Electronegativity: A Force or Energy

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

How to cite this paper: P Ramakrishnan
"Electronegativity: A Force or Energy"
Published in International Journal of Trend in Scientific Research and Development (IJTSRD), ISSN: 2456-6470, Volume-3 | Issue-4, June 2019, pp.665-685, URL: https://www.ijtsrd.com/papers/ijtsrd23864.pdf

Copyright © 2019 by author(s) and International Journal of Trend in Scientific Research and Development Journal. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (CC BY 4.0) (http://creativecommons.org/licenses/by/4).

ABSTRACT

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

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

1. INTRODUCTION

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

He could not exploit the use of correlation to quantify the electronegativity scale by bringing a similar relationship between evolution of heat and difference of electronegativity. In the year 1870, Baker had already inserted three atomic parameters like weight (quantity of matter), valence (quantity of an atom’s combining power), and electronegativity (quality of an atom’s combining power). The caloric theory of heat was discarded completely in 1930s and the birth of thermo-chemistry from the laws of thermodynamics and kinetic molecular theory compelled the scientists to establish a correlation between the heat of reaction and electronegativity. The probable correlation between electronegativity and heat of reaction was suggested by Van’t Hoff1-2, Caven & Lander1-3 and Sackur1-4. Electronegativity was defined with help of terminologies such as heterolytic/homolytic bond dissociation enthalpy data, electron affinity, ionization energy (adiabatic, ground state, ionization, ionization potential and vertical ionization), effective nuclear charge and covalent radius, average electron density, stretching force constants, compactness, configurational energy, dielectric properties, work function, number of valence electrons, pseudopotentials and power. The electronegativity is an intuitive-cum-qualitative construct. This qualitative construct is very difficult to be quantified. The first quantification and assignment of numerical value to electronegativity was given by Linus Pauling4. From 1932, a number of qualitative and quantitative scales for electronegativity have been proposed by different researchers across the globe. The quest for new electronegativity scale study is still going on as this concept is confusing. The concept of electronegativity has been used to sketch the distribution and rearrangement of electronic charge in a molecule6-9. The fundamental descriptors in chemical science like bond energies, bond polarity, dipole moments, and inductive effects are being conceptualized and modeled for evaluation. The scope of this concept is so broad that ionic bond, atom-atom polarizability, equalization of electronegativity, apicophilicity, group electronegativity, principle of maximum hardness, electronic chemical potential, polar effect (inductive effect, effective charge, pi-electron acceptor/donor group), field effect, conjugative mechanism, mesomeric effect could have been explained. The correlations between electronegativity and superconducting transition temperature for solid elements and high temperature superconductors10,11, the chemical shift in NMR spectroscopy12, isomer shift in Mossbauer spectroscopy13 have already been explained. This concept has also been utilized for the design of materials for energy conversion and storage device14. The experimental determination of electronegativity of individual surface atoms using atomic force spectroscopy has already been reported15. In this article, various concepts of electronegativity are overviewed followed by introduction to a new concept based on Hellmann-Feynman theorem.

2. Energy model of electronegativity

2.1 Pauling’s (1932) empirical electronegativity scale

A classical incarnation of electronegativity in terms of an atom’s ability to attract electron towards itself was introduced by Linus Pauling in 19324. 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 ($\Delta$). Again, Pauling and Sherman$^{19}$ have reported that $\Delta$ was not always positive for which Pauling replaced $[DE(A_2)DE(B_2)]/2$ in place of $[DE(A_2)+DE(B_2)]/2$ for his electronegativity equation such as

$$\left| C_A - C_B \right| = 0.208^\circ \text{D}$$  
Eq. 1

Where,

$$D = \frac{1}{2} \left[ D_{A\rightarrow B} + 0.5(D_{A\rightarrow B} + D_{B\rightarrow A}) \right]$$ based on AM  
$$D = \frac{1}{2} \left[ D_{A\rightarrow B} - (D_{A\rightarrow B} - D_{B\rightarrow A}) \right]$$ based on GM  
Eq. 2

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

$DE(AB)$ = Bond dissociation energy of $AB$ (Actual bond energy)

$DE(A_2)$ = Bond dissociation energy of $A_2$

$DE(B_2)$ = Bond dissociation energy of $B_2$

Pauling’s quantum mechanical approach also indicates the dipole moment due to the presence of significant ionic structure $A-B$.

The extra-ionic resonance energy ($\Delta$) arises out of contribution of ionic canonical forms to bonding and it was experimentally verified. 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

$$i_{\text{ionicity}} = 1 - \exp \left( \frac{|X_A - X_B|^2}{4} \right)$$  
Eq. 3

1 (ionicity) = $1 - \exp [-1/4|X_A-X_B|^2]$ and 0(ionicity) = $1 - (N/M)[\exp -1/4|X_A-X_B|^2]$

Pauling’s thermochemical scale was viewed as the culmination of the 19th century concept of electronegativity. Pauling’s empirical electronegativity values derived from bond energies have been used to correlate between chemical and physical properties of a large number of elements followed by theoretical justification. In the year 1932, electronegativity values of ten non-metallic elements was proposed by Pauling$^8$ where $\chi(H)=2.1$ (arbitrary reference to construct a scale) latter changed to 2.2, $\chi(F)=4$. Furthermore, electronegativity values of 29 main group elements was proposed by Linus Pauling in 1939. In 1946, Haissinsky reported electronegativity values for 73 elements. 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). In 1960–61, A. L. Allred updated Pauling’s original electronegativity values for 69 elements where electronegativity of hydrogen was taken as 2.2$^{19}$.$^{24}$ In 1960–61, A. L. Allred updated Pauling’s original electronegativity values for 69 elements where electronegativity of hydrogen was taken as 2.2$^{19}$.$^{24}$ Pauling Electronegativity is not perfect because of the scientific objections like 1) To assign a single electronegativity value to each ‘atom in a molecule at all enough’ is not sufficient as reported by Haissinsky$^{17}$.$^{23}$ and Walsh$^{17}$.$^{25}$ inspite of confirmation of empirical usefulness through several investigations.

To obtain electronegativity is weak one as reported by Ferreira$^{17}$.$^{24}$ because of the assignment of one number to an atom, non – consideration of changes of hybridization, total neglect of effects of atomic charges. 3) Restriction on electronegativity as a fixed atomic character. Further, this scale has been criticized by Iczkowski and Margrave$^{27}$, Pearson$^{29}$, Allen$^{29}$.$^{30}$. The chemical validity of this scale is its continuity as standard for other scales. Pauling type electronegativity is an ambiguity for the elements with several oxidation states of different bond energies$^{31}$.$^{32}$

2.2 Mulliken’s (1934 and 1935) absolute electronegativity

Mulliken$^{20}$.$^{23}$ developed an alternative definition for the electronegativity shortly after Pauling’s definition based on energy concept. He considered three structures (i) $AB$, (ii)$A-B^-$, (iii)$A^{-}B^+$ where the two ionic structures (ii) and (iii) would be of equal weights in the wave function containing ii and iii and so that the complete covalent structure will be possible under the condition

$$IP_A - EA_B + V = IP_B - EA_A + V$$  
Eq. 4

$$\Rightarrow IP_A + EA_A = IP_B + EA_B$$  
Eq. 5

Mulliken suggested the term $IP_A + A_A$ or $IP_B + A_B$ is a measure of electronegativity of atom $A$ or $B$ respectively. $V$ is coulomb potential. With $I_A$ and $I_B$ assumed to be 1 and $A_A$ and $A_B$ assumed to be $A$, Mulliken expressed electronegativity as

$$\chi^M = \frac{(I_A+A_A)}{2}$$ or $$\chi^M = \frac{(I_B+A_B)}{2}$$  
Eq. 6

In general,  

$$\chi^M = \frac{(IP + EA)}{2} \text{ eV}$$  
Eq. 7

Where, $V$=Coulomb Potential

$I_P$ – ionization potential (in eV or kcal/mol)

$EA$ – electron affinity (in eV or kcal/mol)

The values of $IP$ and $EA$ can be computed for atoms in either of states such as ground, excited, or valence state. The scientific reports made by Stark$^{13}$.$^{34}$, Martin$^{13}$.$^{35}$, and Fajans$^{13}$.$^{36}$ have concluded the co-relation between Electronegativity, ionization energy and electron affinity. The rigorous qualitative derivation has also been examined by Moffitt$^{37}$ and Mulliken$^{33}$ himself. The half factor included in eq. 7 represents electronegativity as the average binding energy of the electron in the vicinity of the concerned atom. Mulliken’s electronegativity is an arithmetic average of ionization potential and electron affinity of an atom in the ground state.

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

$$\chi(M) = -\mu(M) = -(IP+EA)/2$$  
Eq. 8
The empirical correlation reported by Mulliken between $\chi_{\text{Mulliken}}$ and $\chi_{\text{Pauling}}$ is given by:

$$\chi_{\text{Pauling}} = \chi_{\text{Mulliken}} \frac{IP + EA}{2.78}$$

Eq. 9

Where $I$, $A$ in kcal/mol, $1/2.78$ is scale adjustment factor. Huheey$^{30}$ reported Mulliken electronegativity as

i. $X = 0.187(I + A) + 0.17$ with $I$ and $A$ in electron volts

ii. $X = [1.97(10^{-3})IP + EA] + 0.19$ with $IP$ and $EA$ in kilojoules per mole

Pritchard and Skinner$^{39,40}$ have reported the correlation between $\chi_{\text{Mulliken}}$ and $\chi_{\text{Pauling}}$ as:

$$\chi_{\text{Mulliken}} = 3.15 \times \chi_{\text{Pauling}}$$

Eq. 10

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

2.2.1 Lang and Smith$^{45,46}$ defined electronegativity as a simple function of

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

where

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

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

2.3 Allen's absolute scale of Spectroscopic Electronegativity

Allen$^{39,40}$ defines Electronegativity as the average one-electron energy of valence shell electrons in ground-state free atom and proposed it as third dimension and also energy dimension of periodic table. So, this type of electronegativity is a Free-atom ground-state quantity with a single defining number which gives its meaning as an extension of periodic table. Allen has introduced two terms – Energy index (in situ $X_{\text{spec}}$ 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 $\Delta X_{\text{spec}}$). The fractional polarity defined from Bond polarity index is equivalent of Pauling's dipole moment referenced 'ionic character percent' Allen has reported a new chemical pattern by mounting a series funnel-shaped potential energy plots (E vs r) along a line of increasing Z i.e along a row of periodic table where a composite curve one-electron energy (vertical axis) vs a part row of periodic table is obtained. This composite curve shows a strong correlation between magnitude of $X_{\text{spec}}$ and energy level spacing (large $X_{\text{spec}}$ with large spacing) like energy level like energy levels of Fermi-Thomas-Dirac atom and in case of other atoms.

