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A New Scale of Electronegativity Based on Electrophilicity Index

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By calculating the energies of neutral and different ionic forms (M^{2+}, M^+, M, M^-, and M^{2-}) of 32 elements (using B3LYP/6-311++G** level of theory) and taking energy (E) to be a *Morse-like function* of the number of electrons (N), the electrophilicity values (ω) are calculated for these atoms. The obtained electrophilicities show a good linearity with some commonly used electronegativity scales such as Pauling and Allred−Rochow. Using these electrophilicities, the ionicities of some diatomic molecules are calculated, which are in good agreement with the experimental data. Therefore, these electrophilicities are introduced as a new scale for atomic electronegativity, χ^0_ω. The same procedure is also performed for some simple polyatomic molecules. It is shown that the new scale successfully obeys Sanderson's electronegativity equalization principle and for those molecules which have the same number of atoms, the ratio of the change in electronegativity during the formation of a molecule from its elements to the molecular electronegativity ($\Delta\chi/\chi_\omega$) is the same.

Introduction

Electronegativity, χ, is one of the most widely used concepts in chemistry[1] and is almost as old as chemistry itself. This concept was introduced for the first time by Pauling[2] as "the desire of an atom in a molecule to attract electrons to itself". Since that time, several attempts have been performed in order to obtain a quantitative measure of atomic electronegativities.[3−33] In the construction of each scale, a property dependent upon electron distribution, not electron distribution itself, is measured. Scales of electronegativity can be also evaluated against an empirical relationship between bond character and χ.[34] Murphy and co-workers[35,36] stated nine elementary rules which all electronegativity scales must obey. They showed that Pauling electronegativity violates more than half of these rules.

Parr et al.[37] identified electronegativity with the negative of the electronic chemical potential (μ). The chemical potential and hardness (η) have been defined within the density functional theory as the first and second derivatives of E with respect to N, respectively.[38,39] Therefore, these parameters for an N-electron atom with energy E are commonly expressed as

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(r)} = -\chi \qquad (1)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(r)} \qquad (2)$$

where the external potential, $\upsilon(r)$, is the potential due to a set of nuclei as well as the external field. A problem associated with these equations is that the number of electrons in an atom or molecule is an integer, and hence, E is not a continuous function of N. If we assume the differentiability of $E(N)$, it is possible to write it as a Taylor series expansion around the point N_0, the number of electrons in the neutral system:

$$E(N) = E(N_0) + \sum_{n=1}^{\infty} \frac{1}{n!}(N - N_0)^n \left(\frac{\partial^n E}{\partial N^n}\right)_{N=N_0} \qquad (3)$$

which according to the definitions of the corresponding derivatives, this equation can be rewritten as

$$E(N) = E(N_0) + (N - N_0)\mu + (N - N_0)^2\eta + (N - N_0)^3\gamma + ... \qquad (4)$$

It is explained[40] that Taylor series expansions of atomic energies essentially terminate after the second-order term if the atoms' ionization energies obey $I_n = n\,(I_1)$. In practice, by finite difference and parabola model approximations, μ and η can be calculated in terms of the ionization potential (IP) and electron affinity (EA) ($\mu = -$ (IP + EA)/2 and $\eta =$ IP − EA); but they are affected if the Taylor series is carried out beyond second order.[40−42]

Parr et al.[43] have defined an index for the global electrophilicity power of a system in terms of its electronic chemical potential and hardness as

$$\omega = \frac{\mu^2}{2\eta} \qquad (5)$$

Such an index is intended to be a measure of the energy lowering of the chemical species due to maximum electron flow from the environment (see Figure 1) and therefore is a measure of the capacity of species to accept an arbitrary number of electrons. In fact it encompasses both, the propensity of the electrophiles to acquire an additional electronic charge driven by μ^2 and resistance of the system to exchange electronic charge with the environment described by η. Therefore, the electrophilicity may have some relation with the power of the system to hold electrons to itself. The usefulness of this index in theoretical studies has been demonstrated by many authors,[44−67] and its utility has been also documented in a comprehensive review article.[68]

