

***Ab initio* calculations, electronegativity equalisation and group electronegativity**

DIPANKAR DATTA

Department of Chemistry, Manipur University, Imphal 795 003, India

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Abstract. A correspondence between *ab initio* calculations, the principle of electronegativity equalisation and group electronegativity has been established within the framework of Mulliken population analysis. Using this we have calculated electronegativities of some 37 groups/atoms. These electronegativities show excellent linear correlation with ${}^1J_{CC}$ coupling constants in monosubstituted benzenes and Inamoto's *i* scale and a satisfactory one with Wells' group electronegativity data. The correspondence however required a scaling of charge (obtained by *ab initio* calculations) and a proportionality between the electronegativity of the neutral group and its hardness. It is shown that using these electronegativity values it is possible to calculate group charges in molecules where groups under consideration interact with each other through σ bond only.

Keywords. *Ab initio* calculations; group charge; group electronegativity.

1. Introduction

Though a sense of "relative electronegativity" developed in the last century (Phillips 1976) in connection with the redox potentials, it was only in 1932 that Pauling first defined it (Pauling 1932, 1960). According to his original definition electronegativity is the power of an atom in a molecule to attract electrons to itself. However, the connection between this definition and his numerical scale is not obvious. Since then various other methods (Pritchard and Skinner 1955; Iczkowski and Margrave 1961; Boyd and Markus 1981; Zhang 1982; Huheey 1983; Robles and Bartolotti 1984; Gazquez and Ortiz 1984; Mullay 1984) have been proposed in attempts to evaluate this parameter theoretically and experimentally. The number of approaches available to date only reveal the ambiguity involved in the concept, which has given rise to a lot of empiricism in the treatments. Nevertheless the usefulness of this parameter, which some authors tend to describe as a fundamental property of an atom, in chemistry to correlate many physical observables is beyond doubt. Few other concepts are used so widely. Probably that is why there is a continuous search for a suitable scale for this parameter.

A comparatively recent but by far the most widely accepted definition (Iczkowski and Margrave 1961; Parr *et al* 1978; Perdew *et al* 1982; Parr and Pearson 1983; Huheey 1983; Gazquez and Ortiz 1984) describes electronegativity (χ_i) as the change in the energy (E_i) of an atom *i* with charge *q* on it,

$$\chi_i = \delta E_i / \delta q = \chi_i^0 + \eta_i q. \quad (1)$$

In (1) χ_i^0 , the electronegativity of the neutral atom ($q = 0$) takes the form of Mulliken's definition (Mulliken 1934, 1935), i.e., $\chi_i^0 = (I_i + A_i)/2$, where I_i and A_i are respectively the ionisation potential and electron affinity of the neutral atom i , and η_i , a companion parameter, is the hardness (Parr and Pearson 1983) of the atom i defined as $(I_i - A_i)$ indicating the resistivity of the atom in deviating from the value χ_i^0 with charge. [Note the difference from the original definition of Parr and Pearson (1983) for hardness. The factor 2 has been dropped for convenience.] It should be mentioned here that definition (1), originally proposed by Iczkowski and Margrave (1961) in a slightly different form is also an approximation. The importance of other terms in the expansion of χ_i in understanding the nature of bonding has been pointed out recently by Nalewajski (1984).

While attempts are on to quantify the notion of electronegativity of an individual atom and of that in a molecule to the extent possible, several workers have been applying this concept to a group of atoms to extend its uses. Consequently a term "group electronegativity" has evolved. It is assumed that a given group of atoms maintains its identity, as far as the power of electron donation or withdrawal is concerned, to considerably the same extent in various molecules; like atomic electronegativities, the numerical values obtained for different groups vary from method to method. Brief reviews on various theoretical and experimental treatments are available (Wells 1968; Huheey 1983; Bratsch 1985). The theoretical varieties are mainly of two types. One type of approach expresses the group electronegativity as a composite function of the electronegativities of the constituent atoms (Hinze *et al* 1963; Huheey 1965, 1966; Bratsch 1985; Mullay 1985). The other type involves group charge calculations through molecular orbital calculations at various levels of sophistication and accuracy in attempts to correlate these charges directly with electronegativity (Topson 1983; Marriott *et al* 1984). We will calculate group electronegativity here from the results of *ab initio* 6-31G**/6-31G* calculations performed by Marriott *et al* (1984) on molecules of type HG where H is hydrogen and G any group of atoms (for a general reference on 6-31G* calculations, see Hariharan and Pople 1972).