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

Electronegativity for representative elements i.e. $X_{\text{spec}} = (a + b\epsilon_p)/a + b$ equation (i) is occupation weighed average per electron ionization energy of an atom where $a,b$ are occupation number and $\epsilon_p$, $\epsilon_s$ are spherical ionization potentials which are determined through multiplet averaging. But for transition elements, $I$ is replaced by $\Delta I$ and $a,b$ are the valence-shell occupancies of s-orbitals and d-orbitals in overlap region.

$$c_{\text{spec}} = \frac{a\hat{I} + b\hat{d}}{a + b}$$

Eq. 11

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

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.
2.4 Jorgensen\textsuperscript{47} introduced optical electronegativity scale ($\chi_{op}$) for rationalizing electron transfer spectra of transition metal complex (MX). In this scale a linear difference in $\chi_{op}$ represent the photon energy ($h\gamma$) as per the following relation.

$$h\gamma = \left[ c_{op}(X) - c_{op}(M) \right] \times 10^4 \text{ cm}^{-1} \quad \text{Eq. 12}$$

A linear relationship of $\chi_{op}$ to the difference in eigen values as introduced by Jorgensen is an idea which can be rationalized in terms of density functional approach to $\chi$.

2.5 J.C.Slater et al.

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

2.6 Simons\textsuperscript{31,50} has reported a theoretical scale to determine atomic electronegativity values where bonds are described by Gaussian Type orbitals. These orbitals are assumed to float to a point of minimum energy between the atoms. The electronegativity values are obtained from Floating Spherical Gaussian Orbital (FSGO wave functions)\textsuperscript{51}. Simons and Frost defined an orbital multiplier ($f_{AB}$= $r_A$/$[r_A+r_B]$) where $r_A$ and $r_B$ label as atomic distances with respect to the orbital center. $f_{AB}$ of 0.5 implies of equal attraction between the atoms. For $f_{AB}$<0.5, A attracts B to a large extent. For $f_{AB}$>0.5, B attracts A to large extent. Simons defined the electronegativity difference as

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

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

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

$$E(n,l) = -0.5Z^2 \left[ n + \hat{l}(l + 1) - l \right]^{-2} \quad \text{Eq. 14}$$

Where

- $Z$ = core charge
- $\hat{l}$ = quantum defect

The orbital electronegativity for valence orbital is defined as

$$\chi_{l}^{IB} = \frac{1}{r_l} \equiv \frac{1}{\hat{l}(\hat{l} + 1)/Z} \quad \text{Eq. 15}$$

where

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

$x\beta$ – orbital electronegativity for valence orbital

$r$ – radius for valence orbital

$l$- orbital quantum number

Atomic electronegativity is represented as

$$\chi = 0.43 \times \sum_{l=0}^{2} \chi_{l}^{IB} + 0.24 \quad \text{Eq. 16}$$

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

3. Energy Charge model of electronegativity

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

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

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

$$a = \frac{IE + EA}{2} \quad \text{Eq. 18}$$

3.2 Huheey’s Idea of Group electronegativity

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

$$[a_i + b_i\delta_i = a_j + b_j\delta_j] \quad \text{-- Group -- wxy}$$

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

$$c_G = a + bd_G \quad \text{Eq. 20}$$

Where $\delta_G$ represents partial charge due to gain/loss of one electron.
a (normal group electronegativity/inherent electronegativity) = (IP-EA)/2
b (charge transfer coefficient) = IP+EA
S G Bratsch has simplified Huheey’s method by using Sanderson’s principle of Electronegativity equalization.

\[ \chi = \chi_A(1+\delta A), \quad X = \frac{(N+\delta g)}{\sum(n)/\chi A} \]  

Eq. 21

Where \( \chi \) represents electronegativity for the molecule or the group, \( n \) represents number of atoms of A, \( N=\Sigma(n) \) represents the total number of atoms, \( \delta A \) is the charge in the group. Mullay has reported the value of ‘b’ as 1.5 times of ‘a’. 

### Weakness

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

#### 3.3 Hinze-Whitehead-Jaffe contribution to Electronegativity

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

\[ \chi_A(atomic\ orbital\ j) = \delta E_A/\delta n \]  

Eq. 22

\[ c_{A,j}(atomic\ orbital\ j) = \frac{dE_A}{dn_j} \]  

Eq. 23

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

\[ dn_A = dn_B \]  

Eq. 24

\[ \frac{dE_A}{dn_A} = \frac{dE_B}{dn_B} \]  

Eq. 25

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

### Strength

The Hinze et al. approach to the electronegativity theory is somewhat simple because it neglects resonance and electrostatic effects. Pritchard suggests the inequality of electronegativity by an order of 10% of the original electronegativity. Bartolotti et al. have suggested the equality of electronegativity in their work. Politzer et. al. have reported the non-importance of the idea of orbitals in electronegativity theory. Mullay and Watson et. al. have reported the potential usefulness of group electronegativity which are obtained from the idea of orbital electronegativity in conjunction with electronegativity equalization.

#### Weakness

The Hinze et al.’s work is simple still then it did not meet the criterion for electronegativity. Some authors suggest that the orbital concept of electronegativity never solves the meaning ‘Atom in Molecule’.

#### 3.4 G Klopman’s atomic electronegativity

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

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

Eq. 26

Where,
- \( Ry \) = Rydberg constant
- \( Z \) = Atomic number
- \( n \) = Principal quantum number
- \( dn \) = Quantum defect
- \( \sigma \) = Screening constant

The screening constant \( \sigma \) is represented as

\[ \sigma = \sum_{j \neq i} q_j \sigma_{ji} \]  

Eq. 27

Where
- \( q_i \) is the occupation number of spin orbital \( j \)
- \( \sigma_{ji} \) is the screening of the electron \( j \) by the electron \( i \)

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

\[ dn = 3.687(Z^*)/IP \]  

Eq. 28

Where,
- \( n \) = Principal quantum number
- \( Z^* \) = effective nuclear charge
- \( IP \) = Ionization potential

Total electronic energy of Valence shell,

\[ E_{val} = \sum_{i} \frac{13.6}{(n_i - d_i)} \frac{1}{2} \left( \sum_{j \neq i} q_j \sigma_{ji} \right) = \sum_{i} \frac{13.6}{(n_i - d_i)} \frac{1}{2} \left( \sum_{j \neq i} q_j A_i^j \right) \]  

Eq. 29

\[ B_s = 13.6 \frac{Z^2}{(n-d)^2} - \frac{1}{2} A_s^s = 2 \left[ \frac{Z^2}{(n-d)^2} \right] \sum_{j} C_j \]  

Eq. 30
Further, Total electronic-energy equation of the diatomic system (AB) at barycenter is represented as,

$$E_{\text{tot}} = \sum_i q_i B_i + \sum_{j \neq i} q_j A_j d_{ij} + \sum_i q_i q_j (1 - d_{ij}) + \sum_i q_i q_j \chi_{ij}$$

Eq. 31

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

$$c_{\text{Atomic-Electronegativity}} = \frac{dE}{dq_i} = B_i + \sum_j q_j A_j d_{ij} + \sum_j q_j A_j (1 - d_{ij}) + \sum_j q_j \chi_{ij}$$

Eq. 32

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

Strength

Klopman’s procedure helps in calculating Neutral Atomic Electronegativity. This procedure provides theoretical support and clarification for electronegativity suggested by Iczkowski and Margrave, Hinze, Whitehead and Jaffe. Weakness: Kolpman’s work has been modified and extended to provide a simple procedure for calculation of atomic or orbital electronegativity and also for group electronegativity.

3.5 Ponec’s idea of Global electronegativity

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

$$\chi_{G(A)} = \frac{1}{2} \left( \rho_A - \frac{1}{2} \right) \chi_A$$

Eq. 33

Where

- $\chi_A$ - orbital electronegativity
- $E_j$ - one electron energy of orbital j
- $\chi$ - electron repulsion integral
- $\rho_A$ - total electron density associated with atom A

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

$$\chi_{G(A)} = \frac{\sum_j P_j \chi_{Aj}}{\sum_j P_j}$$

Eq. 34

Where

- $\chi_{G(A)}$ - Global electronegativity in a molecule
- $P_j$ - charge density on atomic orbital j on A
- $\chi_{Aj}$ - Orbital electronegativity

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

3.6 Iczkowski & Margrave approach

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

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

Eq. 35

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

$$c = - \frac{dE}{dN} \frac{\dot{\delta}}{\delta N} \mid_{N=0}$$

Eq. 36

This also represents (i) the tendency of an atom in a molecule to attract electrons for small charge dislocation during interaction of atoms and (ii) the decrease of energy of 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. Thus, electronegativity characterizes both the internal constitution of atom and the ions which can be formed from it. Again, the electronegativity represents an intensity factor in charge transfer from one atom to the other atom.

Strength

This concept of electronegativity in terms of energy-charge derivative have also been justified through ingenious and laudable efforts of various authors. 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 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.

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

Eq. 37
With this approximation, Jaffe et al. were able to calculate the group orbital electronegativity (i.e., electronegativity of free orbital of an atom bound to other atom). iv) The principle of electronegativity equalization of Sanderson helped in initiating the calculation of charge distribution. V) The above principle has been used by Ferreira for calculation of bond energy and charge distribution in many binuclear molecules.

**Weakness**

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

### 3.7 Parr's density functional electronegativity

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

**Theorem I:**

\[ E[r] = \int \rho(1)v(1)dt_1 + F[r] \quad \text{Eq. 38} \]

**Theorem II:**

\[ E[\rho] = \int \rho \nabla V \cdot \nabla(\rho) dt + F[\rho] \quad \text{Eq. 39} \]

However, theorem I implies that the ground-state electronic energy is a functional of the density. Whereas, theorem II considers inequality with equality holding for \( \rho = \rho_0 \), \( E[\rho] = E_0[\rho] \). The density \( \rho \) 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 \( -\frac{\delta E}{\delta \rho} = \text{constant} \), external potential and Parr et al. identified electronegativity as the negative of Lagrange multiplier which is also considered as chemical potential, \( \mu = -\frac{\delta E}{\delta \rho} \), by the first derivative of energy with respect to \( N \) such as \( \frac{\delta E}{\delta N} \), on the basis of Einhorn et al. [124], where \( v \) stands for fixed potential due to set of nuclei and external field, \( \rho \) represents for electronic density. Parr et al. defined electronegativity as,

\[ c = -m = -\frac{\delta E[\rho]}{\delta N} \quad \text{Eq. 40} \]

by considering the similarity between the above expression for \( \mu \) and electronegativity expression of Iczwoscki and Margrave. The concept of chemical potential has also kept electronegativity as a Global index to characterize the chemical structure. The geometric mean law constitutes a prediction on how molecular electronegativity is related to atomic electronegativity and does not trivially extend to a prediction of molecular electronegativity from functional group electronegativity because the primary sites for electron attraction in a molecule are nuclei of atoms. Parr and Bartolotti have justified that electronegativity is constant throughout an atom or a molecule and also remains constant from orbital to orbital within an atom or a molecule. Again, it is shown how valence state electronegativity differences drive charge transfer on molecule formation. Parr and Pearson have established a Global Electrophilicity Power index.

\[ m = g \frac{IP' - EA}{IP - EA} \quad \text{Eq. 41} \]

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

\[ A^+ + (e) \rightarrow A \rightarrow A^- \]

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

\[ (w) = \mu 2/2\eta \quad \text{Eq. 42} \]

where \( \eta \) chemical hardness.