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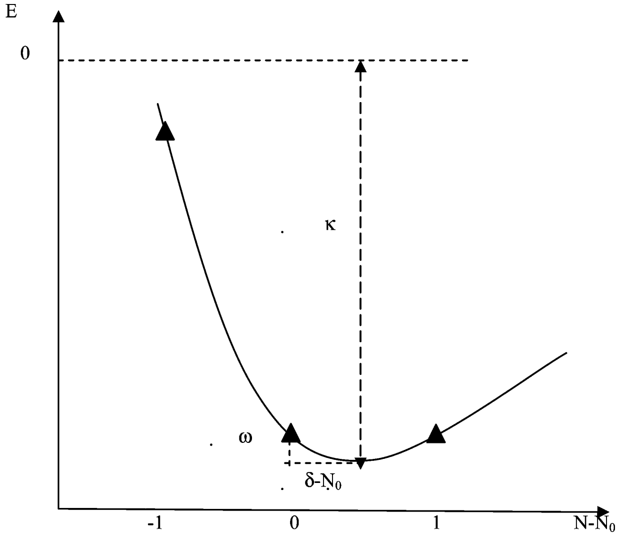

Figure 1. Energy vs the change in the number of electrons. N_0 is the number of electrons in neutral system.

In this article an attempt has been made to introduce a new electronegativity scale for atoms and molecules based on their electrophilicity values, which are obtained by considering a Morse-like function, instead of Taylor series expansion, for $E(N)$. The ability of the obtained values in predicting the bond ionicities of some diatomic molecules is also checked.

Results and Discussion

As has been discussed, the electrophilicity of a system has something to do with both the resistance and the tendency of the system to exchange electrons with the environment. Therefore, it seems that this index can be used as a measure of electronegativity in a given system. In most cases a quadratic form (ground-state parabola model) is considered for the $E(N)$ function and therefore μ, η, and ω of a system are calculated by using IP and EA. According to this approximation and Parr definition, electrophilcities have the following form:

$$\omega_Q = \frac{(IP + EA)^2}{8(IP - EA)} \tag{6}$$

where ionization potential (IP $= E(N-1) - E(N)$) and electron affinity (EA $= E(N) - E(N+1)$) can be easily computed. Therefore, to calculate the electrophilicity values for atoms, the energies of the first four rows elements of the periodic table in neutral (M), anion (M^-), and cation (M^+) forms are calculated. Then the IP, EA, and ω_Q for these atoms are evaluated using the corresponding relations. The calculations are done the commonly used exchange-correlation functional of density functional theory (DFT), B3LYP, and 6-311++G** basis set using the Gaussian 98 program[69] (this basis set is only available for these elements). The results are collected in Table 1. The linear correlation between different scales of electronegativities is the important condition which all scales must obey. But Figure 2 shows that the obtained values for the electrophilicities in this manner are not so correlated with the Allred−Rochow electronegativities ($R^2 = 0.7541$), and therefore they cannot introduce this as a new scale of electronegativity. This difficulty may arise from using the quadratic model in calculating the η and μ, which is caused by a truncation error. It is recalled that the obtained values for the chemical potential, hardness, and therefore electrophilicity depend on the number of terms which are considered in Taylor expansion of $E(N)$ and this approximation is successful only when the atom's ionization potential obeys $I_n = n(I_1)$. In Figure 2 the most *relative deviations* from linearity are observed for N, Mn, and Zn elements; which have the half or full closed shell electronic structures; therefore their I_2 have significant difference with 2 I_1. On the other hand, the relative electrophilicities of the elements in the first transition metal series (Ni > Cu > V > Fe > Cr > Ti > Co > Sc > Zn > Mn) are not in accordance with the relative stabilities of their coordination compounds (Mn < Fe < Co < Ni < Cu > Zn).

