	33.89689825
Sn	6022.84999	145	145	149.86	41.5369	41.5369	40.18984379
Sb	6313.48607	145	133	134.4	43.54128	47.46982	46.97534278
Te	6611.69122	140	123	121.83	47.22637	53.75359	54.2698122
I	6917.8755	140	115	111.41	49.4134	60.15544	62.09384705
Xe	7232.13748	*	108	102.63	*	66.96424	70.4680647
Cs	7553.93311	260	298	424.33	29.05359	25.34877	17.80202463
Ba	7883.54325	215	253	327.53	36.66764	31.16025	24.06968293
La	8220.95071	195	195	266.73	42.15872	42.15872	30.82124512
Ce	8566.37167	185	158	224.94	46.30471	54.21754	38.08291842
Pr	8920.39371	185	247	194.47	48.21834	36.11495	45.87028184
Nd	9283.0449	185	206	171.29	50.17862	45.06332	54.1949028
Pm	9654.39094	185	205	153.03	52.1859	47.09459	63.08822414
Sm	10034.5278	185	238	138.3	54.24069	42.16188	72.55623861
Eu	10423.5496	185	231	126.15	56.34351	45.12359	82.6282172
Gd	10820.5365	180	233	115.96	60.11409	46.44007	93.31266385
Tb	11225.8464	175	225	107.3	64.14769	49.89265	104.6211221
Dy	11640.486	175	228	99.84	66.51706	51.05476	116.5914063

Ho	12064.2689	175	226	93.35	68.93868	53.38172	129.2369459
Er	12497.2944	175	226	87.65	71.41311	55.29776	142.5817958
Tm	12939.6584	175	222	82.61	73.94091	58.28675	156.6354969
Yb	13391.4548	175	222	78.12	76.5226	60.32187	171.4215924
Lu	13851.6806	175	217	74.09	79.15246	63.83263	186.9574922
Hf	14321.0157	155	208	70.56	92.39365	68.85104	202.9622406
Ta	14799.5544	145	200	67.16	102.0659	73.99777	220.3626325
W	15287.3729	135	193	64.16	113.2398	79.20919	238.2695277
Re	15784.5427	135	188	61.41	116.9225	83.96033	257.0353802
Os	16290.4713	130	185	58.9	125.3113	88.0566	276.5784601
Ir	16805.8003	135	180	56.57	124.4874	93.36556	297.0797295
Pt	17330.8587	135	177	54.43	128.3767	97.91446	318.4063696
Au	17865.3992	135	174	52.44	132.3363	102.6747	340.6826697
Hg	18408.9902	150	171	50.6	122.7266	107.6549	363.8140356
Tl	18961.7587	190	156	186.7	99.79873	121.5497	101.562714
Pb	19523.9305	180	154	165.23	108.4663	126.7788	118.1621407
Bi	20095.5875	160	143	148.18	125.5974	140.5286	135.6160582
Po	20676.4142	190	135	134.31	108.8232	153.1586	153.945456
At	21266.7841	*	127	122.83	*	167.455	173.1399829
Rn	21866.7713	*	120	131.15	*	182.2231	166.731005
Fr	22475.8581	*	*	444.79	*	*	50.53139257
Ra	23094.303	215	*	343.32	107.4154	*	67.26757253
Ac	23722.0873	195	*	326.15	121.6517	*	72.73367254
Th	24359.4372	180	*	310.61	135.3302	*	78.42451048
Pa	25006.5117	180	*	227.56	138.9251	*	109.8897508
U	25663.5826	175	*	197.67	146.649	*	129.8304376
Np	26330.6626	175	*	174.73	150.4609	*	150.6934276
Pu	27008.4196	175	*	144.96	154.3338	*	186.3163604
Am	27695.8997	175	*	129.15	158.2623	*	214.4475393
Cm	28392.6577	*	*	129.6	*	*	219.0791489
Bk	29099.5106	*	*	112.47	*	*	258.7313115
Cf	29816.6874	*	*	104.65	*	*	284.9181787
Es	30544.2078	*	*	97.85	*	*	312.1533756

Fm 31282.1408	*	*	91.88	*	*	340.4673574
Md 32030.5533	*	*	86.59	*	*	369.9105359
No 32789.5111	*	*	81.88	*	*	400.4581229
Lr 33557.611	*	*	80.86	*	*	415.008793

Table 2. Electronegativity in terms of Coulomb Force

Element Symbol	r_{slater} pm	$r_{clementi}$ pm	$r_{absloute}$ pm	Z_{slater}^*	$Z_{clementi}^*$	$C_{f-slater}$	$C_{f-clementi}$	$C_{f-absloute}$	H 25	53
									52.92	1
									1	1.6
						0.355998576	0.357075727			
He 120	31	31.13	1.7	1.688	0.118055556	1.756503642	1.741863829			
Li 145	167	162.83	1.3	1.279	0.061831153	0.045860375	0.048239378			
Be 105	112	108.55	1.95	1.912	0.176870748	0.152423469	0.162266262			
B 85	87	81.41	2.6	2.421	0.359861592	0.319857313	0.365291259			
C 70	67	65.13	3.25	3.136	0.663265306	0.698596569	0.73928841			
N 65	56	54.28	3.9	3.834	0.923076923	1.222576531	1.301285021			
O 60	48	46.52	4.55	4.453	1.263888889	1.932725694	2.057658426			
F 50	42	40.71	5.2	5.1	2.08	2.891156463	3.077286782			
Ne 160	38	36.71	57.48	5.758	2.2453125	3.987534626	4.272704829			
Na 180	190	216.5	2.2	2.507	0.067901235	0.069445983	0.053485805			
Mg 150	145	167.11	2.85	3.308	0.126666667	0.157336504	0.118456971			
Al 125	118	136.08	3.5	8.963	0.224	0.643708704	0.484021658			
Si 110	111	114.77	4.15	4.117	0.342975207	0.334144956	0.312553311			
P 100	98	99.22	4.8	4.903	0.48	0.510516451	0.498039109			
S 100	88	87.39	5.45	5.642	0.545	0.72856405	0.738770599			
Cl 100	79	78.08	6.1	6.367	0.61	1.020189072	1.04437205			
Ar 71	71	70.56	6.75	7.068	1.339020036	1.402102757	1.419643821			
K 220	243	329.3	2.2	3.495	0.045454545	0.059188132	0.032230253			
Ca 180	194	254.19	2.85	4.398	0.087962963	0.116856202	0.068067265			
Sc 160	184	241.49	3	4.632	0.1171875	0.136814745	0.079427382			