This index is a measure of lowering energy of the chemical entity during the transfer of electron. This density functional electronegativity encounters with severe differentiability problem where a discontinuous function is put forcibly to differentiation by violating the basic definition of derivative. This above problem was solved partially by ingenious efforts of the proponents. The strength for this concept comes from electronegativity equalization principle. This electronegativity is defined in terms of ground-state energy of a free atom or a free molecule. The conversion of Parr et al. 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, Pearson, Komorowski, and Datta et al. have pointed out that Parr et al. formula implies the transfer of electron between free-atom or free-molecule and external surroundings whereas initial concept of electronegativity is always referred to redistribution of electrons within a molecule.

### 3.8 Politzer 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 has been deduced in terms two physical models where in one model, total energy of molecular system \( AB \) is a function of associated electrons with each atom (\( n_a \) and \( n_b \)) corresponding atomic numbers (\( Z_a \) and \( Z_b \)) and inter-nuclear distance (\( R \)).

\[ E = f(n_a,n_b,Z_a,Z_b,R) \quad \text{Eq. 43} \]

For a molecule ab in the ground state under equilibrium,
\[ \chi(\Delta S/\sqrt{\chi_{SR}} = 2.08 \text{ and } \chi_{SR} \text{ value is expressed in terms of } \sqrt{\chi_P} - 0.77)/0.21 \text{ where } \chi_P = \text{Pauling's value} \]

**Here Electronegativity of A and B**

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

\[ \text{Eq. 45} \]

In another model, total energy of the molecular system \(AB, E = f(n_{a1}, n_{b1}, Z_{a1}, Z_{b1}, n_{a2}, n_{b2}, R)\) is either a function of i.atomic numbers \(Z_{a1}, Z_{b1}\) atoms \(n_{a1}, n_{b1}\) and delocalized atoms inter-nuclear separation or a function of atomic number \(Z_{a1}, Z_{b1}\) atoms \(n_{a2}, n_{b2}\), inter-nuclear separation \(R\).

\[ E = f(Z_{a1}, Z_{b1}, n_{a2}, n_{b2}, \ldots, R) \]

\[ \text{is either a function of } i. \text{atomic numbers } Z_{a1}, Z_{b1} \text{ atoms } n_{a2}, n_{b2}, \ldots, \text{ inter-nuclear separation} \]

4. **Charge model of electronegativity**

4.1 **R T Sanderson approach to electronegativity**

R T Sanderson\(^{58,70,88–90}\) 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) and Sanderson reported equalization of different atomic electronegativity values during the formation of a molecule or a radical. The final value is obtained by considering the geometric mean of all atomic electronegativity values for estimating the atomic charge. He introduced the ratio of electronegativity change in forming the compound to the change in acquisition of a unit positive or negative charge. The unit change in electronegativity (ΔSR) is obtained from the original electronegativity (SR) with the help of the following relation

\[ \chi(\Delta S/\sqrt{\chi_{SR}} = 2.08 \text{ and } \chi_{SR} \text{ value is expressed in terms of } \sqrt{\chi_P} - 0.77)/0.21 \text{ where } \chi_P = \text{Pauling's value} \]

4.2 Gordy has reported various ways for calculation of electronegativity values\(^{91,95}\). One of all the three ways considers the electronegativity in terms of electrostatic potential and covalent radius.

\[ X_{G} = 0.62(Z/r) + 0.5 \]

\[ \text{Eq. 46} \]

4.3 Gordy\(^{90}\) correlated the ionic character with electronegativity difference by the use of nuclear quadrupole couplings constants for halide molecules. Gordy has assumed the use of p-orbitals by halogen atoms in formation of single bonds and has established the ionic character equation

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

Wilmshurst\(^{95}\) has reported different ionic relation: \[|\chi_A - \chi_B|/|\chi_A + \chi_B| = |\text{ Ionic(AB)}| \] which is used to analyse quadrupole coupling constants.

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

4.5 Malone\(^{101}\) suggested in 1933 a rough proportionality between the dipole moment of the bond A-B and electronegativity difference as

\[ \mu \cdot |\chi_A - \chi_B|_{Pauling} \]

\[ \text{Eq. 48} \]

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

The Malone's measure of electronegativity was rejected because of the reports of Coulson\(^{102}\)

4.6 Phillips\(^{103}\) has suggested dielectric definition of electronegativity by proposing a simple model for the static electronic dielectric constants of zinc-blende and wurtzite crystal. The dielectric constants have been correlated with that of diamond crystal which is a sp\(^3\) hybridized net-work. Phillip has extended two dimensional homo-polar model Hamiltonian to a four dimensional space which yields a relation between energy gap (\(E_{gap}\)) and the hetropolar static dielectric constant (\(\epsilon_0\)) such as

\[ \chi^G = 0.31 \times \left(\frac{v+1}{r}\right) + 0.5 \]

\[ \text{Eq. 47} \]

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

Utility:
This scale is very useful because of introducing the idea of the electrostatic potential into electronegativity along with bringing the equivalence of electronegativity with Allred-Rochow force scale\(^{96}\) inspite of the basis of two different parameters. Politzer and Parr\(^{93}\) reported some merit in the Gordy scale which gains theoretical support to some extent from Iczkowski\(^{127}\).
modification and extension of the above ideas were reported

Weakness of this scale is also three fold such as

- independent of electron affinities, bond dissociation energies
- Slater rules for finding effective nuclear charge are empirical
- Covalent radii are known for few elements

5. Force Model OF Electronegativity:

5.1 Allred and Rochow absolute scale

Allred and EG Rochow\(^5\) defined the electronegativity of an atom with electrostatic field and presented an equation for its evaluation and electronegativity will be equal to Coulomb force of attraction between the nucleus and an electron at the covalent radius.

\[
\mathcal{X}_{AR} = 3590 \times \left( \frac{Z'}{r^2} \right) + 0.744 \quad \text{ ..........(ii) Eq. 52}
\]

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

Strength of this scale is two-fold such as

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

5.2. The first extension of Allred-Rochow scale by Huheey\(^17\) is based on two assumptions, r ~ \(1/Z'\) and Z' ~ δ.

\[
\delta = \text{Partial atomic charge} \quad r = \text{Covalent radius}
\]

\[
c^{\prime\prime} = 0.36 \times \left( \frac{Z'-3d}{r^2} \right) + 0.74 \quad \text{ Eq. 53}
\]

5.3. The second extension of Allred-Rochow scale

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

\[
c = \frac{Z}{r} \left( \frac{Z'}{r} \right)^2 \quad \text{ Eq. 54}
\]

Where

- Z = Atomic number
- r = Relative covalent radius
- \(\rho(r)\) = radial charge density
- IP = Ionization potential, r->infinity

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

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

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

Zhang electronegativity is given by,

\[
c = 0.241[F] + 0.775 \quad \text{ Eq. 55}
\]

where

- r= pauling’s covalent radius
- IPz= ultimate ionization potential for outer electron

Yonghe Zhang has reported dual parameter equation\(^111\).
This equation is used as a scale for the strength of Lewis acid.

6. Quantum model of Electronegativity

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

\begin{equation}
\chi_{\text{Putz}} = -\frac{E_{\text{r}}}{\rho_{\text{b}}} = -\mu_{\text{r}} = \left\{ \begin{array}{ll}
\infty & E_{\text{r}} = 0, E_{\text{i}} < 0 \\
E_{\text{i}} & E_{\text{r}} = -\langle \psi_{\text{r}} | \hat{H} | \psi_{\text{r}} \rangle, \rho_{\text{b}} = 1
\end{array} \right.
\end{equation}

Eq. 57

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

7. Ionocovalency model of Electronegativity

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

\begin{equation}
I(IPz)^* C(n^*/r) = \frac{\omega}{R} P_{Q}^{1/2} n^* \frac{n^*}{r} \quad \text{Eq. 58}
\end{equation}

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

\begin{equation}
c_{\text{ic}} = 0.412 \frac{n^* (Iz / R)}{r} + 0.387 \quad \text{Eq. 59}
\end{equation}

where

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

8. Other models

8.1 Huggins (1953) model represents another alternative thermochanical procedure for electronegativity.

8.2 Walsh (1951)model brings relationship between electronegativity and stretching force constants of the bonds of an atom to hydrogen atom.

8.3 Michaelson (1978) model relates atomic electronegativity to the work function.

8.4 Martynov & Batsanov(1980) model gives electronegativity values through the average of successive ionization energies of the valence electrons of an element.