TABLE 1: Calculated Ionization Potential, Electron Affinity, Chemical Potential, Hardness, Electrophilicity, and Allred−Rochow Electronegativity Values for the Selected Atoms

atom	IP	EA	μ	η	ω_Q	χ_{A-R}[a]
H	0.502	0.032	−0.267	0.471	2.063	2.20
Li	0.206	0.021	−0.113	0.186	0.942	0.97
Na	0.199	0.021	−0.113	0.178	0.932	1.01
K	0.165	0.019	−0.922	0.146	0.793	0.91
Be	0.335	−0.008	−0.163	0.343	1.057	1.47
Mg	0.284	−0.008	−0.138	0.292	0.885	1.23
Ca	0.226	0.001	−0.113	0.226	0.775	1.04
B	0.339	0.035	−0.187	0.305	1.562	2.01
Al	0.254	0.038	−0.146	0.216	1.342	1.47
Ga	0.261	0.041	−0.151	0.221	1.405	1.82
C	0.424	0.051	−0.237	0.374	2.045	2.50
Si	0.298	0.049	−0.173	0.249	1.641	1.74
Ge	0.290	0.049	−0.172	0.242	1.619	2.02
N	0.540	0.005	−0.272	0.535	1.886	3.07
P	0.382	0.033	−0.208	0.348	1.684	2.06
As	0.363	0.036	−0.199	0.327	1.655	2.20
O	0.663	0.059	−0.361	0.604	2.937	3.50
S	0.469	0.081	−0.275	0.389	2.646	2.44
Se	0.388	0.081	−0.235	0.307	2.443	2.48
F	0.653	0.128	−0.391	0.525	3.954	4.10
Cl	0.481	0.137	−0.309	0.344	3.772	2.83
Br	0.441	0.132	−0.286	0.308	3.614	2.74
Sc	0.272	−0.006	−0.133	0.277	0.866	1.20
Ti	0.276	0.018	−0.147	0.258	1.143	1.32
V	0.348	0.032	−0.191	0.316	1.558	1.45
Cr	0.258	0.024	−0.141	0.235	1.153	1.56
Mn	0.358	−0.051	−0.153	0.413	0.782	1.60
Fe	0.277	0.025	−0.151	0.252	1.225	1.64
Co	0.371	−0.043	−0.164	0.414	0.887	1.70
Ni	0.284	0.082	−0.183	0.202	2.262	1.75
Cu	0.295	0.045	−0.172	0.251	1.567	1.75
Zn	0.347	−0.038	−0.154	0.384	0.843	1.66

[a] From ref 7.

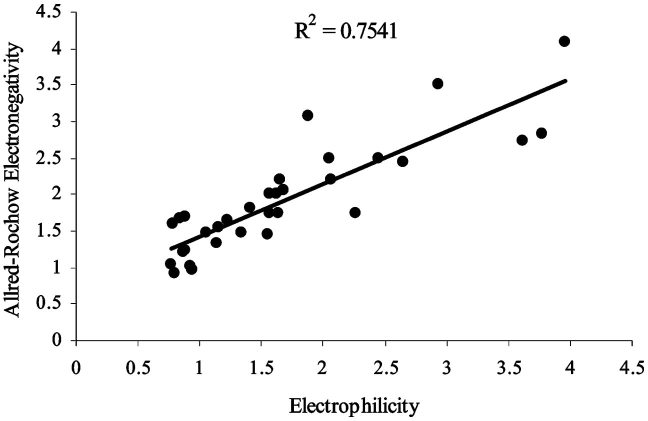

Figure 2. Correlation of Allred−Rochow electronegativity with the electrophilicities obtained from quadratic approximation.

To remove these problems, a *Morse-like function* for $E(N)$, which considers nearly all terms in Taylor expansion, is assumed here. This function has the following simple form

$$E(N) = \alpha\{1 - e^{-\beta(N-\delta)}\}^2 - k \qquad (7)$$

where α, β, δ, and κ are adjustable parameters and each of them has a physical meaning. For example, δ is the amount of electron transfer with respect to the minimum of energy curve ($\delta = N_{\min}$), κ is the depth of such curve ($\kappa = -E(\delta)$) and $\alpha - \kappa$ is the energy of the system when it is saturated with electrons ($\alpha - \kappa = E(\infty)$). Some of these parameters are shown in Figure 1.

