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Electronegativity and Static Electric Dipole Polarizability of Atomic Species. A Semiempirical Relation†

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A quantitative relation between the static electric dipole polarizability (α) and the electronegativity of an atomic species is developed semiempirically. It emerges that the quantity $(q + 1)(1/\alpha)^{1/3}$ can be used as a new measure of the electronegativity of an atomic species with charge $q \geq 0$ quite effectively.

The static electric dipole polarizability (hereafter referred to simply as the polarizability), α, is a measure of the linear response of the electronic cloud of a chemical species to a weak external electric field. This property, which can be determined theoretically and experimentally in various ways, is used extensively in physics to understand a number of phenomena.[1] But its potential use in chemistry has not been exploited properly. Before 1990, the only meaningful application of α in chemistry was probably the development of Rittner's model for understanding the bonding in some singly bonded diatomic molecules in terms of ionic polarizabilities.[2−4] This is because in the past the chemists have always thought of α as a more physical than chemical quantity.[5] In 1990, for the first time, Nagle correlated polarizability with one of the most important concepts in chemistry, which is electronegativity.[6] Subsequently several reports have appeared exploring the relevance of polarizability in chemistry.[7−11] Nagle has demonstrated that for a neutral atom the quantity $(n/\alpha)^{1/3}$ where n is the number of valence electrons (only the outermost s and p electrons are counted), can be used as a measure of its electronegativity, χ. He has found that $(n/\alpha)^{1/3}$ correlates very nicely with the other existing atomic electronegativity scales. However, his work is empirical and moreover restricted to neutral atoms only.[6] Herein we try to examine the relation between α and χ for neutral and ionized atoms quantitatively. All the quantities appearing in the various equations here are expressed in au.

In the statistical theory of atoms, the Fermi−Amaldi model relates the radius r of a monoatomic ion to its chemical potential μ by eq 1.[12] In eq 1, Z is the atomic number and N the number

$$\mu = -(Z - N + 1)/r = -(q + 1)/r \qquad (1)$$

of electrons in the ion under consideration. The charge q on the ion is given by $Z - N$. From the density functional theory,[13] it emerges that $\mu = -\chi$ and hence

$$\chi = (q + 1)/r \qquad (2)$$

An assumption in deriving eq 1 is that the radius of the ion does not vary with the charge q in the range $q \pm 1$. With the same assumption if one considers the charging energy of a conducting sphere of radius r classically, as described elsewhere,[11,14] one obtains $\chi = q/r$, which is incorrect as this relation would mean that the electronegativity of any neutral atom is zero. In terms of the ionization potential I and electron affinity A, χ of a chemical species is given as $(I + A)/2$, which is Mulliken's definition of electronegativity.[13] Recently Allen has proposed a new experimental measure of electronegativity (χ_{Allen}) for a neutral free atom as the "average one-electron energy of the valence-shell electrons".[15,16] Allen's definition is quite different from Mulliken's as it is evident that for H and the alkali atoms χ_{Allen} is simply equal to I. Still, for neutral atoms, there does exist a very good linear correlation between $(I + A)/2$ and χ_{Allen}.[17] Since, at present, Mulliken's definition is very popular among the theoretical chemists, in this article we shall use $(I + A)/2$ as the experimental measure of the electronegativity. Here we would like to point out that the finite difference approximation of eq 1 using the relation $\mu = -\chi$ also yields Mulliken's formula.

Very recently we have shown semiempirically[11] that for an atomic species $r = (\alpha/0.792)^{1/3}$. Substituting this expression for r in eq 2, we get eq 3. Using eq 3, we have estimated the

$$\chi = 0.925(q + 1)(1/\alpha)^{1/3} \qquad (3)$$

electronegativities of some 133 atoms with q ranging from 0 to 7 (Table S; supplementary material), where the polarizability data are available,[18−22] and compared these with their known experimental electronegativity values obtained from ionization potential and electron affinity data (by Mulliken's definition).[14,23] The χ values calculated via eq 3 are found to be uniformly much higher than the actual ones. Details are in Table S; here just to give an idea of the extent of observed deviation, we only mention that in the case of some 55 open shell neutral atoms studied the average value of $\chi_{calcd}/\chi_{exptl}$ is 1.566 (±0.234). The reasons for this kind of behavior of eq 3 will be clear in a subsequent section.