9. New model of electronegativity

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

Born-Oppenheimer Force and Hartree-Fock Force:

This force concept arises out of Born-Oppenheimer energy approximation as well as Hartree-Fock energy approximation. M Born and J R Oppenheimer\textsuperscript{119,120} have contributed a celebrated paper to science that brings the systematic correspondence of the energy of electronic motion, nuclear vibration and rotation to the terms of power series in the fourth root of electron –nucleus mass ratio. Born and Oppenheimer have suggested that total wave function (\(\Psi\)) can be written as the product of the nuclear wave function (\(\Phi_{\text{n}}\)) and electronic wave function (\(\Phi_{\text{e}}\)). This approximation simplifies complicated Schrödinger equation into electronic equation \((\text{He}\Phi_{\text{e}}=\text{E}\Phi_{\text{e}})\) and nuclear equation \((\text{Hn}\Phi_{\text{n}}=\text{E}\Phi_{\text{n}})\). The equation devised by them for the rotation represents a generalization of the treatment of Kramer and Pauli. This approximation also justifies Frank-Condon principle\textsuperscript{121,122} used in explaining the intensity of band lines. In the last several decades, rigorous – mathematical work has been reported on the validity of the B-O approximation. Quite a more no of papers\textsuperscript{66,70–81} contain the study of B-O and also have reported that a reduced Hamiltonian is an appreciable approximation to true molecular Hamiltonian but a few is closely related to works\textsuperscript{112,113,115} on semi-classical Schrödinger matrix operators. B-O approximation is based on “assumption of ignoring motions of nearly stationary nuclei with much larger mass and smaller velocity with respect to motion of electron with much smaller mass and larger velocity”. The approximation holds good for the ground state of molecule and breaks down for the excited state. Complete Hamiltonian is represented as

\begin{equation}
H = H_{\text{n}} + H_{\text{e}} = T_{\text{n}} + T_{\text{e}} + V_{\text{nn}} + V_{\text{en}} + V_{\text{ee}} \quad \text{Eq. 60}
\end{equation}

\begin{equation}
H_{\text{n}} = -\frac{1}{2} \sum_{\alpha} \hat{a}_{\alpha} \hat{a}_{\alpha}^{\dagger} S_{\alpha}^{2} \quad \text{Eq. 61}
\end{equation}

where

- \(\hat{a}_{\alpha}\) is the annihilation operator
- \(S_{\alpha}\) is the orbital angular momentum operator
- \(\hat{a}_{\alpha}^{\dagger}\) is the creation operator
- \(H_{\text{n}}\) is the nuclear Hamiltonian
- \(H_{\text{e}}\) is the electron Hamiltonian
- \(T_{\text{n}}\) is the kinetic energy of the nuclei
- \(T_{\text{e}}\) is the kinetic energy of the electron
- \(V_{\text{nn}}\) is the nuclear-nuclear potential
- \(V_{\text{en}}\) is the electron-nuclear potential
- \(V_{\text{ee}}\) is the electron-electron potential
Again, Molecular Hamiltonian\(^{136}(H_{\text{mol}})\)
\[\begin{align*}
H_{\text{mol}} &= -\frac{1}{2} \sum_{i} \hat{N}^{2}_{i} + \hat{N}^{2} + \sum_{i,j} \hat{Z}_{i} \hat{Z}_{j} \\
&= \sum_{i} \hat{N}_{i} + \frac{1}{2} \sum_{i,j} \hat{Z}_{i} \hat{Z}_{j} + \sum_{i} \hat{Z}_{i} - \sum_{i,j} \hat{Z}_{i} \hat{Z}_{j}
\end{align*}\]
Eq. 62

Where \(\lambda\) is treated as parameter and it may vary between 0 and 1.

The exact solution to the electronic Schrodinger equation, obtained from B-O approximation can be reachable for one electron systems. For multi-electronic systems, Hartree-Fock approximation is a good enough to approximate the energies of electron systems. Hellmann-Feynman theorem for actual motion and also -\(\partial E/\partial R\) replaces the above derivative and it is equal to the B-O force (also Hartree-Fock force) because nuclear co-ordinates are simply treated as external parameters. The term - (\(\partial \hat{E}/\partial R\)) is the operator which represents the force on atom A due to electrons and other atom B. This force is better to be termed as B-O force in the steady state. The electronegativity will be equal to B-O force (also Hartree-Fock force).

**Hellmann-Feynman Force:**

The force concept is the consequence of Hellmann-Feynman\(^{86,136-140}\) theorem. The expression for this theorem has already been reported by different authors\(^{140-144}\). This concept dictates that the actual force on any nucleus can be interpreted in terms of classical electrostatics if three dimensional charge distribution in a system of electrons and nuclei were known from quantum mechanical procedure. The force on a nucleus will be equal to charge on that nucleus times the electric field due to all electrons and other nuclei. R Feynman further stated that a three dimensional electron cloud in a molecule is restricted from collapsing as it obeys Schrödinger equation. The force concept explains the nature of chemical bonding, the change in molecular shape on excitation, chemical reaction. Energy concept is not proved to be satisfactory always because they lack the simplicity and elegant nature. A.C.Hurley\(^{145-148}\) has given the theoretical justification of the actual use of such electrostatic approach and shown that the force calculations are valid even for approximate wave functions. H-F force concept have been used (i) by R.F.W.Bader\(^{149-153}\) for interpreting chemical binding, (ii) by Koga T and H.Nakatsuji\(^{154-156}\) for force modelling of molecular geometry,(iii) by P.Politzer and K.C.Daiker\(^{157,158}\) for models of Chemical Reactivity, (iv) by A.J.Coleman\(^{159-162}\) for calculation of first and second order reduced density matrices and also withstand the critical examination of theoretical physicists and chemists as well. This force concept has certain advantage over the concept of total energy even though the calculation of force always involves an approximate charge density function. The advantage of calculating charge density is possible through molecular orbital method and total force on a nucleus is simple sum of orbital contributions but total energy is not sum of orbital energies. The second advantage is that force is an expectation value of one-electron, momentum independent operator which is more sensitive to any change in wave functions than energy. T Berlin\(^{163}\) gave clear interpretation of this electrostatic force arising out of Hellmann-Feynman theorem. This force will be equivalent to infinitesimal change in energy per change in distance (parameter). Classical physics states that a force is the negative gradient of energy. He proposed a term binding (related force acting on the nucleus) in place of bonding (related to changes in energy) in the picture of chemical bonding.

He has proposed the physical partitioning of three dimensional space of electrons of diatomic system into a binding region(f<1), anti-binding region(f=1) and the nonbinding region(f=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. The net value of f, 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 \(Z_{A}>>Z_{B}\) approaches a plane perpendicular to inter-nuclear axis. The idea of closing of anti-binding region is used to justify to assign more electronegativity value to B. Hellmann-Feynman force equation can be written in various forms\(^{86,136,162}\). See below 1234

Generalized form of Hellmann-Feynman force is represented as,
\[F_{i} = \frac{\partial E}{\partial \lambda} = -\frac{\partial y}{\partial l} y^{y} (\text{V} \cdot \text{dV})\]
Eq. 65
Where \(H_{E} = T+V\), \(\frac{\partial H_{E}}{\partial l} = \frac{\partial V}{\partial l}\) and
\[\frac{\partial y}{\partial l} y^{y} \frac{\partial V}{\partial l} \text{dV} ; \quad \frac{\partial y}{\partial l} y^{y} V \text{dV}\]
Eq. 66

\[F(R_{i}) = -\frac{\partial E}{\partial R_{i}} = \frac{\partial}{\partial R_{i}} \sum_{A} \frac{Z_{i} Z_{A}}{R_{i} - R_{i}} + \frac{\partial}{\partial R_{i}} \sum_{i} \frac{Z_{i}^{2}}{R_{i}^{2}} \text{dR}\]
Eq. 67
Where the first term is independent of the electronic coordinates and is constant during integration over the coordinates. This term gives ordinary columbia force of repulsion between the nuclei. The second term represents charge density distribution due to ith electron.
\[ F(R_A) = -\frac{\nabla E}{\nabla X_A} = -2\left(\frac{\hat{a}}{V_{s.A}} Z_{R_B} - R_A \right) + \frac{\hat{a}}{V_{s.A}} Z \frac{\partial}{\partial \mathbf{r}_i} \mathbf{r}_i \cdot \mathbf{R} - R_A \]  

Eq. 68

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

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

\[ F_A(R_A) = \frac{Z_i}{R_i} Z_B - \hat{a} f_i(R_A) \mathbf{u} \]  

Eq.69.

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

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

Eq. 70

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

\[ F_A(R) = Z_A \int \cdots \int \psi^{\dagger} \sum_{i=1}^{N} \mathbf{\nabla}_i \left( |r_i - R_A| \right)^{-1} \psi dr \]  

Eq. 71

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

\[ F_A(R) = Z_A \int \nabla A \left( |r - R_A| \right)^{-1} \rho(r) dr \]  

Eq. 72

where

\[ \rho(r) = N \int ds_1 \cdots \int \psi^{\dagger}_{(x_1, x_2, \ldots, x_N)} \psi_{(x_1, x_2, \ldots, x_N)} dx_N \]  

Eq. 73

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 ith 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 \( \rho(r) dr \).

9.1 Correlation among Electronegativity, Hellman-Feynman and Hartree-Fock Force

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

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

We propose this new model i.e Electronegativity=Hellmann-Feynman Force=Hartree-Fock Force

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

Eq. 74

ON THE BO approximation

\[ \langle F_A \rangle = \langle F(R) \rangle = -\frac{\nabla E}{\nabla X_A} = -\frac{\hat{a}}{V_{s.A}} Z_{R_B} - R_A - \frac{Z_A}{\mathbf{r}_i} \frac{\partial}{\partial \mathbf{r}_i} \mathbf{r}_i \cdot \mathbf{R} - R_A \]  

Eq. 75

\[ \langle F_A \rangle = \langle F(R) \rangle = -\frac{\nabla E}{\nabla X_A} = -2\frac{\hat{a}}{V_{s.A}} Z_{R_B} - R_A + \frac{Z_A}{\mathbf{r}_i} \frac{\partial}{\partial \mathbf{r}_i} \mathbf{r}_i \cdot \mathbf{R} - R_A \]  

Eq. 76

Where

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

Second terms in Eq 75 AND 76 above represent electronic contribution

\( <F_A> \) Hellmann-Feynman force is a sum of classical contribution due to classical nuclear contribution and electronic contribution

\( F= \) one electron, momentum-independent operator

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

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

\( R_A \) = Distance of nucleus of atom A form electron

\( R_B \) = Distance of nucleus of atom B from electron

9.2 Computation of Electronegativity

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

\[ \langle j \rangle X_e = E(hf)/r(\text{absolute radius}) \]  

\[ \chi_e = \frac{E(hf)}{r_{\text{absolute}}} \]  

Eq. 77

And also, the computational equations for electronegativity have also been considered in terms Coulombic force (au)
\[ \chi = \frac{Z^*}{r^2} \]