Ti	140	176	329.98	3.15	4.871	0.160714286	0.157250775	0.044734531
V	135	171	219.53	3.3	4.981	0.181069959	0.170343012	0.103354356
Cr	140	166	210	3.45	5.133	0.176020408	0.186275221	0.116394558
Mn	140	161	201.24	3.6	5.283	0.183673469	0.203811581	0.130452376
Fe	140	156	193.19	3.75	5.434	0.191326531	0.223290598	0.145596304
Co	135	152	185.75	3.9	5.576	0.21399177	0.24134349	0.161608843
Ni	135	149	178.88	4.05	5.716	0.222222222	0.25746588	0.178635861
Cu	135	145	172.5	4.2	5.842	0.230452675	0.277859691	0.196328502
Zn	135	142	166.54	4.35	5.965	0.238683128	0.295824241	0.215066777
Ga	130	136	144.89	5	6.222	0.295857988	0.336397059	0.296382926
Ge	125	125	128.23	5.65	6.78	0.3616	0.43392	0.412335198
As	115	114	114.5	6.3	7.499	0.47637051	0.5770237	0.571995195
Se	115	103	104.24	6.95	8.2867	0.525519849	0.781100952	0.762628114
Br	115	94	95.32	7.6	9.028	0.574669187	1.021729289	0.993627226
Kr	*	88	87.82	8.25	9.338	*	1.205836777	1.210784922
Rb	235	265	384.87	2.2	4.985	0.03983703	0.070986116	0.033654027
Sr	200	219	297.09	2.85	6.071	0.07125	0.126582015	0.068783483
Y	180	212	282.44	3	6.256	0.092592593	0.139195443	0.078423159
Zr	155	206	268.8	3.15	6.446	0.131113424	0.151899331	0.089213745
Nb	145	198	256.58	3.3	5.921	0.156956005	0.151030507	0.089939291
Mo	145	190	254.43	3.45	6.106	0.164090369	0.169141274	0.094323556
Tc	135	183	235.2	3.6	7.227	0.197530864	0.215802204	0.13064218
Ru	130	178	225.79	3.75	6.485	0.221893491	0.20467744	0.127203943
Rh	135	173	217.11	3.9	6.64	0.21399177	0.221858398	0.140866727
Pd	140	169	209.07	4.05	6.766	0.206632653	0.236896467	0.154792015
Ag	160	165	201.6	4.2	6.756	0.1640625	0.24815427	0.166229686
Cd	155	161	194.65	4.35	8.192	0.181061394	0.31603719	0.216212664
In	155	156	169.34	5	8.413	0.208116545	0.345701841	0.29338086
Sn	145	145	149.86	5.65	10.629	0.268727705	0.505541023	0.473283049
Sb	145	133	134.4	6.3	11.617	0.299643282	0.656735825	0.643125089
Te	140	123	121.83	6.95	12.538	0.354591837	0.828739507	0.844733616
I	140	115	111.41	7.6	11.612	0.387755102	0.878034026	0.935532068
Xe	*	108	102.63	8.25	12.425	*	1.065243484	1.179635244

Cs	260	298	424.33	2.2	2.2	0.032544379	0.024773659	0.012218424
Ba	215	253	327.53	2.85	2.85	0.061654949	0.044524989	0.026567011
La	195	195	266.73	3.5	3.5	0.092044707	0.092044707	0.049195379
Ce	185	158	224.94	4.15	4.15	0.121256392	0.166239385	0.082019046
Pr	185	247	194.47	4.8	4.8	0.140248356	0.078676917	0.126921738
Nd	185	206	171.29	5.45	5.45	0.159240321	0.128428693	0.185751566
Pm	185	205	153.03	6.1	6.1	0.178232286	0.145151695	0.260481377
Sm	185	238	138.3	6.75	6.75	0.197224251	0.119165313	0.352906301
Eu	185	231	126.15	7.4	7.4	0.216216216	0.138678061	0.465004558
Gd	180	233	115.96	8.05	8.05	0.24845679	0.148280499	0.598658933
Tb	175	225	107.3	8.7	8.7	0.284081633	0.171851852	0.755648472
Dy	175	228	99.84	9.35	9.35	0.305306122	0.179863035	0.937999196
Ho	175	226	93.35	10	10	0.326530612	0.195786671	1.147549308
Er	175	226	87.65	10.65	10.65	0.347755102	0.208512804	1.386263431
Tm	175	222	82.61	11.3	11.3	0.368979592	0.229283337	1.655820287
Yb	175	222	78.12	11.95	11.95	0.390204082	0.242472202	1.958138634
Lu	175	217	74.09	12.6	12.6	0.411428571	0.267578415	2.295362888
Hf	155	208	70.56	13.25	12.6	0.551508845	0.291235207	2.530774214
Ta	145	200	67.16	13.9	13.25	0.661117717	0.33125	2.937612472
W	135	193	64.16	14.55	13.9	0.798353909	0.37316438	3.376650332
Re	135	188	61.41	15.2	14.55	0.834019204	0.411668176	3.85820055
Os	130	185	58.9	15.85	15.2	0.937869822	0.444119795	4.381400953
Ir	135	180	56.57	16.5	15.85	0.905349794	0.489197531	4.952869772
Pt	135	177	54.43	17.15	16.5	0.941015089	0.526668582	5.569385446
Au	135	174	52.44	17.8	17.15	0.976680384	0.566455278	6.236468863
Hg	150	171	50.6	18.45	17.8	0.82	0.608734311	6.952147354
Tl	190	156	186.7	5	18.45	0.138504155	0.758136095	0.529307118
Pb	180	154	165.23	5.65	5	0.174382716	0.210828133	0.183143791
Bi	160	143	148.18	6.3	5.65	0.24609375	0.276297129	0.257317467
Po	190	135	134.31	6.95	6.75	0.192520776	0.37037037	0.374185604
At	*	127	122.83	7.6	7.6	*	0.471200942	0.503737971
Rn	*	120	131.15	8.25	8.25	*	0.572916667	0.47964217
Fr	*	*	444.79	2.2	2.2	*	*	0.011120201

Ra	215	*	343.32	2.85	2.85	0.061654949	*	0.024179463
Ac	195	*	326.15	3	3	0.078895464	*	0.028202427
Th	180	*	310.61	3.15	3.15	0.097222222	*	0.032649737
Pa	180	*	227.56	4.3	4.3	0.132716049	*	0.083037947
U	175	*	197.67	4.95	4.95	0.161632653	*	0.126684556
Np	175	*	174.73	5.6	5.6	0.182857143	*	0.183422696
Pu	175	*	144.96	6.75	5.6	0.220408163	*	0.266496596
Am	175	*	129.15	7.4	7.4	0.241632653	*	0.443652465
Cm	*	*	129.6	7.55	7.55	*	*	0.449507506
Bk	*	*	112.47	8.7	8.51	*	*	0.672753816
Cf	*	*	104.65	9.35	9.35	*	*	0.853754775
Es	*	*	97.85	10	10	*	*	1.0444276
Fm	*	*	91.88	10.65	10.65	*	*	1.261559199
Md	*	*	86.59	11.3	11.3	*	*	1.507103104
No	*	*	81.88	11.95	11.95	*	*	1.782428991
Lr	*	*	80.86	12.1	12.1	*	*	1.850622

Conclusion It is argued as to which Electronegativity-model is best approximation because no benchmark for this intuitive concept has been set up till date. Furthermore, the confusion as to what physical picture corresponds Electronegativity and even if non-agreement of proposed units such as Energy, Force and Potential. Numerical values of quantities with different units in computation are not comparable because they are conceptually different. No effort is made to compare the computed values of electronegativity with those of other scales. The computed electronegativity values reproduce the periodicity and also increase monotonically right from representative element to noble gas with maximum value. The exact status of electronegativity might be attributed as triangular concept of force, energy and charge. 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 exists scope of many scales of 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). 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. This will also help design new electrode materials efficiently, electrocatalysts with novel properties for energy conversion devices like Fuel cell, Solar cell etc.

Acknowledgement

The author acknowledges the financial support of Department of Science and Technology, Government of India for pursuing Doctoral program.