From the density functional theory, the hardness η of a system is defined as $\delta\mu/2\delta N$.[13] For a monoatomic ion, from eq 1 it then follows

$$\eta = 1/2r \qquad (4)$$

Incidentally, in terms of I and A, $\eta = (I - A)/2$.[13] From eqs 2 and 4, we have

$$(q + 1)\eta/\chi = 0.5 \qquad (5)$$

This is a very important result which means that for an atomic species with charge q, η is proportional to χ and the proportionality constant is $0.5/(q + 1)$. Such proportionality between η and χ was first indirectly and empirically assumed by Parr and Bartolotti[24] for the neutral atoms and molecules in order to prove Sanderson's geometric mean principle for the equalization

† Dedicated to Professor A. Chakravorty on the occasion of his 60th birthday.

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TABLE 1: The Constancy of $(q + 1)\eta/\chi$ for Some Open and Closed Shell Neutral and Ionized Atoms[a]

atom/ion	$(q+1)\eta/\chi$	atom/ion	$(q+1)\eta/\chi$	atom/ion	$(q+1)\eta/\chi$	atom/ion	$(q+1)\eta/\chi$	atom/ion	$(q+1)\eta/\chi$
				a. Open Shell[b]					
H	0.895	Mo	0.795	Mg^{3+}	0.615	I^{+}	0.587	Mo^{3+}	1.043
Li	0.794	Ru	0.667	Al^{4+}	0.616	Sc^{2+}	0.955	Rh^{3+}	1.062
B	0.935	Rh	0.735	Si^{5+}	0.618	Ti^{2+}	1.016	Hf^{3+}	0.707
C	0.797	Pd	0.874	P^{6+}	0.465	V^{2+}	1.000	W^{3+}	0.864
N	0.990	Ag	0.707	S^{7+}	0.621	Cr^{2+}	0.914	Re^{3+}	0.926
O	0.806	In	0.903	Cl^{8+}	0.623	Mn^{2+}	1.097	Os^{3+}	0.852
F	0.673	Sn	0.709	Ar^{9+}	0.624	Fe^{2+}	0.927	Ir^{3+}	0.845
Na	0.807	Sb	0.783	K^{2+}	0.547	Co^{2+}	0.975	Au^{3+}	0.734
Al	0.858	Te	0.641	Ca^{3+}	0.549	Ni^{2+}	0.956	Ru^{3+}	1.092
Si	0.709	I	0.546	Sc^{4+}	0.551	Cu^{2+}	0.869	Be^{+}	0.646
P	0.868	Cs	0.784	Ti^{5+}	0.553	Y^{2+}	0.758	B^{2+}	0.607
S	0.666	La	0.839	V^{6+}	0.555	Zr^{2+}	0.819	C^{3+}	0.591
Cl	0.564	Hf	0.789	Cr^{7+}	0.546	Nb^{2+}	0.817	N^{4+}	0.582
K	0.793	Ta	0.922	Mn^{8+}	0.545	Mo^{2+}	0.765	O^{5+}	0.577
