Electronegativity of Molecules Through Charge Capacity

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The advent of Density Functional Theory (DFT) has substantiated the insight of electronic structure in atoms and molecules. The most important of these properties are electronegativity and hardness. Few years back, Politzer had stated that electronegativity of an atom in a molecule is a polynomial function. This equation converged when the charge transfer gets equalized between the combining atoms. The present work is devoted to the determination of electronegativity of the molecules and a comparison is made with the geometric mean method used by Mulliken. Furthermore, the Gordy's electronegativity scale is tested by using the effective nuclear charge (Z_{eff}) through ionization potential rather than Slater's rule of effective nuclear charge. In my earlier work, Z_{eff} has been successfully used to calculate dipole polarizability of Na-clusters.

INTRODUCTION

An important conceptual advance introduced by Sanderson was that in a molecule at equilibrium the electronegativities of all the atoms are equal[1,2]. This concept was put to theoretical basis when the electronegativity was related to the chemical potential[3] and it was shown that it is uniform throughout the molecule[4–6]

Equalization of atomic electronegativities implies that their magnitudes must be able to vary as the atoms interact. This is expressed by writing the electronegativity (χ) as a function of the charge 'Q' that develops on the interacting atom and expanding $\chi(Q)$ in a Taylor series around $Q = 0$.[7]

$$\chi(Q) = \chi(0) + Q\left(\frac{\partial \chi}{\partial Q}\right)_{Q=0} + \frac{Q^2}{2}\left(\frac{\partial^2 \chi}{\partial Q^2}\right)_{Q=0} + \ldots \tag{1}$$

The second term in Eq. (1) gives the amount by which the electronegativity of the neutral atom $\chi(0)$ is changed by the development of the change Q. So, the electron-attracting tendency of the atom depends not only upon its intrinsic affinity for electronic charge, but also upon the rate at which this initial affinity increases or decreases as the atom also loses or gains charge. It is the presence of this and succeeding terms in Eq. (1) that makes it possible for the electronegativity to change and equalise as a molecule forms.

When the expansion in Eq. (1) is truncated after the second term, it is similar in form to an electronegativity expression given by Huheey[8–11]:

$$\chi = a + bQ \tag{2}$$

He viewed 'a' as the "inherent" electronegativity of the neutral atom and 'b' as 'an inverse of charge capacity[10], *i.e.*, the ability of the atom to absorb or yield electronic charge. So,

$$a = \chi(0)$$

and

$$\left(\frac{\partial \chi}{\partial Q}\right)_{Q=0} = \frac{1}{k}$$

where 'k' is the charge capacity. It shows that an atom (or group) with a large value of 'k' may be more negative, in a given molecule, than another that has a greater electronegativity and thus a strong initial attraction for electronic charge, but is not able to accmmodate as much of it.

RESULTS AND DISCUSSION

In the present work, the molecular polarizability in terms of their atomic parts is determined by using electronegativity equalization method given by Gazquez and Ortiz[12].

$$\chi_{A\beta} = \frac{2\eta_A \chi_\beta + 2\eta_\beta \chi_A}{2(\eta_A + \eta_\beta)} \tag{3}$$

From equation (1),

$$\Delta q = \frac{|\chi_\beta - \chi_A|}{2(\eta_A + \eta_\beta) + 3Q^2(\eta_A - \eta_\beta)} \tag{4}$$

From equations (3) and (4),

$$\chi_{A\beta} = \frac{(2\eta_A \chi_\beta + 2\eta_\beta \chi_A)\,\Delta q}{|\chi_\beta - \chi_A|} \tag{5}$$

According to Parr and Bartollotti the molecular electronegativity can be written as the geometric mean of atomic electronegativities'as

$$\chi_{A\beta} = (\chi_A \cdot \chi_\beta)^{1/2} \tag{6}$$

The calculated values of Eq. (5) and Eq. (6) are given in Table-1 for various molecules. The results are in good agreement with Eq. (6). A few molecular results have been reported here, though it has been tested on sixtyone molecule.

It seems intuitively reasonable that charge capacity should be related to polarizability[8] which is confirmed quantitatively later[7]. The charge capacity (k) has been utilized to calculate the hardness of various atoms which can be further used to give results for molecular hardness and electronegativity. Recently Hati and Datta[13] derived the relation between 'α' and R as

$$\alpha = kR^3 \tag{7}$$

TABLE-1
ELECTRONEGATIVITY OF VARIOUS MOLECULES THROUGH CHARGE
CAPACITY RELATION

Molecule	Eq. (5) (eV)	Eq. (6) (eV)
NaF	3.78	3.45
NaCl	3.97	4.86
NaBr	3.96	4.65
KI	3.38	4.04
CuCl	5.69	6.10
CuBr	5.61	5.83
CuI	5.47	5.50
CH_3F	6.80	7.19
CH_3Cl	6.63	6.42
CH_3Br	6.27	6.14
CH_3I	5.86	5.79
CH_3Li	3.43	3.86
OHF	8.64	8.84
CH_3OH	6.05	6.10
ICl	7.33	7.49
IBr	7.12	7.16
C_2H_5Cl	6.01	5.76
C_2H_5I	5.39	5.20
HF	8.66	8.64
HCl	7.73	7.72
HBr	7.37	7.38
HOH	7.34	7.34