If we take the ω as the difference between the energy of neutral system and the minimum of E ($\omega = E(N_0) - E(\delta)$),[43] therefore:

$$\omega = \alpha\{1 - e^{-\beta(N_0-\delta)}\}^2 \qquad (8)$$

To calculate the electrophilicity of a given system, we only need to find the adjustable parameters, which can be easily determined by a simple fitting procedure. To apply this method in atomic systems, the energies of the considered atoms in neutral (M), two anionic (M^-, M^{2-}), and two cationic (M^+, M^{2+}) forms are calculated (for hydrogen only one cation form is possible) with the B3LYP/6-311++G** level of theory. Then by a simple fitting procedure using a mathematical software, the values of adjustable parameters are obtained for each atom. By giving these data in hand, the electrophilicity values are calculated from eq 8. The obtained values for the adjustable parameters (in atomic units) and calculated electrophilicity values (in electron volts) for 32 selected atoms are gathered in Table 2. The values of δ and κ show increase left to right across rows and down groups of the periodic table (which are in accordance with the meaning of these parameters); but there are no an obvious trend in the α and β values.

Note that there is no electrophilicity value higher than that of fluorine and the relative electrophilicities of the elements in the first transition series are comparable to the relative stabilities of their co-ordination compounds. It is recalled that the selected basis set, 6-311++G**, is not available for the other elements and therefore this procedure is only applicable for the considered atoms.

Surprisingly the obtained electrophilicities show good linear correlation with the Allred−Rochow ($R^2 = 0.9925$) and Pauling ($R^2 = 0.9787$) electronegativities, for which their plots are drawn in Figure 3 and Figure 4, respectively. Therefore, these electrophilicities can be introduced as a new scale of electronegativity; χ_ω^0. It is mentioned that, this linearity is not achieved when the quadratic form of $E(N)$ is applied with the same basis set or when a lower level basis set (such as 3-21G** or 6-31G**) is performed in calculations; which is due to poor definition of electronic distribution by these basis sets. These data are not presented here. It is the reason that 6-311++G** basis set is selected for these calculations.

TABLE 2: The Obtained Adjustable Parameters of the Considered Function for Energy (α, β, δ and κ) and the Calculated Electrophilicity Values (χ_ω) for the Selected Atoms in This Study[a]

atom	α	β	δ	κ	χ_ω
H	5.830	0.173	1.568	0.564	1.687
Li	0.322	0.369	3.665	7.516	0.676
Na	0.397	0.336	11.671	162.312	0.689
K	0.746	0.242	19.682	599.95	0.656
Be	4.04	0.157	4.612	14.689	1.113
Mg	2.144	0.187	12.624	200.102	0.900
Ca	1.095	0.216	20.694	677.584	0.779
B	0.62	0.293	5.926	24.566	1.637
Al	3.287	0.154	13.713	242.291	1.200
Ga	2.195	0.167	31.886	1924.689	1.514
C	5.502	0.151	6.718	37.920	1.954
Si	1.449	0.226	14.772	289.447	1.430
Ge	5.693	0.12	32.818	2076.985	1.654
N	1.950	0.226	7.869	54.607	2.528
P	6.618	0.129	15.699	341.322	1.611
As	6.934	0.122	33.737	2235.856	1.673
O	11.112	0.132	8.702	75.164	2.841
S	0.873	0.274	16.955	398.167	2.131
Se	3.042	0.177	34.822	2401.559	2.040
F	1.181	0.31	9.921	99.889	3.505
Cl	21.496	0.084	17.74	460.238	2.390
Br	6.756	0.131	35.802	2574.188	2.262
Sc	3.537	0.141	21.657	760.625	0.910
Ti	0.705	0.263	22.781	849.329	0.996
V	0.700	0.339	23.646	943.934	1.141
Cr	14.509	0.076	24.714	1044.449	1.227
Mn	1.265	0.226	25.786	1150.803	1.301
Fe	3.606	0.169	26.649	1263.583	1.314
Co	0.971	0.307	27.663	1382.749	1.343
Ni	13.853	0.096	28.629	1508.303	1.475
Cu	3.028	0.165	29.763	1640.524	1.481
Zn	88.283	0.041	30.564	1779.396	1.293

[a] The parameters are in atomic units, and the electrophilicity values are in electron volts.