2. Calculation of group electronegativity and formulation of a suitable scale

The charges on hydrogen (q_H) in a number of HG molecules as calculated by Marriott *et al* (1984) using Mulliken population analysis are given in table 1. With the knowledge of experimental I and A of hydrogen (in eV) (Parr and Pearson 1983), χ_H in a molecule HG can be expressed as [from (1)]

$$\chi_H = 7.17 + 12.84 q_H. \quad (2)$$

Sanderson's principle of equalisation of electronegativity (Sanderson 1945; Politzer and Weinstein 1979; Parr *et al* 1978; Perdew *et al* 1982; Parr and Pearson 1983; Balbas *et al* 1983; Nalewajski 1985) means that in a molecule AB, $\chi_A = \chi_B$. Thus for the electronegativity of a group, χ_G , in HG, we can write

$$\chi_G = \chi_H = 7.17 + 12.84 q_H. \quad (3)$$

In terms of χ_G^0 and η_G ,

$$\chi_G = \chi_G^0 + \eta_G \cdot q_G. \quad (4)$$

Table 1. Charge on the hydrogen atom (q_H) in a molecule HG and electronegativity χ_G^0 of a group G^a

Group G	q_H	χ_G (eV)	χ_G^0 (eV)	χ_G^0 (eV)	Group G	q_H	χ_G (eV)	χ_G^0 (eV)	χ_G^0 (eV)
CH ₃	0.165	9.29	12.62	4.03	CO ₂ Me	0.186	9.56	13.61	4.37
CH ₂ Me	0.158	9.20	12.31	3.93	CONH ₂	0.144	9.02	11.72	3.73
CHMe ₂	0.153	9.13	12.09	3.86	COF	0.178	9.45	13.22	4.23
CMe ₃	0.155	9.16	12.18	3.88	CF ₃	0.174	9.40	13.03	4.17
CHCH ₂	0.176	9.43	13.13	4.20	NH ₂	0.332	11.43	24.39	7.99
CCH	0.276	10.71	19.19	6.24	NHMe	0.338	11.51	25.06	8.21
CCMe	0.278	10.74	19.34	6.29	NMe ₂	0.335	11.47	24.72	8.10
CH ₂ CCH	0.201	9.75	14.37	4.62	NHCHO	0.389	12.16	32.22	10.62
CH ₂ NH ₂	0.155	9.16	12.18	3.88	NHNH ₂	0.344	11.59	25.77	8.45
CH ₂ OH	0.152	9.12	12.05	3.84	NC	0.430	12.69	40.68	13.46
CH ₂ F	0.155	9.16	12.18	3.88	NCO	0.419	12.55	38.08	12.59
CH ₂ CHO	0.169	9.34	12.80	4.09	NO	0.396	12.25	33.45	11.03
CH ₂ CN	0.228	10.10	15.90	5.14	NO ₂	0.396	12.25	33.45	11.03
CN	0.313	11.19	22.41	7.32	OH	0.434	12.74	41.70	13.80
CNO	0.337	11.50	24.95	8.18	OMe	0.438	12.79	42.76	14.16
CHO	0.140	8.97	11.56	3.68	OCOMe	0.460	13.08	49.53	16.43
COMe	0.145	9.03	11.76	3.74	F	0.517	13.81	79.91	26.64
CO ₂ H	0.181	9.49	13.36	4.28	SiH ₃	-0.133	5.46	4.50	1.30
					Li	-0.177	4.89	3.81	1.07

^aSymbols are as defined in the text. q_H data are from Marriott *et al* (1984)

^bIn Pauling's unit (P). For the conversion, we have used the relation (Huheey 1965) between Mulliken's electronegativity (χ_M), which is obtained in eV, and χ_P : $\chi_P = 0.336(\chi_M - 0.615)$.