Sc	0.958	W	0.814	Fe^{9+}	0.544	Ru^{2+}	0.777	F^{6+}	0.573
Ti	0.977	Re	0.963	Kr^{+}	0.540	Rh^{2+}	0.792	Mg^{+}	0.652
V	0.861	Os	0.775	Kr^{2+}	0.616	Pd^{2+}	0.773	Al^{2+}	0.610
Cr	0.823	Ir	0.704	Kr^{7+}	0.506	Ag^{2+}	0.713	Si^{3+}	0.593
Mn	1.000	Pt	0.625	Rb^{2+}	0.567	Hf^{2+}	0.660	P^{4+}	0.586
Fe	0.938	Au	0.600	Sr^{3+}	0.533	W^{2+}	0.646	S^{5+}	0.574
Co	0.837	Tl	0.906	Y^{4+}	0.547	Os^{2+}	0.767	Cl^{6+}	0.533
Ni	0.739	Pb	0.905	Nb^{6+}	0.689	Pt^{2+}	0.882	Ar^{7+}	0.572
Cu	0.725	Bi	0.797	Mo^{7+}	0.749	Ce^{3+}	1.163	Ne^{7+}	0.570
Ga	0.906	Li^{2+}	0.709	Zn^{+}	0.626	Ti^{3+}	0.892	C^{+}	0.736
Ge	0.739	Be^{3+}	0.687	Cd^{+}	0.611	V^{3+}	0.915	N^{2+}	0.695
As	0.849	B^{4+}	0.674	Hg^{+}	0.570	Cr^{3+}	0.910	N^{+}	0.683
Se	0.657	C^{5+}	0.666	Ba^{+}	0.630	Mn^{3+}	0.830	Si^{+}	0.669
Br	0.556	N^{6+}	0.660	Co^{+}	0.738	Fe^{3+}	1.131	P^{2+}	0.628
Rb	0.791	O^{7+}	0.656	Rh^{+}	0.832	Co^{3+}	0.840	S^{3+}	0.607
Y	1.000	F^{8+}	0.653	Ir^{+}	0.600	Ni^{3+}	0.880	Cl^{4+}	0.591
Zr	0.882	Ne^{9+}	0.650	Cl^{+}	0.589	Zr^{3+}	0.793	Ar^{5+}	0.578
Nb	0.750	Na^{2+}	0.614	Br^{+}	0.595	Nb^{3+}	0.833	Ar^{+}	0.547
				b. Closed Shell[c]					
Be	0.918	Cu^{+}	0.896	Pb^{2+}	1.080	Ge^{4+}	1.716	Se^{6+}	2.176
Mg	1.040	Ag^{+}	0.958	B^{3+}	2.979	Zr^{4+}	2.036	Cr^{6+}	1.962
Ca	1.818	Au^{+}	0.752	Al^{3+}	2.467	Sn^{4+}	1.396	Mo^{6+}	2.113
Sr	1.850	Tl^{+}	1.079	Ga^{3+}	1.447	Pb^{4+}	1.191	Cl^{7+}	4.049
Ba	1.208	Be^{2+}	2.365	In^{3+}	1.268	N^{5+}	4.193	Mn^{7+}	1.956
Zn	1.110	Mg^{2+}	2.052	Sc^{3+}	1.984	P^{5+}	3.359	Br^{7+}	2.429
Cd	1.076	Ca^{2+}	1.866	Y^{3+}	2.000	V^{5+}	1.952	B^{+}	1.008
Hg	1.128	Sr^{2+}	1.791	La^{3+}	1.781	As^{5+}	2.049	C^{2+}	0.976
Li^{+}	1.733	Zn^{2+}	1.132	Lu^{3+}	1.465	Nb^{5+}	2.039	N^{3+}	0.961
Na^{+}	1.608	Ge^{2+}	1.094	Tl^{3+}	1.032	Sb^{5+}	1.902	O^{4+}	0.953
K^{+}	1.516	Cd^{2+}	1.135	C^{4+}	3.587	Bi^{5+}	1.343	F^{5+}	0.949
Rb^{+}	1.465	Sn^{2+}	1.055	Si^{4+}	2.870	S^{6+}	3.659	Ne^{6+}	0.946
Cs^{+}	1.462	Hg^{2+}	0.872	Ti^{4+}	1.963				