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

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

| ELEMENTS | Hartree-Fock Energy (HFE) (au) | Absolute Radii (pm) | \(X(hf) - 2/\text{AbR}(pm)\) |
|----------|-------------------------------|---------------------|-------------------------------|
| H        | 0.499                         | 52.92               | 0.01                          |
| He       | 2.861                         | 31.13               | 0.09                          |
| Li       | 7.432                         | 162.83              | 0.05                          |
| Be       | 14.572                        | 108.55              | 0.13                          |
| B        | 24.414                        | 81.41               | 0.3                           |
| C        | 37.531                        | 65.13               | 0.58                          |
| N        | 54.404                        | 54.28               | 1                             |
| O        | 74.619                        | 46.52               | 1.6                           |
| F        | 99.163                        | 40.71               | 2.44                          |
| Ne       | 128.546                       | 36.71               | 3.5                           |
| Na       | 161.858                       | 216.5               | 0.75                          |
| Mg       | 199.614                       | 167.11              | 1.19                          |
| Al       | 241.802                       | 136.08              | 1.78                          |
| Si       | 288.757                       | 114.77              | 2.52                          |
| P        | 340.718                       | 70.56               | 7.47                          |
| S        | 397.384                       | 87.39               | 4.55                          |
| Cl       | 459.338                       | 78.08               | 5.88                          |
| Ar       | 526.816                       | 70.56               | 7.47                          |
| K        | 599.164                       | 329.3               | 1.82                          |
| Ca       | 676.757                       | 254.19              | 2.66                          |
| Sc       | 759.553                       | 241.49              | 3.15                          |
| Ti       | 848.054                       | 329.98              | 2.57                          |
| V        | 942.482                       | 219.53              | 4.29                          |
| Cr       | 1043.36                       | 210                 | 4.97                          |
| Mn       | 1149.07                       | 201.24              | 5.71                          |
| Fe       | 1262.18                       | 193.19              | 6.53                          |
| Co       | 1380.93                       | 185.75              | 7.43                          |
| Ni       | 1566.33                       | 178.88              | 8.42                          |
| Cu       | 1638.96                       | 172.5               | 9.5                           |
| Zn       | 1777.85                       | 166.54              | 10.68                         |
| Ga       | 1923.19                       | 144.89              | 13.27                         |
| Ge       | 2075.27                       | 128.23              | 16.18                         |
| As       | 2234.24                       | 114.5               | 19.51                         |
| Se       | 2399.76                       | 104.24              | 23.02                         |
| Br       | 2572.32                       | 95.32               | 26.99                         |
| Kr       | 2752.05                       | 87.82               | 31.34                         |
| Rb       | 2938.36                       | 384.87              | 7.63                          |
| Sr       | 3131.55                       | 297.09              | 10.54                         |
| Y        | 3331.56                       | 282.44              | 11.8                          |
| Zr       | 3538.75                       | 268.8               | 13.16                         |
| Nb       | 3753.44                       | 256.58              | 14.63                         |
| Mo       | 3975.55                       | 254.43              | 15.63                         |
| Tc       | 4204.79                       | 235.2               | 17.88                         |
| Ru       | 4441.23                       | 225.79              | 19.67                         |
| Rh       | 4685.54                       | 217.11              | 21.58                         |
| Pd       | 4937.92                       | 209.07              | 23.62                         |
| Ag       | 5197.7                        | 201.6               | 25.78                         |
| Cd       | 5465.13                       | 194.65              | 28.08                         |
| In       | 5740.1                        | 169.34              | 33.9                          |
| Sn       | 6022.85                       | 149.86              | 40.19                         |
| Sb       | 6313.49                       | 134.4               | 46.98                         |
| Te       | 6611.69                       | 121.83              | 54.27                         |
| I        | 6917.88                       | 111.41              | 62.09                         |
Table 2. Force Based Electronegativity data

| ELEMENTS | Absolute Radii(pm) | Z*(Clementi) | X \ Z*(Clementi)/Absolute Radii(pm) | Di-atomic System | Radii(pm) | (force unit) |
|----------|--------------------|--------------|-------------------------------------|------------------|-----------|-------------|
| H        | 52.92              | 1            |                                    |                  | 0.357     |             |
| He       | 31.13              | 1.688        |                                    |                  | 1.742     |             |
| Li       | 162.83             | 1.279        |                                    |                  | 0.048     |             |
| Be       | 108.55             | 1.912        |                                    |                  | 0.162     |             |
| B        | 81.41              | 2.421        |                                    |                  | 0.365     |             |
| C        | 65.13              | 3.136        |                                    |                  | 0.739     |             |
| N        | 54.28              | 3.834        |                                    |                  | 1.301     |             |
| O        | 46.52              | 4.453        |                                    |                  | 2.058     |             |
| F        | 40.71              | 5.1          |                                    |                  | 3.077     |             |
| Ne       | 36.71              | 5.758        |                                    |                  | 4.273     |             |
| Na       | 216.5              | 2.507        |                                    |                  | 0.053     |             |
| Mg       | 167.11             | 3.308        |                                    |                  | 0.118     |             |
| Element | Atomic Mass | Density | Vickers Hardness |
|---------|-------------|---------|-----------------|
| Al      | 136.08      | 2.61    | 4.84            |
| Si      | 28.086      | 2.33    | 0.313           |
| P       | 30.974      | 1.82    | 0.498           |
| S       | 32.06      | 1.87    | 0.739           |
| Cl      | 35.45       | 1.75    | 1.044           |
| Ar      | 39.95       | 1.77    | 1.42            |
| K       | 39.097      | 1.54    | 0.032           |
| Ca      | 40.078      | 1.55    | 0.068           |
| Sc      | 44.96       | 1.78    | 0.079           |
| Ti      | 47.87       | 1.77    | 0.045           |
| V       | 50.942      | 1.78    | 0.103           |
| Cr      | 51.961      | 1.79    | 0.116           |
| Mn      | 54.938      | 1.74    | 0.13            |
| Fe      | 55.847      | 1.75    | 0.146           |
| Co      | 58.934      | 1.77    | 0.162           |
| Ni      | 58.693      | 1.78    | 0.179           |
| Cu      | 63.546      | 1.78    | 0.196           |
| Zn      | 65.385      | 1.79    | 0.215           |
| Ga      | 69.721      | 1.78    | 0.296           |
| Ge      | 72.64      | 1.77    | 0.412           |
| As      | 74.919      | 1.78    | 0.572           |
| Se      | 78.96      | 1.79    | 0.763           |
| Br      | 79.904      | 1.78    | 0.994           |
| Kr      | 83.798      | 1.77    | 1.211           |
| Rb      | 85.47      | 1.78    | 0.034           |
| Sr      | 87.62      | 1.79    | 0.069           |
| Y       | 88.91     | 1.78    | 0.078           |
| Zr      | 91.225     | 1.79    | 0.089           |
| Nb      | 92.93      | 1.78    | 0.09            |
| Mo      | 95.94      | 1.79    | 0.094           |
| Tc      | 98.745     | 1.78    | 0.131           |
| Ru      | 101.07     | 1.79    | 0.127           |
| Rh      | 102.91     | 1.78    | 0.141           |
| Pd      | 106.42     | 1.79    | 0.155           |
| Ag      | 107.87     | 1.78    | 0.166           |
| Cd      | 112.41     | 1.79    | 0.216           |
| In      | 114.82     | 1.78    | 0.293           |
| Sn      | 117.43     | 1.79    | 0.473           |
| Sb      | 121.76     | 1.78    | 0.643           |
| Te      | 127.64     | 1.79    | 0.845           |
| I       | 126.90     | 1.78    | 0.936           |
| Xe      | 131.29     | 1.79    | 1.18            |
| Cs      | 132.91     | 1.78    | 0.012           |
| Ba      | 137.33     | 1.79    | 0.027           |
| La      | 138.91      | 1.78    | 0.049           |
| Ce      | 140.115    | 1.79    | 0.082           |
| Pr      | 140.906    | 1.78    | 0.127           |
| Nd      | 144.24     | 1.79    | 0.186           |
| Pm      | 147.27     | 1.78    | 0.26            |
| Sm      | 150.36     | 1.79    | 0.353           |
| Eu      | 151.96     | 1.78    | 0.465           |
| Gd      | 157.25     | 1.79    | 0.599           |
| Tb      | 158.92     | 1.78    | 0.756           |
| Dy      | 162.50     | 1.79    | 0.938           |
| Ho      | 164.93     | 1.78    | 1.148           |
| Er      | 167.26     | 1.79    | 1.386           |
| Tm      | 168.93     | 1.78    | 1.656           |
| Yb      | 170.95     | 1.79    | 1.958           |
| Lu      | 174.96     | 1.78    | 2.295           |
| Hf      | 178.49     | 1.79    | 2.531           |
| Ta      | 180.95     | 1.78    | 2.938           |
| W       | 183.85     | 1.79    | 3.377           |
| Re      | 186.24     | 1.78    | 3.858           |
| Os      | 189.98     | 1.79    | 4.381           |
| Ir      | 191.22     | 1.78    | 4.953           |
| Pt      | 195.08     | 1.79    | 5.569           |
10. Conclusion
The exact status of electronegativity might be attributed as a dual concept of force and energy. The attempt to measure electronegativity needs reification of this concept for which mathematical formulation is required. Till today, there exists no unique mathematical formulation of this reified noumenon for which there had been scope of many scales 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) and also it will be logical to consider electronegativity equalization in a diatomic as well as polyatomic system. This new approach will be helpful to assign the more accurate electronegativity values to various elements of the periodic table and also more valuable in different areas of chemical science for example to predict the structure and property of materials and also to design efficiently new electrode materials, electrocatalysts with novel properties for energy conversion devices like Fuel cell, Solar cell etc.

Acknowledgement
The author wishes to thank his PhD mentor Abanti Sahu for many stimulating discussions, suggestions and critical comments along with her reading a preprint of this paper and making useful comments. The author is highly indebted to acknowledge the financial support of DST, Government of India for pursuing Doctoral program.

References
[1] Jensen WB. Electronegativity from Avogadro to Pauling: II. Late Nineteenth- and Early Twentieth-Century Developments. J Chem Educ. 2003;80(3):279. doi:10.1021/ed080p279.
[2] van’t Hoff JH. Lectures on Theoretical and Physical Chemistry: III. Relations Between Properties and Composition. London, E Arnold. 1899:94. https://archive.org/details/theoreticallectu2hoffrich/page/94.
[3] Caven RM, Lander GD. Systematic Inorganic Chemistry from the Standpoint of the Periodic Law. In: A Textbook for Advanced Students. Blackie & Son, London; 1907:37-38.
[4] Sackur O. A Text Book of Thermo-Chemistry and Thermodynamics. This Is a Translation of the 1912 German Edition. Macmillan: London; 1917.
[5] Komorowski L. Electronegativity through the energy function. Chem Phys Lett. 1983;103(3):201-204. doi:10.1016/0009-2614(83)80381-9.
[6] Pauling L. THE NATURE OF THE CHEMICAL BOND. IV. THE ENERGY OF SINGLE BONDS AND THE RELATIVE ELECTRONEGATIVITY OF ATOMS. J Am Chem Soc. 1932;54(9):3570-3582. doi:10.1021/ja01348a011.
[7] Politzer P, Murray JS. Electronegativity—a perspective. J Mol Model. 2018;24(8):214. doi:10.1007/s00894-018-3740-6.
[8] Coulson CA. Bond Lengths in Conjugated Molecules: The Present Position. Proc R Soc A Math Phys Eng Sci. 1951;207(1088):91-100. doi:10.1098/rspa.1951.0102.
[9] Fukui K. Role of frontier orbitals in chemical reactions. Science. 1982;218(4574):747-754. doi:10.1126/science.218.4574.747.
[10] Myers RT. Electronegativity, bond energy, and chemical reactivity. J Chem Educ. 1979;56(11):711. doi:10.1021/ed056p711.
[11] Reddy RR, Rao TVR, Viswanath R. Correlation between electronegativity differences and bond energies. J Am Chem Soc. 1989;111(8):2914-2915. doi:10.1021/ja00190a028.
[12] Gutowsky HS, Hoffman CJ. Nuclear Magnetic Shielding
in Fluorine and Hydrogen Compounds. *J Chem Phys.* 1951;19(10):1259-1267. doi:10.1063/1.1748008.