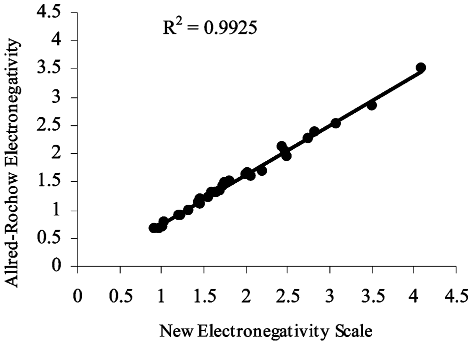

Figure 3. Correlation of Allred−Rochow electronegativity with the new electronegativity scale.

Although this linearity is not the sufficient condition to accept a set of numbers as a new electronegativity scale, but this scale is consistent with Pauling's original definition and also powerful theoretical supports for χ_ω^0 come from the electronegativity theory of Parr and Pearson.[38] First, the dimension of χ_ω^0 is energy, like electronegativity on Parr and Pearson's theory. Second, the value of χ_ω^0 is a "global atomic property". Third, the value of χ_ω^0 is dependent on the valence state and charge of atom. Fourth, and most importantly, there are good linear correlations between χ_ω^0 and the other electronegativity scales for the selected atoms. In addition, χ_ω obeys all of the following fundamental rules which are introduced by Murphy et al.:[35]

(1) The scale has a free atom definition.

(2) A high precision is necessary for each scale.

(3) All of the valence electrons are included in the definition of χ_ω^0.

(4) Electronegativity is associated with energy.

(5) The elements N, O and F have the highest χ_ωs among the main group elements.

(6) Si rule obey: All metals must have χ_ω^0 values which are less than or equal to that Si atom, and Si has the lowest χ_ω^0 in the metalloid band (B, Si, Ge, As, Sb, Te, Bi and Po).

(7) In binary compounds, the electronegativities of the constituted atoms clearly quantify the nature of the bonds; which will be discussed latter.

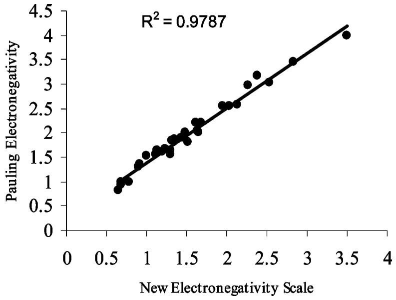

Figure 4. Correlation of Pauling electronegativity with the new electronegativity scale.

TABLE 3: The Calculated Parameters and the Obtained Electrophilicity Values for the Selected Molecules in This Study Using B3LYP/6-311++G Method**

molecule	α	β	δ	κ	χ_ω
HF	27.991	0.087	10.692	100.589	2.926
HCl	32.449	0.073	18.683	460.919	2.307
OH	23.883	0.096	9.6320	75.8560	2.557
SH	10.971	0.106	17.762	398.851	2.128
H_2O	30.107	0.077	10.670	76.5440	2.313
NH_2	23.509	0.080	9.7140	55.9560	2.216
BeH_2	5.269	0.163	6.6350	15.985	1.705
MgH_2	6.133	0.137	14.685	201.324	1.605
BH_3	11.131	0.119	8.6350	26.689	1.857
CH_3	31.823	0.069	9.6680	39.9260	1.931
SiH_3	26.135	0.068	17.727	291.328	1.829
GeH_3	11.344	0.096	35.781	2078.829	1.878
CH_4	8.1710	0.139	10.647	40.606	1.971
SiH_4	12.052	0.113	18.643	291.982	1.846
NH_4^+	33.866	0.059	11.783	57.111	2.065
PH_4^+	71.752	0.040	19.766	343.687	1.872

(8) χ^0_ω has a quantum mechanically definition.