Nomenclature

a, b	-	Valence cell occupation number
a_0	-	Bohr radius in pico meter
$a', a'_x, a'_y, a'_w, a'_z$	-	Normal group electronegativity
$b', b'_x, b'_y, b'_w, b'_z$	-	Charge transfer coefficient
A, B, X	-	Atoms symbol
B_i	-	Spectroscopic Parameter
C	-	Mean Value C_{ji}
dn	-	Quantum defect
dq	-	Infinitesimal electronic charge under transfer from A to B
$D_{E A_2}, D_{E B_2}, D_{E AB}$	-	Bond dissociation energy
e	-	Charge of one electron
eV	-	Electron volt
E, E_A, E_B	-	Energy
\bar{E}	-	Average energy
E_0	-	Eigen Energy
E_e	-	Electronic energy
E_{g0}	-	Energy gap
E_{hf}	-	Hartree Fork Energy
E_{total}	-	Total Energy
$E[r]$	-	Energy functional of electron density

$E_v[r']$	-	Energy functional of approximated electron density
$EA, EA_A, EA_B, EA_k, EA_v$	-	Electron Affinity (in eV or kcal/mol)
E_{g0}	-	Energy gap
E_j^A	-	One electron energy of orbital j
f_{AB}	-	Orbital multiplier
f_i	-	Atomic force or overlap force or Screening force
$f_i(R_A)$	-	Atomic force or overlap force or Screening force at R_A
$F(R_A), F(R_B)$	-	Force at position of nuclei A and B
$f(r)$	-	Atomic/overlap/screening force at r, berlin quantity
F	-	Force
F_ζ	-	Hellmann-Feynman force
$F_{\zeta'}$	-	Hellmann-Feynman force (unsteady state)
$F_{\zeta A}$	-	Hellmann-Feynman on atom A
$F(r)$ density	-	Sum of electronic kinetic energy and electron repulsion energy functional of density
h	-	Planck's constant
H	-	Hamiltonian operator
H_e	-	Electronic Hamiltonian
H^{mol}	-	Molecular Hamiltonian
H_n	-	Nuclear Hamiltonian
$hw_p / 2p$	-	Plasma energy
$i^{ionicity}$	-	Iconicity
Iz	-	Ultimate ionization potential for outer electron
IE, IE_v	-	Ionization energy
$IP, IP_A, IP_B, IP_k, IP_s, IP_p$	-	Ionization potential (in ev or kcal/mol)
IP_z	-	Ultimate ionization potential
j	-	Atomic orbital
k	-	Orbital multiplier coefficient

k_s	-	Thomas Fermi screening radius for a free electron gas
l	-	Orbital quantum number
\hat{l}	-	Orbital quantum defandant parameter
n	-	Principal quantum number
n^*	-	Effective Principal quantum number
n_{Ae}, n_{Be}	-	Electron transfer number of A, B
n_1, n_2, n_3	-	Atom number
n_A, n_B, n_X	-	No of associated electrons
n_j	-	Electron occupancy
N	-	Net charge
P_j	-	Charge density on atomic orbital j on A
q	-	Ionic charge (+1 for cataion, -1 for anion)
q_j	-	Occupation number of spin orbital j
r	-	Covalent radius, electronic positional coordinate
r_{ionic}	-	Ionic radius
r_i, r_n	-	Electronic space co-ordinate of electron I and n respectively
r_j	-	Electronic space co-ordinate of electron j
r_l	-	Radius for valence orbital
r_A, r_B	-	Atomic distance w.r.t. orbital center
r_{A0}, r_{B0}	-	Thomas Fermi ground state radius
R	-	Inter nuclear separation
R_A, R_B	-	Nuclear co-ordinate of A and B
R_E	-	Equilibrium inter nuclear separation between A and B
Ry	-	Rydberg constant
s, p, d	-	Atomic orbital
s_i	-	Spin coordinate
T	-	Kinetic energy operator
T_e	-	Kinetic energy Operator(electron)
T_n	-	Kinetic energy operator(nucleus)
V	-	Fixed potential

$v(1)$	-	Fixed external applied potential
V	-	Coulomb Potential (in eV or kcal/mol)
V_{ee}	-	Electron-electron repulsion term
V_{en}	-	Electron-nuclear attraction term
V_{nn}	-	Nuclear-nuclear repulsion term
(w)	-	Electrophilic power index
w, x, y, z	-	Group numbers
x_i	-	Product of space coordinate r_i and spin coordinate s_i of the i th electron
Z, Z_A, Z_B	-	Atomic number or Nuclear Charge
Z^*	-	Effective nuclear charge
Z'	-	Screen charge by Gordy's technique
Greek Letters		
$\langle \alpha \zeta \alpha \rangle$	-	One-electron integral
$\langle \alpha \alpha \beta \beta \rangle$	-	Two-electron Coulomb integral
$\langle \alpha \beta \beta \alpha \rangle$	-	Exchange integral
a_1, a_2, a_3, a_4	-	Constants
n	-	Frequency of photon
g	-	Fall-off parameter
g_A	-	Electron repulsion integral
d_w, d_x, d_y, d_z	-	Partial atomic charge due to gain/loss of one electron
∂t_1 applied potential	-	Differential of spin free ground-state electron density and fixed external applied potential
q	-	Charge transfer coefficient
∂v	-	Spatial electronic distribution
d_{ij}	-	Kronecker delta symbol, equal to 1 for same spin and 0 for opposite spin
l	-	Parameter of value lying between 0 and 1
V	-	Extra ionic resonance energy
\tilde{N}_A^2	-	Laplacian operator related to co-ordinate of nucleus A
\tilde{N}_i^2	-	Laplacian operator related to Cartesian co-ordinate of electron i

$z(a)$	-	One-electron operator
$h(a,b)$	-	Two-electron operator
h	-	Chemical hardness
ζ, ζ'	-	Explicit Parameters (steady and Perturbation) in Hamiltonian
V_A	-	Parameter in Hamiltonian for a coordinate of nucleus A
e_0	-	Dielectric constant
y	-	Wave function
y_0	-	Unperturbed wave-state
y_n	-	Nuclear wave function
y_e	-	Electronic wave function
y^*	-	Conjugate wave function
r_A	-	Total electron density associated with atom A
r	-	Exact ground-state electron density
r_0	-	Unperturbed occupancy
r'	-	Approximation to exact ground-state electron density
$r(1)$	-	Spin free ground-state electron density
$r(r)$	-	Radial charge density (always positive)
s	-	Screening constant or slater constant
s_{ij}	-	Screening of the electron i by the electron j
m	-	Chemical potential
m_0	-	Ground state chemical potential
m_{dipole}	-	dipole moment
μ_M	-	Chemical potential (Mulliken)
χ, χ_A, χ_B	-	Electronegativity
$\chi_{Pa}, \chi_{Pa}^A, \chi_{Pa}^B$	-	Pauling's Electronegativity
$\chi_M, \chi_M^A, \chi_M^B, \chi_M^k$	-	Mulliken electronegativity
c_{LS}	-	Lang-Smith electronegativity
c_{spec}	-	Spectroscopic electronegativity

C_{OP}	-	Optical electronegativity
C_l^{JB}, C_{Aj}^{JB}	-	Orbital electronegativity for valence orbital
$C_{G(A)}$	-	Global electronegativity in a molecule
C_g, C_g^A, C_g^B	-	Gordy electronegativity
C_H	-	Huheey electronegativity
C_Z	-	Zhang electronegativity
C_{Putz}	-	Putz electronegativity
C_{ic}	-	Ionocovalency electronegativity