A significant observation of recent times is that for neutral atoms and molecules $\eta = \gamma\chi$ where γ is the proportionality constant (Nalewajski 1985; Yang *et al* 1985; Datta 1986) and takes the same value (Yang *et al* 1985), $1.6(\pm 0.25)$, for atoms and molecules. (This is a direct consequence of the fact that I and A are proportional to each other in the atoms, Parr and Bartolotti 1982, and in the molecules, Yang *et al* 1985. Incidentally the proportionality between I and A forms the basis for the vindication, Parr and Bartolotti 1982, of Sanderson's geometric mean principle of the equalisation of electronegativity, Sanderson 1945.) Assuming that this relation holds good for groups as well, we rewrite (4) as

$$\chi_G = (1 + 1.6 q_G) \chi_G^0 \quad (5)$$

Charge conservation requires $q_G = -q_H$. Hence,

$$\chi_G = (1 - 1.6 q_H) \chi_G^0 \quad (6)$$

Combining (3) and (6) we have

$$\chi_G^0 = (7.17 + 12.84 q_H) / (1 - 1.6 q_H) \quad (7)$$

Group electronegativities calculated by (7) are given in table 1. These are found to be unrealistically high. These need scaling. In order to make these values comparable to other scales available, we have calibrated q_H in HG by

$$q'_H = q_H / 2.5 \quad (8)$$

The factor 2.5 is arbitrary and the choice is made by the observation that q'_H values are comparable to the results of *STO-3G* calculations (Marriott *et al* 1984) available on some of the molecules considered (see table 2). Incidentally, that atomic elec-

Table 2. Group electronegativities (χ'_G) and comparison with other scales^a.

Group G	q'_H	χ'_G (eV)	χ''_G (eV)	χ''_G (P)	Mullay's ^b data	Wells ^c data	${}^1J_{CC}$ ^d	i^e	σ_I^f
CH ₃	0.066 0.064 ^g	8.02	8.96	2.80	2.32	2.3	1.07	2.14	-0.01
CH ₂ Me	0.063	7.98	8.87	2.77	2.35		1.09	2.15	-0.01
CHMe ₂	0.061	7.95	8.81	2.75	2.38		1.5		-0.01
CMe ₃	0.062	7.97	8.84	2.76	2.41		1.90	2.16	-0.01
CHCH ₂	0.070 0.062 ^g	8.07	9.09	2.85	2.56	(3.0)	1.61	2.34	0.11
CCH	0.110 0.109 ^g	8.58	10.41	3.29	3.10	(3.3)	3.37	2.52	0.29
CCMe	0.111	8.59	10.45	3.30					0.30
CH ₂ CCH	0.080	8.20	9.40	2.95					0.14
CH ₂ NH ₂	0.062	7.97	8.84	2.76	2.42		1.42	2.18	
CH ₂ OH	0.061	7.95	8.81	2.75	2.50		1.65	2.22	0.11
CH ₂ F	0.062	7.97	8.84	2.76	2.55		2.00	2.24	
CH ₂ CHO	0.068	8.04	9.02	2.82					
CH ₂ CN	0.091	8.34	9.76	3.07	2.28		3.07	2.20	0.20
CN	0.125 0.149 ^g	8.77	10.97	3.48	3.46	3.3	4.11	2.61	0.57
CNO	0.135	8.90	11.36	3.61					
CHO	0.056	7.89	8.66	2.70	2.89		2.0	2.39	
COMe	0.058	7.91	8.72	2.72	2.93		1.9	2.36	0.30
CO ₂ H	0.072	8.09	9.15	2.87	3.15	(2.85)		2.37	0.30
CO ₂ Me	0.074	8.12	9.21	2.89	3.16		2.4		0.32
CONH ₂	0.058	7.91	8.72	2.72	3.06		1.89	2.30	0.28
COF	0.071	8.08	9.12	2.86			3.3		
CF ₃	0.070	8.07	9.09	2.85	3.10	3.35	3.57	2.47	0.40
NH ₂	0.133 0.160 ^g	8.88	11.28	3.58	3.15	3.35	5.2	2.47	0.17
NHMe	0.135	8.90	11.36	3.61	3.19		5.8	2.50	0.13
NMe ₂	0.134	8.89	11.32	3.60	3.24	(3.0)	6.89	2.48	0.17
NHCHO	0.156	9.17	12.22	3.90	3.30		6.87		0.33
NHNH ₂	0.138	8.94	11.48	3.65	3.34		5.8	2.50	
NC	0.172	9.38	12.94	4.14					0.63
NCO	0.168	9.33	12.76	4.08	4.20		10.0	2.83	
NO	0.158	9.20	12.31	3.93					
NO ₂	0.158	9.20	12.31	3.93	4.08	3.4		2.75	0.67
OH	0.174 0.186 ^g	9.40	13.03	4.17	3.97	3.7	11.43 9.7	2.79	0.24
OMe	0.175	9.42	13.08	4.19	4.03	(3.7)	11.09	2.82	0.30
OCOMe	0.184	9.53	13.51	4.33	4.18		12.78	2.80	0.38
F	0.207 0.209 ^g	9.83	14.69	4.73	4.73		14.84	3.10	0.54
SiH ₃	-0.053	6.49	5.98	1.80	1.97	(2.2)	-6.5	1.79 ^h	-0.11 ^h
Li	-0.071	6.26	5.62	1.68	1.01			1.15	