[a] Symbols are explained in the text. Experimental η and χ values are from refs 14 and 23. [b] The average value of $(q + 1)\eta/\chi = 0.742$ (± 0.152). [c] The average value of $(q + 1)\eta/\chi = 1.718$ (± 0.801).

of electronegativity. Later this proportionality was used only as an experimental observation in several works in various contexts.[25-29] However, for monoatomic ions the proportionality implied by eq 5 remains to be shown. Here we have tested it for a number of ionized and neutral atoms where the experimental I and A values are known.[14,23] For some 105 open shell monoatomic cations of various charges (q varying from 1 to 9) and some 55 open shell atoms (Table 1a), the averge value of the quantity $(q + 1)\eta/\chi$ is found to be 0.742 with a standard deviation (σ) of 0.152. Earlier Yang et al. have found that for some 33 open shell neutral atoms the average value of η/χ is 0.775 (± 0.110).[29] On the other hand, for some 63 closed shell neutral and cationic atoms (Table 1b) the average value of $(q + 1)\eta/\chi$ comes out as 1.718 (± 0.801). Nevertheless, in view of our results, for an open shell atomic species we assume the working form of eq 5 to be

$$\chi = (q + 1)\eta/0.742 \tag{6}$$

Using the relation between r and α described in an earlier section, η can be expressed in terms of α as (from eq 4)[11]

$$\eta = {}^1/_2(0.792/\alpha)^{1/3} \tag{7}$$

A combination of eqs 6 and 7 gives us a quantitative relation between χ and α (eq 8). Using eq 8, we have determined the

$$\chi = 0.623(q + 1)(1/\alpha)^{1/3} \tag{8}$$

electronegativity of some 55 open shell neutral atoms (Table 2a) and some 22 open shell monoatomic cations with $q = 1-7$ (Table 2b). Among the neutral atoms, the significant deviants are H and the group IIIA elements; when these deviants are not counted, the average error in reproducing the experimental χ is only 8.6% ($\pm 6.5\%$). In the open shell cationic atoms, the χ values calculated by eq 8 are found to be lower than the experimental ones on the average by 11.7% ($\pm 6.4\%$).

The performance of eq 3 can be understood only with reference to that of eq 7. Earlier we found that eq 7 reproduces the experimental hardness data in a number of open shell atoms

TABLE 2: Calculation of Electronegativities of Some Open Shell Neutral Atoms and Monoatomic Cations by Eq 8 and Comparison with the Experimental Data[a]

atom/ion	α	χ exptl	χ from eq 8	% error	atom/ion	α	χ exptl	χ from eq 8	% error
				a. Neutral Atoms[b]					
H	4.521	0.264	0.377	42.80	Rb	319.190	0.086	0.091	5.81
Li	163.981	0.111	0.114	2.70	Y	153.184	0.117	0.116	0.85
B	20.447	0.158	0.228	44.30	Zr	120.793	0.134	0.126	5.97
C	11.877	0.230	0.273	18.70	Nb	105.947	0.147	0.132	10.20
N	7.423	0.268	0.319	19.03	Mo	86.377	0.143	0.141	1.40
O	5.412	0.277	0.355	28.16	Ru	64.783	0.165	0.155	6.06
F	3.779	0.383	0.400	4.44	Rh	58.034	0.158	0.161	1.90
Na	159.257	0.105	0.115	9.52	Pd	32.391	0.163	0.195	19.63
Al	56.280	0.119	0.163	36.97	Ag	53.176	0.163	0.166	1.84
Si	36.305	0.175	0.188	7.43	In	68.832	0.114	0.152	33.33
P	24.496	0.206	0.214	3.88	Sn	51.961	0.158	0.167	5.70
S	19.570	0.229	0.231	0.87	Sb	44.538	0.178	0.176	1.12
Cl	14.711	0.305	0.254	16.72	Te	37.115	0.202	0.187	7.43
K	292.872	0.089	0.094	5.62	I	33.134	0.248	0.194	21.77
Sc	120.118	0.123	0.126	2.44	Cs	402.193	0.080	0.084	5.00
Ti	98.524	0.127	0.135	6.30	La	209.869	0.114	0.105	7.89
V	83.678	0.132	0.142	7.58	Hf	109.321	0.140	0.130	7.14
Cr	78.279	0.137	0.146	6.57	Ta	88.401	0.151	0.140	7.28
Mn	63.433	0.137	0.156	13.87	W	74.905	0.162	0.148	8.64
Fe	56.685	0.149	0.162	8.72	Re	65.457	0.148	0.155	4.73
Co	50.611	0.158	0.168	6.33	Os	57.360	0.180	0.161	10.55
Ni	45.888	0.162	0.174	7.41	Ir	51.286	0.198	0.168	15.15
Cu	45.247	0.165	0.175	6.06	Pt	43.863	0.206	0.177	14.08
Ga	54.795	0.118	0.164	38.98	Au	39.139	0.212	0.183	13.68
Ge	40.962	0.169	0.181	7.10	Tl	51.286	0.118	0.168	42.37
As	29.085	0.195	0.203	4.10	Pb	45.888	0.143	0.174	21.68
Se	25.441	0.216	0.212	1.85	Bi	49.937	0.172	0.169	1.74
Br	20.582	0.279	0.227	18.64					
				b. Monoatomic Cations[c]					
Be^-	24.70	0.506	0.428	15.41	Cl^{6+}	2.00	3.899	3.461	11.23
B^{2+}	7.92	1.159	0.938	19.07	Ar^{7+}	1.50	4.920	4.354	11.50
C^{3+}	3.50	2.065	1.641	20.53	C^+	6.032	0.655	0.684	4.43
N^{4+}	1.81	3.222	2.556	20.67	N^+	3.718	0.811	0.804	0.86
O^{5-}	1.05	4.631	3.678	20.58	N^{2-}	2.611	1.416	1.357	4.17
F^{6-}	0.65	6.290	5.034	19.97	Si^+	19.635	0.450	0.462	2.67
Mg^-	35.10	0.417	0.380	8.87	P^{2+}	9.581	0.917	0.880	4.03
Al^{2+}	14.40	0.869	0.768	11.62	S^{3+}	5.533	1.509	1.409	6.63
Si^{3+}	9.03	1.445	1.197	17.16	Cl^{4+}	3.576	2.228	2.037	8.57
P^{4+}	4.50	2.139	1.887	11.78	Ar^{5+}	2.429	3.051	2.781	8.85
S^{5+}	2.95	2.953	2.606	11.75	Ar^+	6.714	0.797	0.660	17.19