By definition, the hardness through difference method is

$$\eta = \frac{I - A}{2} \tag{8}$$

So by combining the two equations, the resultant equation is

$$\eta = \frac{1}{2}\left(\frac{k}{\alpha}\right)^{1/3} \tag{9}$$

where 'k' is constant, and has been tested for various values of k as 1.0, 0.585 and 0.792. The results have been reported elsewhere. Since 'K' does not carry any physical significance, so it requires some physical weightage. In the present work, the value of K has been replaced by effective nuclear charge (Z_{eff}) and results have been reported in Table-2. This concepts have been extended to clusters of sodium and is given in Table-3. The comparison of calculated values with the experimental ones is striking.

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TABLE-2

CALCULATED VALUES OF HARDNESS FOR SOME ATOMS

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Atom	I_1 (eV)	I_0 (eV)	Z_{eff}	η_{cal}	η_{exp}
Li	75.64	5.39	0.609	0.079	0.088
Na	47.29	5.14	0.679	0.082	0.084
K	31.63	4.39	0.764	0.070	0.071
Rb	27.28	4.18	0.806	0.067	0.068
Cs	25.10	3.89	0.827	0.065	0.063
Cu	20.29	7.73	1.205	0.151	0.119
Ag	21.49	7.58	1.132	0.140	0.115
Au	20.50	9.23	1.353	0.164	0.127
Tl	20.43	6.10	1.061	0.139	0.107
Co	17.06	7.80	1.461	0.155	0.132
Rh	18.08	7.46	1.322	0.143	0.116
Ir	16.90	9.10	1.724	0.163	0.140
I	19.13	10.45	1.678	0.186	0.136

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TABLE-3

CALCULATED 'η' VALUES FOR SODIUM CLUSTERS Na_n

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n	α^a	$\eta_{cal.}$	η^b
4	545.929	0.055 (0.056)	0.057
5	725.418	0.050 (0.052)	0.061
10	1296.356	0.041 (0.042)	0.045
12	1494.470	0.039 (0.041)	0.044
15	1751.036	0.037 (0.038)	0.043
17	1822.291	0.037 (0.038)	0.042
18	1874.778	0.037 (0.037)	0.046
20	2076.718	0.035 (0.036)	0.049
34	3422.127	0.030 (0.030)	0.041
40	4013.289	0.028 (0.029)	0.034

a. Reference 14; b. Reference 15.

It shows that the physical significance of 'K' is based on the Z_{eff}.

Conclusion

With the use of charge capacity relation the electronegativity and hardness can be calculated with fair amount of accuracy with some physical meaning occurring in the atomic and molecular arrangements.

REFERENCES

1. R.T. Sanderson, *J. Am. Chem. Soc.*, **74,** 272 (1952).

2. ——————— , *Science*, **121,** 207 (1955).

3. R.G. Parr, R.A. Donnelly, M. Levy and W.E. Palke, *J. Chem. Phys.*, **68,** 3801 (1978).

4. R.A. Donnelly and R.G. Parr, *J. Chem. Phys.*, **69,** 4431 (1978).

5. P. Politzer and H. Weinstein, *J. Chem. Phys.*, **71,** 4218 (1979).

6. R.G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York (1989).

7. P. Politzer, *J. Chem. Phys.*, **86,** 1072 (1987).

8. J.E. Huheey, *J. Phys. Chem.*, **69,** 3284 (1965).

9. ——————— , *J. Org. Chem.*, **36,** 204 (1971).

10. R.S. Evans and J.E. Huheey, *Chem. Phys. Lett.*, **19,** 114 (1973).

11. G.A.L. Filgueiras and J.E. Huheey, *J. Org. Chem.*, **41,** 49 (1976).

12. J.L. Gazquez and E. Ortiz, *J. Chem. Phys.*, **81,** 2741 (1984).

13. S. Hati and D. Datta, *J. Phys. Chem.,* **98,** 10451 (1994).

14. K. Selby, M. Vllmer, J. Mosui, V. Kresin, W.A. de Heer and W.D. Knight, *Phys. Rev.*, **B40,** 5417 (1989).

15. D.E. Beck, *Solid State Commun.*, **49,** 381 (1984).