(9) This scale shows a systematic increase left to right across rows of the periodic table and a general decrease down groups.

It is clear that there are no severe flaws in this electronegativity scale.

To check the applicability of this method in determining the electronegativities of larger systems, the same procedure is performed for some simple polyatomic molecules, which are given in Table 3. Notice that charged molecules are also considered in this series. Vibrational frequencies are calculated for optimized structures without any scaling factor in order to check if there is a true minimum. The obtained parameters and electrophilicities for these molecules are summerized in Table 3. The calculated molecular electronegativities (χ_ω), the arithmetic means (χ_{AM}) and the geometric means (χ_{GM}) of the electronegativities of the constituted atoms for each case are also given for comparison in the first, second, and third columns of Table 4, respectively. It is clear from this table that the χ_{AM} and χ_{GM} are nearly the same and even in some cases (BH_3, GeH_3, SiH_4, and PH_4^+) are equal, but in other molecules χ_{AM} values are little more than the corresponding χ_{GM}.

The values of the two first columns (χ_ω and χ_{AM}) are nearly the same (a linear correlation with slope near to unity and $R^2 = 0.9973$), and therefore, it is concluded that in the new scale the molecular electronegativity is simply related to the atomic electronegativities as

$$\chi_\omega = \frac{\sum_{i=1}^{m} \chi^0_{\omega_i}}{m} \tag{9}$$

TABLE 4: Molecular (χ_ω), Arithmetic Mean (χ_{AM}), Geometric Mean (χ_{GM}) and the Change in Electronegativity during the Formation ($\Delta\chi$) of Some Selected Molecules

molecule	χ_ω	χ_{AM}	χ_{GM}	$\Delta\chi$	$\Delta\chi/\chi_\omega$
HF	2.926	2.596	2.432	−2.266	−0.774
HCl	2.307	2.039	2.008	−1.771	−0.768
OH	2.557	2.264	2.189	−1.971	−0.771
SH	2.128	1.909	1.896	−1.690	−0.794
H_2O	2.313	2.072	2.007	−3.902	−1.687
NH_2	2.216	1.968	1.848	−3.686	−1.663
BeH_2	1.705	1.496	1.469	−2.782	−1.632
MgH_2	1.605	1.425	1.368	−2.699	−1.663
BH_3	1.857	1.675	1.674	−4.841	−2.607
CH_3	1.931	1.754	1.816	−5.084	−2.633
SiH_3	1.829	1.623	1.619	−4.662	−2.549
GeH_3	1.878	1.679	1.679	−4.837	−2.576
CH_4	1.971	1.741	1.738	−6.732	−3.416
SiH_4	1.846	1.636	1.632	−6.333	−3.431
NH_4^+	2.065	1.856	1.829	−7.213	−3.493
PH_4^+	1.872	1.672	1.672	−6.488	−3.466

where m is the number of atoms in the considered molecule and $\chi^0_{\omega_i}$ is the electronegativity of the ith free atom of the molecule. It seems that each atom has a χ^0_i/m contribution in the molecular electronegativity. It is the essence of Sanderson's electronegativity equalization principle and indicates that the new scale obeys this principle. It is another advantage for the introduced scale. This property makes further calculations with these electronegativities easier.

The change in electronegativities during the formation of the selected molecules from their elements ($\Delta\chi = \chi_\omega - \sum_{i=1}^{m} \chi^0_i$) are also calculated, which are given in the fourth column of Table 4. It can be easily shown that in the introduced scale:

$$\Delta\chi = (1 - m)\chi_\omega \tag{10}$$

Therefore, it is expected that for those compounds which have the same number of atoms, $\Delta\chi/\chi_\omega$ ratio is nearly the same $(1 - m)$. This is such as a *corresponding state principle* in atomic scale. These ratios are calculated for the considered molecules and are gathered in the fifth column of Table 4. It is found that for $m = 2$, 3, 4, and 5 these ratios are nearly −0.8, −1.7, −2.6, and −3.5, respectively, which are in accordance with our expectation, but as the size of the system increases, the difference between $\Delta\chi/\chi_\omega$ ratio and $1 - m$ increases too.