- [1] W. B. Jensen, "Electronegativity from Avogadro to Pauling: II. Late Nineteenth- and Early Twentieth-Century Developments," *J. Chem. Educ.*, vol. 80, no. 3, p. 279, Mar. 2003.
- [2] J. H. van't Hoff, "Lectures on Theoretical and Physical Chemistry: III. Relations Between Properties and Composition," *London, E. Arnold*, p. 94, 1899.
- [3] R. M. Caven and G. D. Lander, "Systematic Inorganic Chemistry from the Standpoint of the Periodic Law," in *A Text-book for Advanced Students*, Blackie & Son, London, 1907, pp. 37–38.
- [4] O. Sackur, *A Text Book of Thermo-Chemistry and Thermodynamics. This is a translation of the 1912 German edition*. Macmillan: London, 1917.
- [5] C. A. Coulson, "Bond Lengths in Conjugated Molecules: The Present Position," *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 207, no. 1088, pp. 91–100, Jun. 1951.
- [6] K. Fukui, "Role of frontier orbitals in chemical reactions.," *Science*, vol. 218, no. 4574, pp. 747–54, Nov. 1982.
- [7] R. T. Myers, "Electronegativity, bond energy, and chemical reactivity," *J. Chem. Educ.*, vol. 56, no. 11, p. 711, Nov. 1979.
- [8] R. R. Reddy, T. V. R. Rao, and R. Viswanath, "Correlation between electronegativity differences and bond energies," *J. Am. Chem. Soc.*, vol. 111, no. 8, pp. 2914–2915, Apr. 1989.
- [9] H. S. Gutowsky and C. J. Hoffman, "Nuclear Magnetic Shielding in Fluorine and Hydrogen Compounds," *J. Chem. Phys.*, vol. 19, no. 10, pp. 1259–1267, Oct. 1951.
- [10] S. Motiejūnas, D. Baltrūnas, V. I. Garasim, and P. M. Starik, "A Correlation between Ligand Electronegativity and the Value of the Mössbauer Isomer Shift of Stannous Chalcogenides," *Phys. status solidi*, vol. 148, no. 2, pp. K161–K164, Aug. 1988.
- [11] M. E. Arroyo-de Dompablo, M. Armand, J. M. Tarascon, and U. Amador, "On-demand design of polyoxianionic cathode materials based on electronegativity correlations: An exploration of the Li₂MSiO₄ system (M = Fe, Mn, Co, Ni)," *Electrochem. commun.*, vol. 8, no. 8, pp. 1292–1298, Aug. 2006.
- [12] L. Komorowski, "Electronegativity through the energy function," *Chem. Phys. Lett.*, vol. 103, no. 3, pp. 201–204, Dec. 1983.
- [13] L. Pauling, "THE NATURE OF THE CHEMICAL BOND. IV. THE ENERGY OF SINGLE BONDS AND THE RELATIVE ELECTRONEGATIVITY OF ATOMS," *J. Am. Chem. Soc.*, vol. 54, no. 9, pp. 3570–3582, Sep. 1932.
- [14] P. Politzer and J. S. Murray, "Electronegativity—a perspective," *J. Mol. Model.*, vol. 24, no. 8, p.

214, Aug. 2018.

- [15] J. Onoda, M. Ondráček, P. Jelínek, and Y. Sugimoto, "Electronegativity determination of individual surface atoms by atomic force microscopy," *Nat. Commun.*, vol. 8, p. 15155, Apr. 2017.
- [16] L. Pauling and J. Sherman, "A Quantitative Discussion of Bond Orbitals," *J. Am. Chem. Soc.*, vol. 59, no. 8, pp. 1450–1456, Aug. 1937.
- [17] J. Mullay, "Atomic and group electronegativities," *J. Am. Chem. Soc.*, vol. 106, no. 20, pp. 5842–5847, Oct. 1984.
- [18] L. Pauling and D. M. Yost, "The Additivity of the Energies of Normal Covalent Bonds.," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 18, no. 6, pp. 414–6, Jun. 1932.
- [19] A. L. Allred, "Electronegativity values from thermochemical data," *J. Inorg. Nucl. Chem.*, vol. 17, no. 3–4, pp. 215–221, Jun. 1961.
- [20] R. S. Mulliken, "Electronic structures of molecules XII. Electroaffinity and molecular orbitals, polyatomic applications," *J. Chem. Phys.*, vol. 3, no. 9, pp. 586–591, Sep. 1935.
- [21] R. G. Pearson, "The Calculation of Ionic Resonance Energies," *J. Chem. Phys.*, vol. 17, no. 10, pp. 969–971, Oct. 1949.
- [22] L. Pauling, "Chapter 2," in *The Nature of the Chemical Bond*, Cornell University Press, 1939.
- [23] M. Haissinsky, "Scale of Pauling electronegativities and heats of formation of inorganic compounds," *J. Phys. Radium*, vol. 7, no. 1, pp. 7–11, 1946.
- [24] M. L. Huggins, "Bond Energies and Polarities ¹," *J. Am. Chem. Soc.*, vol. 75, no. 17, pp. 4123–4126, Sep. 1953.
- [25] A. D. Walsh, "The properties of bonds involving carbon," *Discuss. Faraday Soc.*, vol. 2, no. 0, p. 18, Jan. 1947.
- [26] R. Ferreira, "Electronegativity and Chemical Bonding," *Adv. Chem. Phys.*, vol. 13, pp. 55–84, Mar. 1967.
- [27] R. P. Iczkowski and J. L. Margrave, "Electronegativity," *J. Am. Chem. Soc.*, vol. 83, no. 17, pp. 3547–3551, Sep. 1961.
- [28] R. G. Pearson, "Electronegativity Scales," *Acc. Chem. Res.*, vol. 23, no. 1, pp. 1–2, Jan. 1990.
- [29] L. C. Allen, "Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state free atoms," *J. Am. Chem. Soc.*, vol. 111, no. 25, pp. 9003–9014, Dec. 1989.
- [30] L. C. Allen, "Electronegativity scales," *Acc. Chem. Res.*, vol. 23, no. 6, pp. 175–176, Jun. 1990.
- [31] J. E. Huheey, "Variable electronegativity," *J. Inorg. Nucl. Chem.*, vol. 27, no. 9, pp. 2127–2129, Sep. 1965.
- [32] J. E. Huheey, "Electronegativity, acids, and bases. IV. Concerning the inductive effect of alkyl groups," *J. Org. Chem.*, vol. 36, no. 1, pp. 204–205, Jan. 1971.
- [33] R. S. Mulliken, "A new electroaffinity scale; Together with data on valence states and on valence ionization potentials and electron affinities," *J. Chem. Phys.*, vol. 2, no. 11, pp. 782–793, Nov. 1934.
- [34] J. Stark, "Die Dissoziierung und Umwandlung chemischer Atome," *Vieweg Braunschweig, Ger.*, pp. 7–8, 1903.
- [35] G. Martin, "Researches on the affinities of the elements and on the causes of the chemical similarity or dissimilarity of elements and compounds." *J. & A. Churchill*, pp. 226–228, 1905.
- [36] K. Fajans, "Über eine Beziehung zwischen der Art einer radioaktiven Umwandlung und dem elektrochemischen Verhalten der betreffenden Radioelemente," *Phys. Zeitschrift*, vol. 14, pp. 131–136, 1913.
- [37] W. Moffitt, "Term Values in Hybrid States," *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 202, no. 1071, pp. 534–548, Aug. 1950.