[13] Motiejūnas S, Baltrūnas D, Garasim VI, Starik PM. A Correlation between Ligand Electronegativity and the Value of the Mössbauer Isomer Shift of Stannous Chalcogenides. *Phys status solidi.* 1988;148(2):K161-K164. doi:10.1002/pssb.2221480247.

[14] Arroyo-de Dompablo ME, Armand M, Tarascon JM, Amador U. On-demand design of polyoxianionic cathode materials based on electronegativity correlations: An exploration of the Li2MSiO4 system (M = Fe, Mn, Co, Ni). *Electrochem commun.* 2006;8(8):1292-1298. doi:10.1016/j.elecom.2006.06.003.

[15] Onoda J, Ondráček M, Jelinek P, Sugimoto Y. Electronegativity determination of individual surface atoms by atomic force microscopy. *Nat Commun.* 2017;8:15155. doi:10.1038/ncomms15155.

[16] Pauling L, Sherman J. A Quantitative Discussion of Bond Orbitals. *J Am Chem Soc.* 1937;59(8):1450-1456. doi:10.1021/ja01287a012.

[17] Mullay J. Atomic and group electronegativities. *J Am Chem Soc.* 1984;106(20):5842-5847. doi:10.1021/ja00332a014.

[18] Pauling L, Yost DM. The Additivity of the Energies of Normal Covalent Bonds. *Proc Natl Acad Sci U S A.* 1932;18(6):414-416. doi:10.1073/PNAS.18.6.414.

[19] Allred AL. Electronegativity values from thermochemical data. *J Inorg Nucl Chem.* 1961;17(3-4):215-221. doi:10.1016/0022-1902(61)80142-5.

[20] Mulliken RS. Electronic structures of molecules XII. Electroaffinity and molecular orbitals, polyatomic applications. *J Chem Phys.* 1935;3(9):586-591. doi:10.1063/1.1749732.

[21] Pearson RG. The Calculation of Ionic Resonance Energies. *J Chem Phys.* 1949;17(10):969-971. doi:10.1063/1.1747096.

[22] Pauling L. Chapter 2. In: The Nature of the Chemical Bond. Cornell University Press; 1939.

[23] Haissinsky M. Scale of Pauling electronegativities and heats of formation of inorganic compounds. *J Phys Radioam.* 1946;7(1):7-11.

[24] Huggins ML. Bond Energies and Polarities 1. *Am Chem Soc.* 1953;75(17):4123-4126. doi:10.1021/ja01113a001.

[25] Walsh AD. The properties of bonds involving carbon. *Discuss Faraday Soc.* 1947;2(0):18. doi:10.1039/df9470200018.

[26] Ferreira R. Electronegativity and Chemical Bonding. *Adv Chem Phys.* 1967;13:55-84. doi:10.1002/9780470140154.ch4.

[27] Iczkowski RP, Marggrave JL. Electronegativity. *J Am Chem Soc.* 1961;83(17):3547-3551. doi:10.1021/ja01478a001.

[28] Pearson RG. Electronegativity Scales. *Acc Chem Res.* 1990;23(1):1-2. doi:10.1021/ar00169a001.

[29] Allen LC. Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state free atoms. *J Am Chem Soc.* 1989;111(25):9003-9014. doi:10.1021/ja00207a003.

[30] Allen LC. Electronegativity scales. *Acc Chem Res.* 1990;23(6):175-176. doi:10.1021/ar00174a001.

[31] Huheey JE. Variable electronegativity. *J Inorg Nucl Chem.* 1965;27(9):2127-2129. doi:10.1016/0022-1902(65)80077-X.

[32] Huheey JE. Electronegativity, acids, and bases. IV. Concerning the inductive effect of alkyl groups. *J Org Chem.* 1971;36(1):204-205. doi:10.1021/jo00800a044.

[33] Mulliken RS A new electroaffinity scale; Together with data on valence states and on valence ionization potentials and electron affinities. *J Chem Phys.* 1934;2(11):782-793. doi:10.1063/1.1749394.

[34] Stark J. Die Dissoziation und Umwandlung chemischer Atome. *Vieweg Braunschweig, Ger.* 1903:7-8.

[35] Martin G. Researches on the affinities of the elements and on the causes of the chemical similarity or dissimilarity of elements and compounds. 1905:226-228.

[36] Fajans K. Über eine Beziehung zwischen der Art einer radioaktiven Umwandlung und dem elektrochemischen Verhalten der betreffenden Radioelemente. *Phys Zeitschrift.* 1913:141-136.

[37] Moffitt W. Term Values in Hybrid States. *Proc R Soc A Math Phys Eng Sci.* 1950;202(1071):534-548. doi:10.1098/rspa.1950.0118.

[38] Huheey JE, Keiter EA, Keiter RL, Medhi OK. Electronegativity. In: Inorganic Chemistry : Principles of Structure and Reactivity. 4th ed. Harper Collins college, New York; 1993:182.

[39] Kloppman G. Electronegativity. *J Chem Phys.* 1965;43(10):S124-S129. doi:10.1063/1.1701474.

[40] Pritchard HO, Skinner HA. The Concept Of Electronegativity. *Chem Rev.* 1955;55(4):745-786. doi:10.1021/cr50004a005.

[41] Pearson RG. Absolute electronegativity and absolute hardness of Lewis acids and bases. *J Am Chem Soc.* 1985;107(24):6801-6806. doi:10.1021/ja00310a009.

[42] Hinze J, Jaffé HH. Electronegativity. I. Orbital Electronegativity of Neutral Atoms. *J Am Chem Soc.* 1962;84(4):540-546. doi:10.1021/ja00863a008.

[43] Hinze J, Whitehead MA, Jaffé HH. Electronegativity. II. Bond and Orbital Electronegativities. *J Am Chem Soc.* 1963;85(2):148-154. doi:10.1021/ja00858a008.

[44] Mulliken RS, S. R. Quelques aspects de la théorie des orbitales moléculaires. *J Chim Phys.* 1949;46:497-542. doi:10.1051/jcp/1949460497.

[45] Lang PF, Smith BC. Electronegativity effects and single covalent bond lengths of molecules in the gas phase. *Dalt Trans.* 2014;43(21):8016-8025. doi:10.1039/C4DT00807C.
[47] Klixbüll Jørgensen C. Electron Transfer Spectra. Prog Inorg Chem. March 1970;101-158. doi:10.1002/9780470166310.ch2.

[48] Slater JC, Johnson KH. Self-consistent-field Xa cluster method for polyatomic molecules and solids. Phys Rev B. 1972;5(3):844-853. doi:10.1103/PhysRevB.5.844.

[49] Slater JC, Phillips JC. Quantum Theory of Molecules and Solids Vol. 4: The Self-Consistent Field for Molecules and Solids. Phys Today. 1974;27(12):49. doi:10.1063/1.3129035.

[50] Simons G, Zandler ME, Talaty ER. Nonempirical electronegativity scale. J Am Chem Soc. 1976;98(24):7869-7870. doi:10.1021/ja00440a093.

[51] ohn J, Bloch AN. Quantum-Defect Electronegativity Scale for Nontransition Elements. Phys Rev Lett. 1974;33(18):1095-1098. doi:10.1103/PhysRevLett.33.1095.

[52] Simons G. New Model Potential for Pseudopotential Calculations. J Chem Phys. 1971;55(2):756-761. doi:10.1063/1.1676142.

[53] Huheey JE. The Electronegativity of Groups. J Phys Chem. 1965;69(10):3284-3291. doi:10.1021/j100894a011.

[54] Huheey JE. The Electronegativity of Multiply Bonded Groups. J Phys Chem. 1966;70(7):2086-2092. doi:10.1021/ja00879a003.

[55] Klopman G. A Semiempirical Treatment of Molecular Structures I. Electronegativity and Atomic Terms. J Am Chem Soc. 1964;86(8):1463-1469. doi:10.1021/ja01062a001.

[56] Klopman G. A Semiempirical Treatment of Molecular Structures. II. Molecular Terms and Application to diatomic Molecules. J Am Chem Soc. 1964;86(21):4550-4557. doi:10.1021/ja01075a008.

[57] Ponec R. Generalization of electronegativity concept. Theor Chim Acta. 1981;59(6):629-637. doi:10.1007/BF00552856.

[58] Parr RG, Donnelly RA, Levy M, Palke WE. Electronegativity: The density functional viewpoint. J Chem Phys. 1978;66(8):3801-3807. doi:10.1063/1.436185.

[59] Parr RG, Bartolotti LJ. On the geometric mean principle for electronegativity equalization. J Am Chem Soc. 1982;104(14):3801-3803. doi:10.1021/ja00378a004.

[60] Parr RG, Pearson RG. Absolute hardness: companion parameter to absolute electronegativity. J Am Chem Soc. 1983;105(26):7512-7516. doi:10.1021/ja00364a005.

[61] Watson RE, Bennett LH, Davenport JW. Ionic character of polar crystals: An extended Mulliken scheme for electronegativities. Phys Rev B. 1983;27(10):6428-6438. i:10.1103/PhysRevB.27.6428.

[62] Bratsch SG. A group electronegativity method with Pauling units. J Chem Educ. 1985;62(2):101. doi:10.1021/ed062p101.

[63] Hancock JR, Hardstaff WR, Johns PA, Langler RF, Mantle WS. Regiochemistry and reactivity in the chlorination of sulfides. Can J Chem. 1983;61(7):1472-1480. doi:10.1139/v83-257.

[64] Pritchard HO. Equalization of Electronegativity. J Am Chem Soc. 1963;85(12):1876. doi:10.1021/ja00895a043.

[65] Evans RS, Huheey JE. Electronegativity, acids, and bases—I: Hard and soft acids and bases and Pauling’s electronegativity equation. J Inorg Nucl Chem. 1970;32(2):373-381. doi:10.1016/0022-1902(70)80244-5.