Now it is attempted to extend the application of the new electronegativity scale by calculating dipole moment charges, q, of some simple diatomic molecules. A comparison has been also made by means of an already known electronegativity scale (Allred−Rochow). Since bond character (ionic, covalent and metallic) is directly conditioned by the peculiar capacity of bonded atoms to exchange electrons,[70] the electronegativity difference between the bonded atoms is the most suitable one for the problem under discussion and the type of bond formed is largely determined by this difference. Electronegativity can be used to predict the degree of ionic character (ionicity) of a bond between two dissimilar elements. It was shown that compounds will be ionic if the electronegativity difference between the A and B atoms of a B−A bond is more than the half the electronegativity value of the most electronegative element.[71] A new approach to the relationship between bond energy and electronegativity is also given by Smith.[72] Although the dipole moment charge of the bond can be related to the difference between the two atomic electronegativities, but it must be noticed that q could not be a simple function of $\chi_B - \chi_A$ and it is difficult to formulate a reliable relation between the ionicity of a bond and the difference in electronegativity of the

TABLE 5: Comparison between Calculated Dipole Moment Charges with Eqs 1−5 by Using New Electronegativity Scale and Allred−Rochow Electronegativity (in Parentheses)[a] for Some Selected Diatomic Molecules

molecule	q_1	q_2	q_3	q_4	q_5	exptl
LiF	0.865	0.917	0.936	0.807	0.677	0.839
	(0.914)	(0.860)	(0.898)	(0.763)	(0.617)	
NaF	0.862	0.913	0.933	0.803	0.671	0.879
	(0.908)	(0.846)	(0.889)	(0.754)	(0.605)	
KF	0.869	0.924	0.940	0.813	0.685	0.822
	(0.921)	(0.880)	(0.912)	(0.778)	(0.637)	
LiCl	0.520	0.791	0.847	0.717	0.559	0.731
	(0.579)	(0.696)	(0.762)	(0.657)	(0.489)	
NaCl	0.515	0.783	0.840	0.712	0.552	0.801
	(0.563)	(0.673)	(0.740)	(0.643)	(0.474)	
KCl	0.528	0.804	0.857	0.726	0.569	0.801
	(0.602)	(0.730)	(0.794)	(0.678)	(0.513)	
LiBr	0.467	0.766	0.826	0.701	0.540	0.593
	(0.543)	(0.677)	(0.745)	(0.646)	(0.477)	
NaBr	0.461	0.757	0.818	0.695	0.533	0.758
	(0.527)	(0.654)	(0.721)	(0.631)	(0.461)	
KBr	0.475	0.780	0.838	0.710	0.550	0.783
	(0.567)	(0.713)	(0.779)	(0.668)	(0.501)	
BrF	0.32	0.254	0.243	0.355	0.216	0.153
	(0.370)	(0.228)	(0.211)	(0.332)	(0.199)	
BrCl	0.004	0.013	0.005	0.054	0.028	0.055
	(0.002)	(0.006)	(0.002)	(0.032)	(0.016)	

[a] From ref 73.

two atoms between which the bond is formed. The following relations were frequently used to match experimental data with electronegativity values of the constituted atoms of an A−B bond based on an empirical basis:[2,70,72]