^aSymbols as defined in the text; ^bdata for all the groups except Li are from Mullay (1985). The value for Li is taken from Mullay (1984); ^cWells (1968); ^din Hertz, from Marriott *et al* (1984); ^eInamoto and coworkers (1977, 1978, 1982); ^fCharton (1980); ^g q'_H calculated at *STO-3G* level (Marriott *et al* 1984); ^hFor SiMe₃.

tron populations obtained at one basis seem to be linearly related to those obtained at another has been recognised earlier (Topsom 1983). Here we would like to note a comment of Marriott *et al* (1984) – “Since the definition of an electronegativity scale involves an arbitrary scaling factor, one needs only relative hydrogen charge densities in order to define an electronegativity scale”. A point revealed in retrospect is that since q'_H is much smaller in magnitude, the hydrogen atom (and the groups in turn) is (are) kept closer to the neutral point so that (1) applies better (actually the expansion of E as a quadratic function in q is done around $q = 0$). The electronegativities calculated using (7) with q'_H are given in table 2 as $\chi_G^{0'}$. These are reasonable and comparable with other existing scales. For ready comparison corresponding values obtained by Mullay (1985) and those of Wells (1968) in cases where available are also given in table 2.

3. Correlations with other scales and measures of group electronegativity

At present the NMR coupling constants $^1J_{CC}$ (ortho-*ipso*) for monosubstituted benzenes (Marriott *et al* 1984) are considered to be very good measures of the electronegativities of various chemical groups (Mullay 1985; Marriott *et al* 1984). A very strong linear correlation of these constants with our $\chi_G^{0'}$ values is obtained ($r = 0.969$, figure 1) through

$$^1J_{CC} = 17.975 + 2.186 \chi_G^{0'} \quad (9)$$

The goodness of correlation is comparable to that of Mullay (1985) who has obtained the best correlation so far ($r = 0.940$) of the electronegativity values with $^1J_{CC}$ constants. It should be mentioned here that Marriott *et al* (1984) have earlier found an empirical relation between $^1J_{CC}$ and $(q_H)^2$.

Another scale which is claimed to represent substituent electronegativity is the i scale developed by Inamoto and co-workers (Inamoto and Masuda 1977, 1978; Inamoto *et al* 1982) again through extensive correlation with NMR data for a wide variety of groups. The i values also correlate well with $\chi_G^{0'}$ ($r = 0.935$, figure 2). However, Mullay (1985) has obtained a much better correlation ($r = 0.975$) with these i values. A fair amount of correlation is found with the data of Wells (1968)