- [38] J. E. Huheey, E. A. Keiter, R. L. Keiter, and O. K. Medhi, "Electronegativity," in *Inorganic chemistry: principles of structure and reactivity*, 4th ed., Harper Collins college, New York, 1993, p. 182.
- [39] G. Klopman, "Electronegativity," *J. Chem. Phys.*, vol. 43, no. 10, pp. S124–S129, Nov. 1965.
- [40] H. O. Pritchard and H. A. Skinner, "The Concept Of Electronegativity," *Chem. Rev.*, vol. 55, no. 4, pp. 745–786, Aug. 1955.
- [41] R. G. Pearson, "Absolute electronegativity and absolute hardness of Lewis acids and bases," *J. Am. Chem. Soc.*, vol. 107, no. 24, pp. 6801–6806, Nov. 1985.
- [42] J. Hinze and H. H. Jaffé, "Electronegativity. I. Orbital Electronegativity of Neutral Atoms," *J. Am. Chem. Soc.*, vol. 84, no. 4, pp. 540–546, Feb. 1962.
- [43] J. Hinze, M. A. Whitehead, and H. H. Jaffé, "Electronegativity. II. Bond and Orbital Electronegativities," *J. Am. Chem. Soc.*, vol. 85, no. 2, pp. 148–154, Jan. 1963.
- [44] R. S. Mulliken and R. S., "Quelques aspects de la théorie des orbitales moléculaires," *J. Chim. Phys.*, vol. 46, pp. 497–542, Jun. 1949.
- [45] P. F. Lang and B. C. Smith, "An equation to calculate internuclear distances of covalent, ionic and metallic lattices," *Phys. Chem. Chem. Phys.*, vol. 17, no. 5, pp. 3355–3369, Jan. 2015.
- [46] P. F. Lang and B. C. Smith, "Electronegativity effects and single covalent bond lengths of molecules in the gas phase," *Dalt. Trans.*, vol. 43, no. 21, pp. 8016–8025, May 2014.
- [47] C. Klixbüll Jørgensen, "Electron Transfer Spectra," *Prog. Inorg. Chem.*, pp. 101–158, Mar. 1970.
- [48] J. C. Slater and K. H. Johnson, "Self-consistent-field $X\alpha$ cluster method for polyatomic molecules and solids," *Phys. Rev. B*, vol. 5, no. 3, pp. 844–853, Feb. 1972.
- [49] J. C. Slater and J. C. Phillips, "Quantum Theory of Molecules and Solids Vol. 4: The Self-Consistent Field for Molecules and Solids," *Phys. Today*, vol. 27, no. 12, p. 49, Dec. 1974.
- [50] G. Simons, M. E. Zandler, and E. R. Talaty, "Nonempirical electronegativity scale," *J. Am. Chem. Soc.*, vol. 98, no. 24, pp. 7869–7870, Nov. 1976.
- [51] J. John and A. N. Bloch, "Quantum-Defect Electronegativity Scale for Nontransition Elements," *Phys. Rev. Lett.*, vol. 33, no. 18, pp. 1095–1098, Oct. 1974.
- [52] G. Simons, "New Model Potential for Pseudopotential Calculations," *J. Chem. Phys.*, vol. 55, no. 2, pp. 756–761, Jul. 1971.
- [53] W. Gordy, "A New Method of Determining Electronegativity from Other Atomic Properties," *Phys. Rev.*, vol. 69, no. 11–12, pp. 604–607, Jun. 1946.
- [54] D. C. Ghosh, "A new scale of electronegativity based on absolute radii of atoms," *J. Theor. Comput. Chem.*, vol. 04, no. 01, pp. 21–33, Mar. 2005.
- [55] B. Fricke, "On the correlation between electric polarizabilities and the ionization potential of atoms," *J. Chem. Phys.*, vol. 84, no. 2, pp. 862–866, Jan. 1986.
- [56] J. K. Nagle, "Atomic polarizability and electronegativity," *J. Am. Chem. Soc.*, vol. 112, no. 12, pp. 4741–4747, Jun. 1990.
- [57] I. K. Dmitrieva and G. I. Plindov, "Dipole Polarizability, Radius and Ionization Potential for Atomic Systems," *Phys. Scr.*, vol. 27, no. 6, pp. 402–406, Jun. 1983.
- [58] J. E. Huheey, "The Electronegativity of Groups," *J. Phys. Chem.*, vol. 69, no. 10, pp. 3284–3291, Oct. 1965.
- [59] J. E. Huheey, "The Electronegativity of Multiply Bonded Groups," *J. Phys. Chem.*, vol. 70, no. 7, pp. 2086–2092, Jul. 1966.
- [60] G. Klopman, "A Semiempirical Treatment of Molecular Structures. I. Electronegativity and Atomic Terms," *J. Am. Chem. Soc.*, vol. 86, no. 8, pp. 1463–1469, Apr. 1964.

- [61] G. Klopman, "A Semiempirical Treatment of molecular Structures. II. Molecular Terms and Application to diatomic Molecules," *J. Am. Chem. Soc.*, vol. 86, no. 21, pp. 4550–4557, Nov. 1964.
- [62] R. Ponc, "Generalization of electronegativity concept," *Theor. Chim. Acta*, vol. 59, no. 6, pp. 629–637, 1981.
- [63] R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, "Electronegativity: The density functional viewpoint," *J. Chem. Phys.*, vol. 68, no. 8, pp. 3801–3807, Apr. 1978.
- [64] R. G. Parr and L. J. Bartolotti, "On the geometric mean principle for electronegativity equalization," *J. Am. Chem. Soc.*, vol. 104, no. 14, pp. 3801–3803, Jul. 1982.
- [65] R. G. Parr and R. G. Pearson, "Absolute hardness: companion parameter to absolute electronegativity," *J. Am. Chem. Soc.*, vol. 105, no. 26, pp. 7512–7516, Dec. 1983.
- [66] R. E. Watson, L. H. Bennett, and J. W. Davenport, "Ionic character of polar crystals: An extended Mulliken scheme for electronegativities," *Phys. Rev. B*, vol. 27, no. 10, pp. 6428–6438, May 1983.
- [67] S. G. Bratsch, "A group electronegativity method with Pauling units," *J. Chem. Educ.*, vol. 62, no. 2, p. 101, Feb. 1985.
- [68] J. R. Hancock, W. R. Hardstaff, P. A. Johns, R. F. Langler, and W. S. Mantle, "Regiochemistry and reactivity in the chlorination of sulfides," *Can. J. Chem.*, vol. 61, no. 7, pp. 1472–1480, Jul. 1983.
- [69] H. O. Pritchard, "Equalization of Electronegativity," *J. Am. Chem. Soc.*, vol. 85, no. 12, p. 1876, Jun. 1963.
- [70] R. S. Evans and J. E. Huheey, "Electronegativity, acids, and bases—I: Hard and soft acids and bases and Pauling's electronegativity equation," *J. Inorg. Nucl. Chem.*, vol. 32, no. 2, pp. 373–381, Feb. 1970.
- [71] J. L. Reed, "Electronegativity. An isolated atom property," *J. Phys. Chem.*, vol. 85, no. 2, pp. 148–153, Jan. 1981.
- [72] L. J. Bartolotti, S. R. Gadre, and R. G. Parr, "Electronegativities of the Elements from Simple. Xa Theory," *J. Am. Chem. Soc.*, vol. 102, no. 9, pp. 2945–2948, Apr. 1980.
- [73] P. Politzer and H. Weinstein, "Some relations between electronic distribution and electronegativity," *J. Chem. Phys.*, vol. 71, no. 11, pp. 4218–4220, Dec. 1979.
- [74] M. A. Whitehead, N. C. Baird, and M. Kaplansky, "Group orbital electronegativities," *Theor. Chim. Acta*, vol. 3, no. 2, pp. 135–146, 1965.
- [75] E. P. Gyftopoulos and G. N. Hatsopoulos, "Quantum-Thermodynamic Definition of Electronegativity," *Proc. Natl. Acad. Sci.*, vol. 60, no. 3, pp. 786–793, 1968.
- [76] M. B. Einhorn and R. Blankenbecler, "Bounds on scattering amplitudes," *Ann. Phys. (N. Y.)*, vol. 67, no. 2, pp. 480–517, Oct. 1971.
- [77] M. S. Gopinathan and M. A. Whitehead, "On the Dependence of Total Energy on Occupation Numbers," *Isr. J. Chem.*, vol. 19, no. 1–4, pp. 209–214, 1980.
- [78] P. Geerlings, F. De Proft, and W. Langenaeker, "Conceptual Density Functional Theory," *Chem. Rev.*, vol. 103, no. 5, pp. 1793–1874, May 2003.
- [79] C. K. Jørgensen, *Orbitals in Atoms and Molecules*. Academic Press Inc., New York, 1962.
- [80] J. Hinze, M. A. Whitehead, and H. H. Jaffe, "Electronegativity. II. Bond and Orbital Electronegativities," *J. Am. Chem. Soc.*, vol. 85, no. 2, pp. 148–154, Jan. 1963.
- [81] R. T. Sanderson, "An interpretation of bond lengths and a classification of bonds," *Science (New York, N.Y.)*, vol. 114, no. 2973. American Association for the Advancement of Science, pp. 670–672, 1951.
- [82] R. Ferreira, "Principle of electronegativity equalization. Part 1.—Bond moments and force constants," *Trans. Faraday Soc.*, vol. 59, no. 0, pp. 1064–1074, Jan. 1963.
- [83] N. H. March, "The ground-state energy of atomic and molecular ions and its variation with the