[66] Reed JL. Electronegativity. An isolated atom property. J Phys Chem. 1981;85(2):148-153. doi:10.1021/j150602a010.

[67] Bartolotti LJ, Gadre SR, Parr RG. Electronegativities of the Elements from Simple. Xa Theory. J Am Chem Soc. 1980;102(9):2945-2948. doi:10.1021/ja00529a013.

[68] Politzer P, Weinstein H. Some relations between electronic distribution and electronegativity. J Chem Phys. 1979;71(11):4218-4220. doi:10.1063/1.438228.

[69] Whitehead MA, Baird NC, Kaplansky M. Group orbital electronegativities. Theor Chim Acta. 1965;3(2):135-146. doi:10.1007/BF00527344.

[70] Gyftopoulos EP, Hatsopoulos GN. Quantum-Thermodynamic Definition of Electronegativity. Proc Natl Acad Sci. 1968;60(3):786-793. doi:10.1073/pnas.60.3.786.

[71] Einhorn MB, Blankenbecler R. Bounds on scattering amplitudes. Ann Phys (N Y). 1971;67(2):480-517. doi:10.1016/0003-4916(71)90151-5.

[72] Gophathorn MS, Whitehead MA. On the Dependence of Total Energy on Occupation Numbers. Isr J Chem. 1980;19(1-4):209-214. doi:10.1021/ji8000022.

[73] Geerlings P, De Proft F, Langenaeker W. Conceptual Density Functional Theory. Chem Rev. 2003;103(5):1793-1874. doi:10.1021/cr990029p.

[74] Jørgensen CK. Orbitals in Atoms and Molecules. Academic Press Inc., New York; 1962.

[75] Sanderson RT. An interpretation of bond lengths and a classification of bonds. Science. 1951;114(2973):670-672. doi:10.1126/science.114.2973.670.

[76] Ferreira R. Principle of electronegativity equalization. Part 1.—Bond moments and force constants. Trans Faraday Soc. 1963;59(0):1064-1074. doi:10.1039/TF9635901064.

[77] March NH. The ground-state energy of atomic and molecular ions and its variation with the number of electrons. In: Chemical Hardness. Berlin/Heidelberg: Springer-Verlag; 1993:71-86. doi:10.1007/BFb0036800.

[78] Nguyen-Dang TT, Bader RFW, Essén H. Some properties of the Lagrange multiplier μ in density functional theory. Int J Quantum Chem. 1982;22(5):1049-1058. doi:10.1002/qua.560220517.

[79] Hinze J. The concept of electronegativity of atoms in molecules. Theor Comput Chem. 1999;6:189-212. doi:10.1016/S1380-7323(99)80009-0.

[80] Chemette H. Chemical reactivity indexes in density functional theory. J Comput Chem. 1999;20(1):129-154. doi:10.1002/(SICI)1096-987X(19990115)20:1<129::AID-JCC13>3.0.CO;2-A.
[81] Hohenberg P, Kohn W. Inhomogeneous Electron Gas. Rev. Phys. 1964;136(3B):B864-B871. doi:10.1103/PhysRev.136.B864.

[82] Miranda-Quintana RA, Ayers PW. Interpolation of property-values between electron numbers is inconsistent with ensemble averaging. J. Chem. Phys. 2016;144(24):244112. doi:10.1063/1.4953557.

[83] Heidar-Zadeh F, Miranda-Quintana RA, Verstraeten T, Bultink P, Ayers PW. When is the Fukui Function Not Normalized? The Danger of Inconsistent Energy Interpolation Models in Density Functional Theory. J. Chem. Theory Comput. 2016;12(12):5777-5787. doi:10.1021/acs.jctc.6b00494.

[84] Komorowski L. Electronegativity through the energy function. Chem. Phys. Lett. 1983;103(3):201-204. doi:10.1016/0009-2614(83)80381-9.

[85] Datta D, Shee NK, Von Szentpály L. Chemical potential of molecules contrasted to averaged atomic electronegativities: Alarming differences and their theoretical rationalization. J. Phys. Chem. A. 2013;117(1):200-206. doi:10.1021/jp310336e.

[86] Feynman RP. Forces in Molecules. Phys. Rev. 1939;56(4):340-343. doi:10.1103/PhysRev.56.340.

[87] Berlin T. Binding Regions in Diatomic Molecules. J. Chem. Phys. 1951;19(2):208-213. doi:10.1063/1.1748161.

[88] Sanderson RT. Electronegativities in inorganic chemistry. J. Chem. Educ. 1952;29(11):539. doi:10.1021/ed029p539.

[89] Sanderson RT. Relation of Stability Ratios to Pauling Electronegativities. J. Chem. Phys. 1955;23(12):2467-2468. doi:10.1063/1.1741939.

[90] Anderson AB, Parr RG. Vibrational Force Constants from Electron Densities. J. Chem. Phys. 1970;53(8):3375-3376. doi:10.1063/1.1674492.

[91] Sanderson RT. Electronegativities in inorganic chemistry: (II). J. Chem. Educ. 1954;31(1):2. doi:10.1021/ed031p2.

[92] Sanderson RT. Electronegativities in inorganic chemistry. III. J. Chem. Educ. 1954;31(5):238. doi:10.1021/ed031p238.

[93] Sanderson RT. Principles of electronegativity Part I. General nature. J. Chem. Educ. 1988;65(2):112. doi:10.1021/ed065p112.

[94] Gordy W. A New Method of Determining Electronegativity from Other Atomic Properties. Phys. Rev. 1946;69(11-12):604-607. doi:10.1103/PhysRev.69.604.

[95] Gordy W. A Relation between Bond Force Constants, Bond Orders, Bond Lengths, and the Electronegativities of the Bonded Atoms. J. Chem. Phys. 1946;14(5):305-320. doi:10.1063/1.1724138.

[96] Allred AL, Rochow EG. A scale of electronegativity based on electrostatic force. J. Inorg. Nucl. Chem. 1958;5(4):264-268. doi:10.1016/0022-1902(58)80003-2.

[97] Politzer P, Parr RG, Murphy DR. Relationships between atomic chemical potentials, electrostatic potentials, and covalent radii. J. Chem. Phys. 1983;79(8):3859-3861. doi:10.1063/1.446251.

[98] Gordy W. Interpretation of Nuclear Quadrupole Couplings in Molecules. J. Chem. Phys. 1951;19(6):792-793. doi:10.1063/1.1748359.

[99] Gordy W, Thomas WJO. Electronegativities of the Elements. J. Chem. Phys. 1956;24(2):439-444. doi:10.1063/1.1742493.

[100] Boyd RJ, Edgecombe KE. Atomic and Group Electronegativities from the Electron Density Distributions of Molecules. J. Am. Chem. Soc. 1988;110(13):4182-4186. doi:10.1021/ja00221a014.

[101] Malone JG. The Electric Moment as a Measure of the Ionic Nature of Covalent Bonds. J. Chem. Phys. 1933;1(3):197-199. doi:10.1063/1.1749274.

[102] Coulson CA. The dipole moment of the C—H bond. Trans. Faraday Soc. 1942;38(0):433-444. doi:10.1039/TP9423800433.

[103] Phillips JC. Dielectric Definition of Electronegativity. Phys. Rev. Lett. 1968;20(11):550-553. doi:10.1103/PhysRevLett.20.550.

[104] Pauling L. Atomic Radii and Interatomic Distances in Metals. J. Am. Chem. Soc. 1947;69(3):542-553. doi:10.1021/ja01195a024.

[105] Slater JC. Atomic Shielding Constants. Phys. Rev. 1930;36(1):57-64. doi:10.1103/PhysRev.36.57.

[106] Housecroft C.E. and Sharpe A.G. Electronegativity values. In: Inorganic Chemistry. Pearson Education Limited; 2005:38.

[107] Boyd RJ, Markus GE. Electronegativities of the elements from a nonempirical electrostatic model. J. Chem. Phys. 1981;75(11):5385-5388. doi:10.1063/1.441984.

[108] Clementi E, Roetti C. Roothaan-Hartree-Fock atomic wavefunctions: Basis functions and their coefficients for ground and certain excited states of neutral and ionized atoms, Z≤54. At. Data Nucl. Data Tables. 1974;14(3-4):177-478. doi:10.1016/S0002-740X(74)80016-1.

[109] Bunge CF, Barrientos JA, Bunge AV. Roothaan-Hartree-Fock Ground-State Atomic Wave Functions: Slater-Type Orbital Expansions and Expectation Values for Z=2-54. At. Data Nucl. Data Tables. 1993;53(1):113-162. doi:10.1006/ADND.1993.1003.

[110] Mande C, Deshmukh P, Deshmukh P. 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. 1977;10(12):2293-2300. doi:10.1088/0022-3700/10/12/008.

[111] Zhang Y. Electronegativities of Elements in Valence States and Their Applications. 2. A Scale for Strengths of Lewis Acids. Inorg. Chem. 1982;21(11):3889-3893. doi:10.1021/si1044-013-9376-5.

[112] Putz M.V. Systematic formulations for electronegativity and hardness and their atomic scales within density functional softness theory. Int. J. Quantum Chem. 2006;106(2):361-389. doi:10.1002/qua.20787.

[113] PUTZ M.V. SEMICLASSICAL ELECTRONEGATIVITY AND CHEMICAL HARDNESS. J. Theor. Comput. Chem. 2007;06(01):33-47.
[114] Putz M, Putz, V. M. Density Functionals of Chemical Bonding. *Int J Mol Sci.* 2008;9(6):1050-1095. doi:10.3390/ijms9061050.

[115] Putz M V. Electronegativity: Quantum observable. *Int J Quantum Chem.* 2009;109(4):733-738. doi:10.1002/qua.21957.

[116] Bergmann D, Hinze J. Electronegativity and charge distribution. In: *Electronegativity.* Berlin/Heidelberg: Springer-Verlag; 1987:145-190. doi:10.1007/BFb0029840.

[117] Zhang Y. Electronegativity from Ionization Potentials. *J Mol Sci (Chinese).* 1981;1:125.

[118] Zhang Y, Zhang, Yonghe. Ionocovality and Applications 1. Ionocovalency Model and Orbital Hybrid Scales. *Int J Mol Sci.* 2010;11(11):4381-4406. doi:10.3390/ijms11114381.

[119] Jecko T. On the mathematical treatment of the Born-Oppenheimer approximation. *J Math Phys.* 2014;55(5):053504. doi:10.1063/1.4870855.