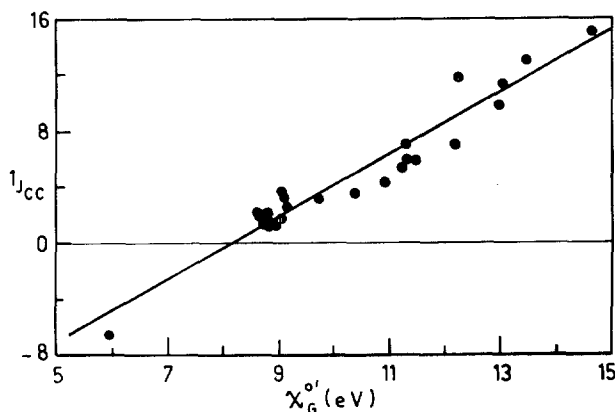


Figure 1. Variation of $^1J_{CC}$ with $\chi_G^{0'}$. χ_G^0 also correlates satisfactorily ($r, 0.913$).

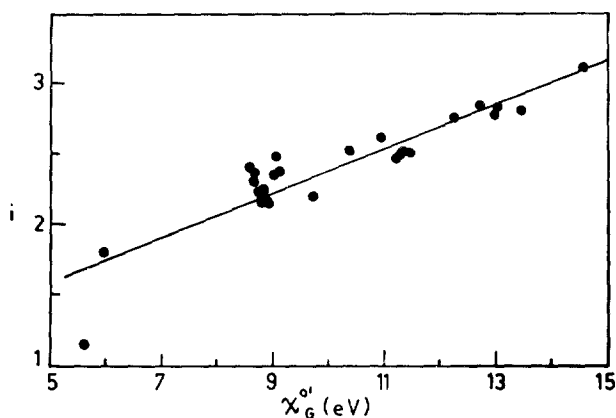


Figure 2. Correlation between $\chi_G^{0'}$ and i scale.

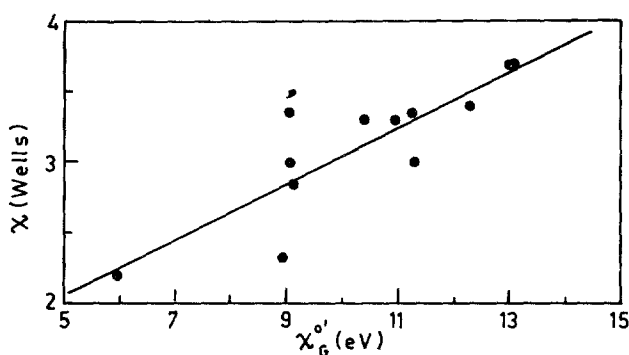


Figure 3. Correlation between Wells' data and $\chi_G^{0'}$.

($r = 0.854$, figure 3) which was earlier regarded the "best" (Huheey 1983). A very poor correlation is achieved with Taft's σ_I constants (Charton 1980) ($r = 0.610$) showing that these are not much related to the electronegativities of the groups.

4. Nature of $\chi_G^{0'}$ and group charge calculation in molecules

Radom and coworkers (Pross and Radom 1980) have done extensive calculations on monosubstituted benzenes at the *STO-3G* level to separate the charges donated by a substituent to the phenyl ring through the σ -path (q_σ) and the π -path (q_π). The q_σ values calculated by them for some of these molecules are given in table 3. From (7) with $q'_H = 0.063$ (table 3), $\chi_{Ph}^{0'}$ is found to be 8.87 eV. With this value charges donated to the phenyl ring by the various substituents considered in table 3 are calculated using

$$q = \frac{\chi_G^{0'} - \chi_{Ph}^{0'}}{\eta_G + \eta_{Ph}} = \frac{\chi_G^{0'} - \chi_{Ph}^{0'}}{1.6(\chi_G^{0'} - \chi_{Ph}^{0'})}, \quad (10)$$

a consequence of equalisation of electronegativity and charge conservation, and given there as q . An excellent linear correlation ($r = 0.983$, figure 4) is obtained

Table 3. σ -Donation by a group to the phenyl ring in monosubstituted benzenes— q_σ as calculated at the *STO-3G* level and q as calculated using (10).

Substituent	q_σ^a	q
H	0.063	—
CH ₃	-0.007	0.005
NH ₂	0.140	0.075
OH	0.185	0.119
OCH ₃	0.192	0.119
F	0.215	0.154
NO ₂	0.227	0.101
CN	0.104	0.066
CHO	-0.001	-0.007
CF ₃	0.021	0.008
Li	-0.265	-0.140

^aPross and Radom (1980).