$$q_1 = 1 - \exp\{-(\chi_B - \chi_A)^2/4\} \tag{11}$$

$$q_2 = 1 - \exp\{-(\chi_B - \chi_A)^2/\chi_{GM}{}^{3/2}\} \tag{12}$$

$$q_3 = 1 - \exp\{-3(\chi_B - \chi_A)^2/\chi_{AM}{}^2\} \tag{13}$$

$$q_4 = \frac{\chi_B - \chi_A}{\chi_B} \tag{14}$$

$$q_5 = \frac{\chi_B - \chi_A}{\chi_B + \chi_A} \tag{15}$$

where χ_{AM} and χ_{GM} are the arithmetic and geometric means of the two atomic electronegativities (χ_A and χ_B), respectively. These relations are used here to calculate the ionicity of some diatomic molecules by using the corresponding $\chi^0_{\omega_i}$ s. The results are collected in Table 5. We have also chosen Allred−Rochow's electronegativity scale (in parenthesis) in order to compare the calculated ionicities with those computed from the new scale. The range of dipole moment charges is sufficiently broad to state some general conclusions. Although the ionicity values agree only roughly with the experimental points, but comparing the values show the incapability of eqs 11, 13, and 15 to give reliable estimations for the dipole moment charges, in contrast with eq 12, which is more successful. There is no advantage in using the more complex eqs 11 and 13 instead of the much simpler eq 14. To simplify this comparison, the correlation between the obtained dipole moment charges from both of the Allred−Rochow and introduced scales with experimental values are drawn for q_2 (Figure 5) and q_4 (Figure 6). If we compare the results, we see that our scale is nearly as good as or a little better than the Allred−Rochow scale; which is another advantage for the new scale.

It seems that other molecular properties such as dissociation energy, heat of formation etc. can be predicted successfully using this scale. Research along this line is being made in our group, and results will be published in a forthcoming paper.

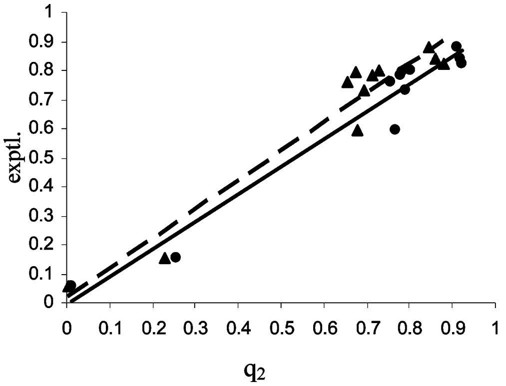

Figure 5. Correlation between the experimental and calculated dipole moment charges (q_2) using Allred−Rochow (dashed line, ▲, $R^2 = 0.9364$) and new (filled line, ●, $R^2 = 0.9521$) scales.

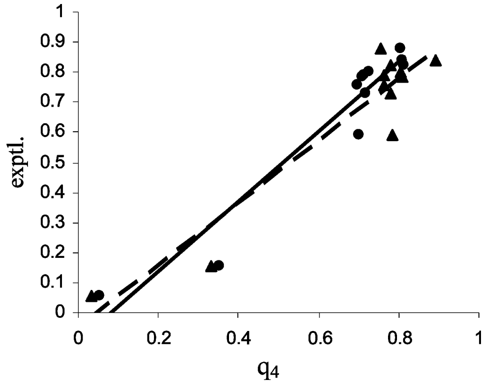

Figure 6. Correlation between the experimental and calculated dipole moment charges (q_4) using Allred−Rochow (dashed line, ▲, $R^2 = 0.8941$) and new (filled line, ●, $R^2 = 0.9196$) scales.

Conclusion

By considering a Morse-like function for $E(N)$, and calculating the electrophilicities of some atoms and molecules, a new scale of electronegativity is introduced based on these electrophilicities; which is not achieved when a parabola model approximation is used. This scale is strongly linked with Allred−Rochow and Pauling electronegativities. It also obeys Sanderson's electronegativity equalization principle and all of the other fundamental rules which are introduced for an acceptable scale of electronegativity. This fact suggests that the new scale is theoretically reasonable. It is shown that for those molecules which have the same number of atoms, the ratio of the change in the electronegativities during the formation of the molecules from their elements to the molecular electronegativities ($\Delta\chi/\chi_\omega$) is the same. The obtained atomic electronegativity values also successfully determine the bond character of diatomic molecules, and it is expected that they can be used in predicting the other molecular properties such as bond dissociation energy and heat of formation of molecules.

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