[120] Born M, Oppenheimer R Zur Quantentheorie der Molekeln. *Ann Phys.* 1927;389(20):437-484. doi:10.1002/andp.19273892002.

[121] Franck J, Society ED-T of the F, 1926. undefined. Elementary processes of photochemical reactions. pubs.rsc.org. http://pubs.rsc.org/en/content/articlepdf/1926/tf/tf9262100536. Accessed October 14, 2018.

[122] Condon E. A Theory of Intensity Distribution in Band Systems. *Phys Rev.* 1926;28(6):1182-1201. doi:10.1103/PhysRev.28.1182.

[123] Hagedorn GA. A time dependent Born-Oppenheimer approximation. *Commun Math Phys.* 1980;77(1):1-19. doi:10.1007/BF01205036.

[124] Hagedorn GA. High order corrections to the time-independent Born-Oppenheimer approximation II: Diatomic Coulomb systems. *Commun Math Phys.* 1988;116(1):23-44. doi:10.1007/BF01239023.

[125] HAGEDORN GA, JOYE A. MOLECULAR PROPAGATION THROUGH SMALL AVOIDED CROSSINGS OF ELECTRON ENERGY LEVELS. *Rev Math Phys.* 1999;11(01):41-101. doi:10.1142/S0129055X99000040.

[126] Hagedorn GA, Joye A. A Time-Dependent Born-Oppenheimer Approximation with Exponentially Small Error Estimates. *Commun Math Phys.* 2001;223(3):583-626. doi:10.1007/s002200100562.

[127] HAGEDORN GA, JOYE A. A MATHEMATICAL THEORY FOR VIBRATIONAL LEVELS ASSOCIATED WITH HYDROGEN BONDS II: THE NON-SYMMETRIC CASE. *Rev Math Phys.* 2009;21(02):279-313. doi:10.1142/S0129055X09003621.

[128] Klein M, Martinez A, Wang XP. On the Born-Oppenheimer approximation of wave operators in molecular scattering theory. *Commun Math Phys.* 1993;152(1):73-95. doi:10.1007/BF02097058.

[129] Klein M, Martinez A, Wang XP. On the Born–Oppenheimer approximation of diatomic wave operators. II. Singular potentials. *J Math Phys.* 1998;38(3):1373. doi:10.1063/1.532189.

[130] Martinez A, Messirdi B. Resonances of diatomic molecules in the born-oppenheimer approximation. *Commun Partial Differ Equations.* 1994;19(7-8):1139-1162. doi:10.1080/03605309408821048.

[131] Spohn H, Teufel S. Adiabatic Decoupling and Time-Dependent Born–Oppenheimer Theory. *Commun Math Phys.* 2001;224(1):113-132. doi:10.1007/s002200100535.

[132] Teufel S, Wachsmuth J. Spontaneous Decoy of Resonant Energy Levels for Molecules with Moving Nuclear. *Commun Math Phys.* 2012;315(3):699-738. doi:10.1007/s00220-012-1547-3.

[133] Sutcliffe BT, Woolley RG. On the quantum theory of molecules. *J Chem Phys.* 2012;137(22):22A544. doi:10.1063/1.4755287.

[134] Sutcliffe BT, Woolley RG. Comment on “On the quantum theory of molecules” [J. Chem. Phys. 122 (2010)]. *J Chem Phys.* 2014;140(3):037101. doi:10.1063/1.4861897.

[135] Kammerer CF, Rousve V. Resolvent Estimates and Matrix-Valued Schrödinger Operator with Eigenvalue Crossings: Application to Strichartz Estimates. *Commun Partial Differ Equations.* 2008;33(1):19-44. doi:10.1080/03605300701454925.

[136] Wilson EB. Four-Dimensional Electron Density Function. *J Chem Phys.* 1962;36(8):2232-2233. doi:10.1063/1.1732864.

[137] Stanton RE. Hellmann-Feynman Theorem and Correlation Energies. *J Chem Phys.* 1962;36(5):1298-1300. doi:10.1063/1.1732731.

[138] Andrae D, ed. *Hans Hellmann: Einführung in Die Quantenchemie.* Berlin, Heidelberg: Springer Berlin Heidelberg 2015. doi:10.1007/978-3-662-45967-6.

[139] Levine IN. *Quantum Chemistry.* 5th ed. Pearson/Prentice Hall; 2009.

[140] Politzer P, Murray JS. The Hellmann-Feynman theorem: a perspective. *J Mol Model.* 2018;24(9):266. doi:10.1007/s00894-018-3784-7.

[141] Pauli W. Die allgemeinen Prinzipien der Wellenmechanik In: *Quantentheorie.* Berlin, Heidelberg: Springer Berlin Heidelberg; 1933:83-272. doi:10.1007/978-3-642-52619-0-2.

[142] Hellmann H. Zur Rolle der kinetischen Elektronenenergie für die zwischenatomären Kräfte. *Zeitschrift für Phys.* 1933;85(3-4):180-190. doi:10.1007/BF01342053.

[143] Güttinger P. Das Verhalten von Atomen im magnetischen Drehfeld. *Zeitschrift für Phys.* 1932;73(3-4):169-184. doi:10.1007/BF01351211.

[144] Schrödinger E. Quantisierung als Eigenwertproblem. *Ann Phys.* 1926;385(13):437-490. doi:10.1002/andp.19263851302.

[145] Hurley AC. The Electrostatic Calculation of Molecular Energies. I. Methods of Calculating Molecular Energies. *Proc R Soc A Math Phys Eng Sci.* 1954;226(1165):170-178. doi:10.1098/rspa.1954.0246.
[146] Hurley AC. The Electrostatic Calculation of Molecular Energies. II. Approximate Wave Functions and the Electrostatic Method. *Proc R Soc A Math Phys Eng Sci*. 1954;226(1165):179-192. doi:10.1098/rspa.1954.0247.

[147] Hurley AC. The Electrostatic Calculation of Molecular Energies. III. The Binding Energies of Saturated Molecules. *Proc R Soc A Math Phys Eng Sci*. 1954;226(1165):193-205. doi:10.1098/rspa.1954.0248.

[148] Hurley AC. The Electrostatic Calculation of Molecular Energies. IV. Optimum Paired-Electron Orbitals and the Electrostatic Method. *Proc R Soc A Math Phys Eng Sci*. 1956;235(1201):224-234. doi:10.1098/rspa.1956.0078.

[149] Bader RFW. Binding Regions in Polyatomic Molecules and Electron Density Distributions. *J Am Chem Soc*. 1964;86(23):5070-5075. doi:10.1021/ja01077a005.

[150] Bader RFW, Henneker WH. The Ionic Bond. *J Am Chem Soc*. 1965;87(14):3063-3068. doi:10.1021/ja01092a008.

[151] Bader RFW, Preston HJT. A CRITIQUE OF PAULI REPULSIONS AND MOLECULAR GEOMETRY. *Can J Chem*. 1961;39(6):1253-1265. doi:10.1139/v61-159.

[152] Bader RFW. THE USE OF THE HELLMANN–FEYNMAN THEOREM TO CALCULATE MOLECULAR ENERGIES. *Can J Chem*. 1960;38(11):2117-2127. doi:10.1139/v60-287.

[153] Bader RFW, Jones GA. the Hellmann–Feynman Theorem and Chemical Bonding *Can J Chem*. 1964;41(10):1131-1145. doi:10.1139/v64-170.

[154] Koga T, Nakatsui H. The Hellmann–Feynman theorem applied to long-range forces. *Theor Chim Acta*. 1976;41(2):19-131. doi:10.1007/BF00117807.

[155] Koga T, Nakatsui H, Yonezawa T. Generalized Berlin diagram for polyatomic molecules. *J Am Chem Soc*. 1978;100(24):7522-7527. doi:10.1021/ja00492a014.

[156] Koga T, Nakatsui H, Yonezawa T. Force and density study of the chemical reaction process OH + H → OH₂. *Mol Phys*. 1980;39(1):239-249. doi:10.1080/00268978000102021.

[157] Politzer P. A Study of the Bonding in the Hydrogen Molecule 1. *J Phys Chem*. 1966;70(4):1174-1178. doi:10.1021/j10876a033.

[158] Politzer P, Daiker KC. Molecular electrostatic potentials. Negative potentials associated with some methyl and methylene groups. *Chem Phys Lett*. 1975;34(2):294-297. doi:10.1016/0009-2614(75)85277-8.

[159] Coleman AJ. Structure of Fermion Density Matrices. II. Antisymmetrized Geminal Powers. *J Math Phys*. 1965;6(9):1425-1431. doi:10.1063/1.1704794.

[160] Coleman AJ. INFINITE RANGE CORRELATION AND LARGE EIGENVALUES OF THE 2-MATRIX. *Can J Phys*. 1967;45(3):1271-1273. doi:10.1139/p67-094.

[161] Coleman AJ. Necessary Conditions for N -Representability of Reduced Density Matrices. *J Math Phys*. 1972;13(2):214-222. doi:10.1063/1.1665956.

[162] Slater JC. Hellmann–Feynman and Virial Theorems in the Xα Method. *J Chem Phys*. 1972;57(6):2389-2396. doi:10.1063/1.1678599.

[163] Larsen A, Poulsen RS, Garm TP. Applied Hartree-Fock Methods Atomic and Diatomic Energy Computations. Denmark; 2015. https://www.aau.dk/digitalAssets/281/281541_speciale--applied-hartree-fock-methods.pdf. Accessed October 21, 2018.

[164] Slater JC. Atomic Shielding Constants. *Phys Rev*. 1930;36(1):57-64. doi:10.1103/PhysRev.36.57.

[165] Bader RFW, Henneker WH. The Ionic Bond. *J Am Chem Soc*. 1965;87(14):3063-3068. doi:10.1021/ja01092a008.

[166] Slater JC. Atomic Radii in Crystals. *J Chem Phys*. 1964;41(10):3199-3204. doi:10.1063/1.1725697.

[167] Clementi E, Raimondi DL. Atomic Screening Constants from SCF Functions. *J Chem Phys*. 1963;38(11):2686-2689. doi:10.1063/1.1733573.

[168] Clementi E, Raimondi DL, Reinhardt WP. Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons. *J Chem Phys*. 1967;47(4):1300-1307. doi:10.1063/1.1712084.

[169] Rahm M, Hoffmann R, Ashcroft NW. Atomic and Ionic Radii of Elements 1–96. *Chem - A Eur J*. 2016;22(41):14625-14632. doi:10.1002/chem.201602949.

[170] Ghosh DC, Chakraborty T, Mandal B. The electronegativity scale of Allred and Rochow: revisited. *Theor Chem Acc*. 2009;124(3-4):295-301. doi:10.1007/s00214-009-0610-4.