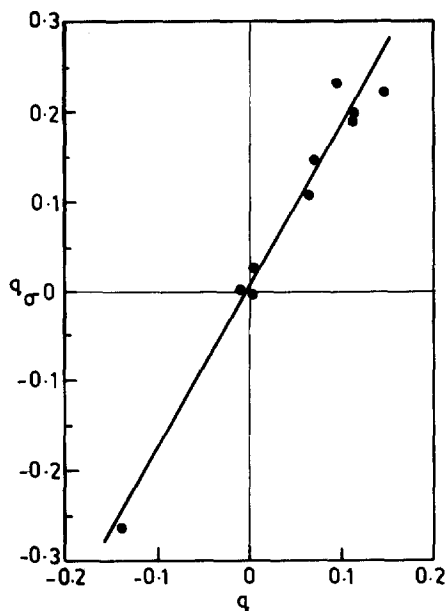


Figure 4. Correspondence between q_σ and q . (For symbol definitions, see text.)

between q_σ and q . Since no significant correlation is found with q_π or $(q_\sigma + q_\pi)$, we recognise that our $\chi_G^{0'}$ values indicate only a σ -inductive effect. This is probably because these are calculated with reference to hydrogen which does not give scope for multiple bonding.

It is well known that in methyl compounds, hyperconjugative effects are operative; however, these are expected to be small (Wiberg 1980). Using the $\chi_G^{0'}$ values of table 2, we have tried to calculate the charge on the methyl group in molecules of type CH₃G by

$$q'_{\text{CH}_3} = \frac{\chi_G^{0'} - \chi_{\text{CH}_3}^{0'}}{1.6(\chi_G^{0'} + \chi_{\text{CH}_3}^{0'})}, \quad (11)$$

Table 4. Results of the calculation of the charge on the methyl group in-CH₃G molecules using (11) and comparison with 6-31G*//6-31G* results.

Group G	$2.5 \cdot q'_{\text{CH}_3}$ ^a	q_{CH_3} ^b	Δq ^c
CHCH ₂	0.011	0.000	0.011
CHO	-0.027	0.012	-0.039
CN	0.157	0.153	0.004
CCH	0.117	0.171	-0.054
NH ₂	0.179	0.175	0.004
NO	0.174	0.237	0.063
OH	0.289	0.292	0.003
OCH ₃	0.292	0.296	-0.004
F	0.378	0.403	-0.025

^a q'_{CH_3} is the methyl charge calculated using (11); ^b*Ab initio* results, from Marriott *et al* (1984); ^c $\Delta q = 2.5 \cdot q'_{\text{CH}_3} - q_{\text{CH}_3}$.

The results given in table 4 show satisfactory reproduction of *ab initio* 6-31G*//6-31G* values. The deviations Δq may be due to hyperconjugation, which suggests that such group charge calculations can be done only for those groups which do not form multiple bonds between them.

5. Concluding remarks

Thus we have established a correspondence between *ab initio* calculations, the principle of electronegativity equalisation and group electronegativity within the framework of Mulliken population analysis (for a very good discussion on Mulliken population analysis see Huzinaga and Narita 1980). We have also shown that the electronegativity values of the various groups, though calculated with reference to the hydrogen atom, are transferable to other molecules.

In an earlier section, we have indicated that there is a proportionality between the group charges obtained at the 6-31G* level and at the 3G level. However, there are cases where this proportionality is lost to a considerable extent. For example, we find in table 2 that our scaled 6-31G* charges differ significantly in H₂O, HCN or NH₃ from those calculated at the 3G level. The differences are mainly due to the incorporation of polarisation functions in the 6-31G* level. A comparison of the various results obtained by *ab initio* calculations at these two levels has been made earlier by Topsom (1983). In any case we have seen that group charges yielded at the 6-31G* level are useless for calculating group electronegativity unless properly scaled. In this respect the 3G group charges seem to be better suited (table 2). Thus it would be interesting to carry out the *ab initio* calculations at the STO-3G level to obtain the electronegativities of various groups and compare them with our present results.

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