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Hardness and Electric Dipole Polarizability

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Pearson, in 1963, classified the Lewis acids and bases in terms of "hardness". A less polarizable species is hard and more polarizable is soft. This proved to be quite successful in rationalizing a variety of chemical observations, especially the exchange reactions. In the present work, a relation between hardness and polarizability has been found, which is further used to calculate the electronegativity of various atoms. It is interesting to note that these calculated values are very close to the experimental values. Further the electrostatic potentials of various atoms have been calculated and compared with the experimental values for better agreement.

INTRODUCTION

Pearson in 1963, using the idea of polarizability, classified the Lewis acids and bases in terms of "hardness".[1]

A less polarizable species is hard and a more polarizable species is soft. This hard-soft classification proved to be quite successful in rationalizing a variety of chemical observations, especially in exhange reactions[2, 3]. The meaning of polarizability is the ease of deforming the valence electron cloud of a chemical species. A closely related experimental quantity is electric dipole polarizability 'α' which actually describes the response of the electron cloud of a chemical species to an external electric field much lower than what would be needed to ionize the system. The proportionality constant for the dipole moment (μ) induced by the appiied electric field (F) is 'α',[4] *i.e.*,

$$\mu = F\alpha \tag{1}$$

The connection of 'η' and 'α' could not be ascertained due to lack of quantitative definition of hardness. So, the polarizability originally rested on the nature of the charge and the size of chemical species.

In 1983, Pearson and Parr gave a quantitative definition of hardness (η).

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right) = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right) \tag{2}$$

where 'E' is the electronic energy of the system having N number of electrons and 'μ' is the chemical potential of the electron cloud[5]. Eq. (1) is based on density functional theory. The other definition of 'η' is the approximate finite difference of ionization potential and electron affinity.

$$\eta = \frac{(I - A)}{2} \tag{3}$$

Recently Ghanty and Ghosh[6] have empirically found that softness $\left(\frac{1}{\eta}\right)$ correlates linearly with $\alpha^{1/3}$ for number of atoms and sodium cluster. Similar observations have been reported by Fuentealba and Reyes[7] for certain atoms and monoatomic ions.

The energy E(q) required to charge a conducting sphere of radius 'R' with 'q' is classically given by

$$E(q) = \frac{q^2}{2R}$$

$$E(q + 1) = (q + 1)^2/2R$$

Now

$$I = E(q + 1) - E(q)$$
$$A = E(q) - E(q - 1)$$

Hence

$$\frac{(I - A)}{2} = \frac{1}{2R} \tag{4}$$

The drawback of this eq. (4) is non-dependence of charge, rather used through the radius. This equation is valid for metallic cluster where the unit charge added or subtracted, does not give change in radius. However, for atoms and molecules it is not.

Recently, Hati and Datta[8] derived the relation between 'α' and 'R' as

$$\alpha = kR^3$$

where K is proportionality constant. Combining the eqs. (2–4),

$$\eta = \frac{1}{2}\left(\frac{k}{\alpha}\right)^{1/3} \tag{5}$$

The above equation gives explicit values for 'k' as 1.0, 0.585 and 0.792 which does not depict the physical significance of this parameter. Hence to correlate 'η' and 'α' it requires the entity which has some connection with the electronic charge cloud. In the present work we have attemped to use the effective nuclear charge (Z_{eff}) to re-relate hardness and polarizability. According to the following formula the effective nuclear charge 'Z_{eff}' is as follows:

$$Z_{eff} = \frac{1}{2}\left(\frac{I_1 + I_0}{I_1 - I_0}\right) \tag{6}$$

where I_1 and I_0 are the ionization energies for first and second stage of an atom.

RESULTS AND DISCUSSION

Since hardness is defined as the tight binding of electrons in the atom, so it has some relation to the effective nuclear charge. The results are reported in Table-1, calculated by Hati and Datta[8] for ready reference.

TABLE-1
APPLICATION OF EQ. (5) TO ATOMS

Atom	α^a	$\eta_{cal.}$ (a.u.)			$\eta^b_{exp.}$
		k = 1	k = 0.585	k = 0.792	
Li	163.918	0.091	0.084	0.084	0.088
Na	159.257	0.092	0.077	0.085	0.084
K	292.872	0.075	0.063	0.069	0.071
Rb	319.190	0.073	0.061	0.067	0.068
Cs	402.193	0.068	0.057	0.063	0.063
Cu	45.247	0.140	0.117	0.129	0.119
Ag	53.176	0.133	0.111	0.123	0.115
Au	39.139	0.147	0.123	0.136	0.127
Tl	51.286	0.135	0.113	0.125	0.107
Co	50.611	0.135	0.113	0.125	0.132
Rh	58.034	0.129	0.108	0.119	0.116
Ir	51.286	0.135	0.113	0.125	0.140

a. Reference 9 b. Reference 10

The calculated values for hardness through effective nuclear charge have been shown in Table–2 for some atoms. Although the values have been calculated for 61 atoms for which the results have been reported but in the present work only few of the atoms have been reported. It is interesting to note that for most of the atoms, calculated values are closely compared with the application of Eq. (5) and experimental values. It gives us the idea of 'k' to have the physical significance in terms of effective nuclear charge.

TABLE-2
CALCULATED VALUES OF HARDNESS FOR SOME ATOMS

Atom	I_1 (ev)	I_0 (ev)	$Z_{eff.}$	$\eta_{cal.}$	$\eta_{exp.}$
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

The relation has been further extended to cluster of atoms. The results of sodium cluster have been reported in Table-3. The comparison of the calculated values of hardness in the present work and the earlier one shows strikingly close proximity with each other. The use of effective nuclear charge is also valid for monoatomic ions whose results along with other cluster of atoms will be reported in due course.

TABLE-3
CALCULATED 'η' VALUES FOR SODIUM CLUSTERS Na_n

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 11 b. Reference 12

Conclusion

The relation between hardness and polarizability can be defined and quantified by invoking the nuclear charge of an atom, which has the physical significance. This concept can be extended to the molecules which further become helpful to understand the reaction path of chemical reactions.

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