number of electrons,” in *Chemical Hardness*, Berlin/Heidelberg: Springer-Verlag, 1993, pp. 71–86.

- [84] T. T. Nguyen-Dang, R. F. W. Bader, and H. Essén, “Some properties of the Lagrange multiplier μ in density functional theory,” *Int. J. Quantum Chem.*, vol. 22, no. 5, pp. 1049–1058, Nov. 1982.
- [85] J. Hinze, “The concept of electronegativity of atoms in molecules,” *Theor. Comput. Chem.*, vol. 6, pp. 189–212, Jan. 1999.
- [86] H. Chermette, “Chemical reactivity indexes in density functional theory,” *J. Comput. Chem.*, vol. 20, no. 1, pp. 129–154, Jan. 1999.
- [87] P. Hohenberg and W. Kohn, “Inhomogeneous Electron Gas,” *Phys. Rev.*, vol. 136, no. 3B, pp. B864–B871, Nov. 1964.
- [88] R. A. Miranda-Quintana and P. W. Ayers, “Interpolation of property-values between electron numbers is inconsistent with ensemble averaging,” *J. Chem. Phys.*, vol. 144, no. 24, p. 244112, Jun. 2016.
- [89] F. Heidar-Zadeh, R. A. Miranda-Quintana, T. Verstraelen, P. Bultinck, and P. W. Ayers, “When is the Fukui Function Not Normalized? The Danger of Inconsistent Energy Interpolation Models in Density Functional Theory,” *J. Chem. Theory Comput.*, vol. 12, no. 12, pp. 5777–5787, Dec. 2016.
- [90] L. Komorowski, “Electronegativity through the energy function,” *Chem. Phys. Lett.*, vol. 103, no. 3, pp. 201–204, 1983.
- [91] D. Datta, N. K. Shee, and L. Von Szentpály, “Chemical potential of molecules contrasted to averaged atomic electronegativities: Alarming differences and their theoretical rationalization,” *J. Phys. Chem. A*, vol. 117, no. 1, pp. 200–206, Jan. 2013.
- [92] R. P. Feynman, “Forces in Molecules,” *Phys. Rev.*, vol. 56, no. 4, pp. 340–343, Aug. 1939.
- [93] T. Berlin, “Binding Regions in Diatomic Molecules,” *J. Chem. Phys.*, vol. 19, no. 2, pp. 208–213, Feb. 1951.
- [94] R. T. Sanderson, “Electronegativities in inorganic chemistry,” *J. Chem. Educ.*, vol. 29, no. 11, p. 539, Nov. 1952.
- [95] R. T. Sanderson, “Relation of Stability Ratios to Pauling Electronegativities,” *J. Chem. Phys.*, vol. 23, no. 12, pp. 2467–2468, Dec. 1955.
- [96] A. B. Anderson and R. G. Parr, “Vibrational Force Constants from Electron Densities,” *J. Chem. Phys.*, vol. 53, no. 8, pp. 3375–3376, Oct. 1970.
- [97] R. T. Sanderson, “Electronegativities in inorganic chemistry: (II),” *J. Chem. Educ.*, vol. 31, no. 1, p. 2, Jan. 1954.
- [98] R. T. Sanderson, “Electronegativities in inorganic chemistry. III,” *J. Chem. Educ.*, vol. 31, no. 5, p. 238, May 1954.
- [99] R. T. Sanderson, “Principles of electronegativity Part I. General nature,” *J. Chem. Educ.*, vol. 65, no. 2, p. 112, Feb. 1988.
- [100] W. Gordy, “A Relation between Bond Force Constants, Bond Orders, Bond Lengths, and the Electronegativities of the Bonded Atoms,” *J. Chem. Phys.*, vol. 14, no. 5, pp. 305–320, May 1946.
- [101] A. L. Allred and E. G. Rochow, “A scale of electronegativity based on electrostatic force,” *J. Inorg. Nucl. Chem.*, vol. 5, no. 4, pp. 264–268, Jan. 1958.
- [102] P. Politzer, R. G. Parr, and D. R. Murphy, “Relationships between atomic chemical potentials, electrostatic potentials, and covalent radii,” *J. Chem. Phys.*, vol. 79, no. 8, pp. 3859–3861, Oct. 1983.
- [103] W. Gordy, “Interpretation of Nuclear Quadrupole Couplings in Molecules,” *J. Chem. Phys.*, vol. 19, no. 6, pp. 792–793, Jun. 1951.
- [104] W. Gordy and W. J. O. Thomas, “Electronegativities of the Elements,” *J. Chem. Phys.*, vol. 24, no. 2, pp. 439–444, 1956.

- [105] R. J. Boyd and K. E. Edgecombe, "Atomic and Group Electronegativities from the Electron Density Distributions of Molecules," *J. Am. Chem. Soc.*, vol. 110, no. 13, pp. 4182–4186, Jun. 1988.
- [106] J. G. Malone, "The Electric Moment as a Measure of the Ionic Nature of Covalent Bonds," *J. Chem. Phys.*, vol. 1, no. 3, pp. 197–199, Mar. 1933.
- [107] C. A. Coulson, "The dipole moment of the C—H bond," *Trans. Faraday Soc.*, vol. 38, no. 0, pp. 433–444, Jan. 1942.
- [108] J. C. Phillips, "Dielectric Definition of Electronegativity," *Phys. Rev. Lett.*, vol. 20, no. 11, pp. 550–553, Mar. 1968.
- [109] L. Pauling, "Atomic Radii and Interatomic Distances in Metals," *J. Am. Chem. Soc.*, vol. 69, no. 3, pp. 542–553, Mar. 1947.
- [110] J. C. Slater, "Atomic Shielding Constants," *Phys. Rev.*, vol. 36, no. 1, pp. 57–64, Jul. 1930.
- [111] Housecroft C.E. and Sharpe A.G., "Electronegativity values," in *Inorganic chemistry*, Pearson Education Limited, 2005, p. 38.
- [112] R. J. Boyd and G. E. Markus, "Electronegativities of the elements from a nonempirical electrostatic model," *J. Chem. Phys.*, vol. 75, no. 11, pp. 5385–5388, Dec. 1981.
- [113] E. Clementi and C. Roetti, "Roothaan-Hartree-Fock atomic wavefunctions: Basis functions and their coefficients for ground and certain excited states of neutral and ionized atoms, $Z \leq 54$," *At. Data Nucl. Data Tables*, vol. 14, no. 3–4, pp. 177–478, Sep. 1974.
- [114] C. F. Bunge, J. A. Barrientos, and A. V. Bunge, "Roothaan-Hartree-Fock Ground-State Atomic Wave Functions: Slater-Type Orbital Expansions and Expectation Values for $Z = 2-54$," *At. Data Nucl. Data Tables*, vol. 53, no. 1, pp. 113–162, Jan. 1993.
- [115] C. Mande, P. Deshmukh, and P. Deshmukh, "A new scale of electronegativity on the basis of calculations of effective nuclear charges from X-ray spectroscopic data," *J. Phys. B At. Mol. Phys.*, vol. 10, no. 12, pp. 2293–2300, Aug. 1977.
- [116] Y. Zhang, "Electronegativities of Elements in Valence States and Their Applications. 2. A Scale for Strengths of Lewis Acids," *Inorg. Chem.*, vol. 21, no. 11, pp. 3889–3893, Nov. 1982.
- [117] M. V. Putz, "Systematic formulations for electronegativity and hardness and their atomic scales within density functional softness theory," *Int. J. Quantum Chem.*, vol. 106, no. 2, pp. 361–389, Jan. 2006.
- [118] M. V. PUTZ, "SEMICLASSICAL ELECTRONEGATIVITY AND CHEMICAL HARDNESS," *J. Theor. Comput. Chem.*, vol. 06, no. 01, pp. 33–47, Mar. 2007.
- [119] M. Putz, Putz, and M. V., "Density Functionals of Chemical Bonding," *Int. J. Mol. Sci.*, vol. 9, no. 6, pp. 1050–1095, Jun. 2008.
- [120] M. V. Putz, "Electronegativity: Quantum observable," *Int. J. Quantum Chem.*, vol. 109, no. 4, pp. 733–738, Mar. 2009.
- [121] D. Bergmann and J. Hinze, "Electronegativity and charge distribution," in *Electronegativity*, Berlin/Heidelberg: Springer-Verlag, 1987, pp. 145–190.
- [122] Y. Zhang, "Electronegativity from Ionization Potentials," *J. Mol. Sci.(Chinese)*, vol. 1, p. 125, 1981.
- [123] Y. Zhang, Zhang, and Yonghe, "Ionocovalency and Applications 1. Ionocovalency Model and Orbital Hybrid Scales," *Int. J. Mol. Sci.*, vol. 11, no. 11, pp. 4381–4406, Nov. 2010.
- [124] M. L. Huggins, "Bond Energies and Polarities," *J. Am. Chem. Soc.*, vol. 75, no. 17, pp. 4123–4126, Sep. 1953.
- [125] A. D. Walsh and M. G. Evans, "I. A possible new definition of electronegativity," *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, vol. 207, no. 1088, pp. 13–22, Jun. 1951.
- [126] H. B. Michaelson, "Relation Between an Atomic Electronegativity Scale and the Work Function," *IBM J. Res. Dev.*, vol. 22, no. 1, pp. 72–80, Jan. 1978.

- [127] S. S. Batsanov, "Dielectric Methods of Studying the Chemical Bond and the Concept of Electronegativity," *Russ. Chem. Rev.*, vol. 51, no. 7, pp. 684–697, Jul. 1982.
- [128] A. I. Martynov and S. S. Batsanov, "A new approach to the determination of the electronegativity of atoms," *Russ. J. Inorg. Chem.*, vol. 25, pp. 1737–1739, 1980.
- [129] T. Jecko, "On the mathematical treatment of the Born-Oppenheimer approximation," *J. Math. Phys.*, vol. 55, no. 5, p. 053504, May 2014.
- [130] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," *Ann. Phys.*, vol. 389, no. 20, pp. 457–484, 1927.
- [131] W. Pauli, "Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren English Translated version available," *Zeitschrift für Phys.*, vol. 31, no. 1, pp. 765–783, Feb. 1925.
- [132] H. A. Kramers, "The general theory of paramagnetic rotation in crystals," in *Proc. Acad. Amst*, 1930, pp. 959–972.
- [133] J. Franck, E. D.-T. of the F. Society, and undefined 1926, "Elementary processes of photochemical reactions," *pubs.rsc.org*.
- [134] E. Condon, "A Theory of Intensity Distribution in Band Systems," *Phys. Rev.*, vol. 28, no. 6, pp. 1182–1201, Dec. 1926.
- [135] G. A. Hagedorn, "A time dependent Born-Oppenheimer approximation," *Commun. Math. Phys.*, vol. 77, no. 1, pp. 1–19, Feb. 1980.
- [136] G. A. Hagedorn, "High order corrections to the time-independent Born-Oppenheimer approximation II: Diatomic Coulomb systems," *Commun. Math. Phys.*, vol. 116, no. 1, pp. 23–44, Mar. 1988.
- [137] G. A. HAGEDORN and A. JOYE, "MOLECULAR PROPAGATION THROUGH SMALL AVOIDED CROSSINGS OF ELECTRON ENERGY LEVELS," *Rev. Math. Phys.*, vol. 11, no. 01, pp. 41–101, Jan. 1999.
- [138] G. A. Hagedorn and A. Joye, "A Time-Dependent Born-Oppenheimer Approximation with Exponentially Small Error Estimates," *Commun. Math. Phys.*, vol. 223, no. 3, pp. 583–626, Nov. 2001.
- [139] G. A. HAGEDORN and A. JOYE, "A MATHEMATICAL THEORY FOR VIBRATIONAL LEVELS ASSOCIATED WITH HYDROGEN BONDS II: THE NON-SYMMETRIC CASE," *Rev. Math. Phys.*, vol. 21, no. 02, pp. 279–313, Mar. 2009.
- [140] M. Klein, A. Martinez, and X. P. Wang, "On the Born-Oppenheimer approximation of wave operators in molecular scattering theory," *Commun. Math. Phys.*, vol. 152, no. 1, pp. 73–95, Feb. 1993.
- [141] M. Klein, A. Martinez, and X. P. Wang, "On the Born–Oppenheimer approximation of diatomic wave operators. II. Singular potentials," *J. Math. Phys.*, vol. 38, no. 3, p. 1373, Jun. 1998.
- [142] A. Martinez and B. Messirdi, "Resonances of diatomic molecules in the born-oppenheimer approximation," *Commun. Partial Differ. Equations*, vol. 19, no. 7–8, pp. 1139–1162, Jan. 1994.
- [143] H. Spohn and S. Teufel, "Adiabatic Decoupling and Time-Dependent Born–Oppenheimer Theory," *Commun. Math. Phys.*, vol. 224, no. 1, pp. 113–132, Nov. 2001.
- [144] S. Teufel and J. Wachsmuth, "Spontaneous Decay of Resonant Energy Levels for Molecules with Moving Nuclei," *Commun. Math. Phys.*, vol. 315, no. 3, pp. 699–738, Nov. 2012.
- [145] B. T. Sutcliffe and R. G. Woolley, "On the quantum theory of molecules," *J. Chem. Phys.*, vol. 137, no. 22, p. 22A544, Dec. 2012.
- [146] B. T. Sutcliffe and R. G. Woolley, "Comment on 'On the quantum theory of molecules' [J. Chem. Phys. 137, 22A544 (2012)]," *J. Chem. Phys.*, vol. 140, no. 3, p. 037101, Jan. 2014.
- [147] C. F. Kammerer and V. Rousse, "Resolvent Estimates and Matrix-Valued Schrödinger Operator with Eigenvalue Crossings; Application to Strichartz Estimates," *Commun. Partial Differ. Equations*, vol. 33, no. 1,

pp. 19–44, Jan. 2008.

[148] E. B. Wilson, “Four-Dimensional Electron Density Function,” *J. Chem. Phys.*, vol. 36, no. 8, pp. 2232–2233, Apr. 1962.

[149] R. E. Stanton, “Hellmann-Feynman Theorem and Correlation Energies,” *J. Chem. Phys.*, vol. 36, no. 5, pp. 1298–1300, Mar. 1962.

[150] B. M. Deb, “Chapter 1,” in *The Force concept in chemistry*, Van Nostrand Reinhold, 1981, p. Page 9.

[151] D. Andrae, Ed., *Hans Hellmann: Einführung in die Quantenchemie*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2015.

[152] I. N. Levine, *Quantum Chemistry*, 5th ed. Pearson/Prentice Hall, 2009.

[153] P. Politzer and J. S. Murray, “The Hellmann-Feynman theorem: a perspective,” *J. Mol. Model.*, vol. 24, no. 9, p. 266, Sep. 2018.

[154] W. Pauli, “Die allgemeinen Prinzipien der Wellenmechanik,” in *Quantentheorie*, Berlin, Heidelberg: Springer Berlin Heidelberg, 1933, pp. 83–272.

[155] H. Hellmann, “Zur Rolle der kinetischen Elektronenenergie für die zwischenatomaren Kräfte,” *Zeitschrift für Phys.*, vol. 85, no. 3–4, pp. 180–190, Mar. 1933.

[156] P. Güttinger, “Das Verhalten von Atomen im magnetischen Drehfeld,” *Zeitschrift für Phys.*, vol. 73, no. 3–4, pp. 169–184, Mar. 1932.

[157] E. Schrödinger, “Quantisierung als Eigenwertproblem,” *Ann. Phys.*, vol. 385, no. 13, pp. 437–490, Jan. 1926.

[158] A. C. Hurley, “The Electrostatic Calculation of Molecular Energies. I. Methods of Calculating Molecular Energies,” *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 226, no. 1165, pp. 170–178, Nov. 1954.

[159] A. C. Hurley, “The Electrostatic Calculation of Molecular Energies. II. Approximate Wave Functions and the Electrostatic Method,” *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 226, no. 1165, pp. 179–192, Nov. 1954.

[160] A. C. Hurley, “The Electrostatic Calculation of Molecular Energies. III. The Binding Energies of Saturated Molecules,” *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 226, no. 1165, pp. 193–205, Nov. 1954.

[161] A. C. Hurley, “The Electrostatic Calculation of Molecular Energies. IV. Optimum Paired-Electron Orbitals and the Electrostatic Method,” *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 235, no. 1201, pp. 224–234, Apr. 1956.

[162] R. F. W. Bader, “Binding Regions in Polyatomic Molecules and Electron Density Distributions,” *J. Am. Chem. Soc.*, vol. 86, no. 23, pp. 5070–5075, Dec. 1964.

[163] R. F. W. Bader and W. H. Henneker, “The Ionic Bond,” *J. Am. Chem. Soc.*, vol. 87, no. 14, pp. 3063–3068, Jul. 1965.

[164] R. F. W. Bader and H. J. T. Preston, “A CRITIQUE OF PAULI REPULSIONS AND MOLECULAR GEOMETRY,” *Can. J. Chem.*, vol. 44, no. 10, pp. 1131–1145, May 1966.

[165] R. F. W. Bader, “THE USE OF THE HELLMANN-FEYNMAN THEOREM TO CALCULATE MOLECULAR ENERGIES,” *Can. J. Chem.*, vol. 38, no. 11, pp. 2117–2127, Nov. 1960.

[166] R. F. W. Bader and G. A. Jones, “the Hellmann-Feynman Theorem and Chemical Binding,” *Can. J. Chem.*, vol. 39, no. 6, pp. 1253–1265, Jun. 1961.

[167] T. Koga and H. Nakatsuji, “The Hellmann-Feynman theorem applied to long-range forces,” *Theor. Chim. Acta*, vol. 41, no. 2, pp. 119–131, 1976.

[168] T. Koga, H. Nakatsuji, and T. Yonezawa, “Generalized Berlin diagram for polyatomic molecules,” *J. Am. Chem. Soc.*, vol. 100, no. 24, pp. 7522–7527, Nov. 1978.

- [169] T. Koga, H. Nakatsuji, and T. Yonezawa, "Force and density study of the chemical reaction process $\text{OH}_2 + \text{H}^+ \rightarrow \text{OH}_3^+$," *Mol. Phys.*, vol. 39, no. 1, pp. 239–249, Jan. 1980.
- [170] P. Politzer, "A Study of the Bonding in the Hydrogen Molecule 1 ," *J. Phys. Chem.*, vol. 70, no. 4, pp. 1174–1178, Apr. 1966.
- [171] P. Politzer and K. C. Daiker, "Molecular electrostatic potentials. Negative potentials associated with some methyl and methylene groups," *Chem. Phys. Lett.*, vol. 34, no. 2, pp. 294–297, Jul. 1975.
- [172] A. J. Coleman, "Structure of Fermion Density Matrices. II. Antisymmetrized Geminal Powers," *J. Math. Phys.*, vol. 6, no. 9, pp. 1425–1431, Sep. 1965.
- [173] A. J. Coleman, "INFINITE RANGE CORRELATION AND LARGE EIGENVALUES OF THE 2-MATRIX," *Can. J. Phys.*, vol. 45, no. 3, pp. 1271–1273, Mar. 1967.
- [174] A. J. Coleman, "Necessary Conditions for N -Representability of Reduced Density Matrices," *J. Math. Phys.*, vol. 13, no. 2, pp. 214–222, Feb. 1972.
- [175] J. C. Slater, "Hellmann-Feynman and Virial Theorems in the $X\alpha$ Method," *J. Chem. Phys.*, vol. 57, no. 6, pp. 2389–2396, Sep. 1972.
- [176] T. Berlin, "Binding Regions in Diatomic Molecules," *J. Chem. Phys.*, vol. 19, no. 2, pp. 208–213, Feb. 1951.
- [177] A. Larsen, R. S. Poulsen, and T. P. Garm, "Applied Hartree-Fock methods Atomic and diatomic energy computations," Denmark, 2015.
- [178] J. C. Slater, "Atomic Shielding Constants," *Phys. Rev.*, vol. 36, no. 1, pp. 57–64, Jul. 1930.
- [179] E. Clementi and D. L. Raimondi, "Atomic Screening Constants from SCF Functions," *J. Chem. Phys.*, vol. 38, no. 11, pp. 2686–2689, Jun. 1963.
- [180] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, "Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons," *J. Chem. Phys.*, vol. 47, no. 4, pp. 1300–1307, Aug. 1967.
- [181] J. C. Slater, "Atomic Radii in Crystals," *J. Chem. Phys.*, vol. 41, no. 10, pp. 3199–3204, Nov. 1964.
- [182] D. C. Ghosh, T. Chakraborty, and B. Mandal, "The electronegativity scale of Allred and Rochow: revisited," *Theor. Chem. Acc.*, vol. 124, no. 3–4, pp. 295–301, Oct. 2009.