[a] Polarizability (α) and electronegativity (χ) values are given in au. [b] Sources of data: α, ref 11; exptl χ, ref 14. The average value of the % error is, excluding H and the group IIIA elements, 8.6 (±6.5); including all, 12.0 (±11.6). [c] Sources of data: α, refs 8 and 19; exptl χ, ref 23. The average value of the % error is 11.7 (±6.4).

with $q \geq 0$ very well. A comparison of eq 7 with eq 3 shows that with the same α data, for an open shell neutral atom eq 3 will produce a χ value twice its η value. For an open shell neutral atom, since experimentally the proportionality constant between η and χ comes out as 0.742 instead of the predicted value of 0.5 (see eq 5), the χ value is expected to be only 1.35 times its η value. Thus eq 3 will generate a value of χ which is 2/1.35, i.e., 1.48 times the experimental data for an open shell neutral atom.

The possible reasons for the departure from eq 8 are now discussed. First, in principle r of an atomic species cannot be treated as constant in the range of charge $q \pm 1$, contrary to one of our assumptions in deriving eq 8; but from our previous experience with the evaluation of η by eq 7 where the same assumption is involved, we can say that in reality the variation of r with charge is not likely to play any significant role here. Second, the α values used here are not very accurate. For example, the error involved in the polarizability data for most of the neutral atoms is reported to be 50%.[11] Recently Fricke[30] has tried to correct these data to 20−30%. Since the approach of Fricke is purely empirical, we have chosen not to use his data. The third and probably the most important reason is the constancy of the quantity $(q + 1)\eta/\chi$; as indicated by the magnitude of σ (vide supra), this quantity can be said to be constant only within ±61% (which is 3σ). It can be shown that when the constant is lower than 0.742, eq 8 will give a χ value higher than the experimental one and when the constant is higher than 0.742, the calculated χ will be lower than the actual one.

Though eq 8 is specifically designed for an open shell atomic species, we have applied it to some 56 closed shell neutral and positively charged atoms also (Table 3). Excepting Ca, Sr, and the cations with $1s^2$, $2p^6$, and $3d^{10}$ configurations which are found to deviate most, the experimental χ values are reproduced on the average within 5.8% (±3.7%). This unexpected matching of the χ values calculated by eq 8 with the experimental values in the closed shell cases deserves some comments. Earlier we found that for a closed shell species the hardness calculated by eq 7, from which eq 8 is derived using eq 6, is much lower than the experimental data; this deviation has been attributed to the failure of eq 7 to reveal the "extra" thermodynamic stability of a closed shell system.[11] Here we find that the actual electronegativity of a number of closed shell atomic species is related to the theoretical hardness (yielded by eq 7)

TABLE 3: Calculation of Electronegativities of Some Closed Shell Neutral and Cationic Atoms by Eq 8 and Comparison with the Experimental Data[a]

		χ					χ		
atom/ion	α	exptl	from eq 8	% error	atom/ion	α	exptl	from eq 8	% error
Be	37.790	0.180	0.186	3.33	Y^{3+}	4.048	1.514	1.564	3.20
Mg	71.531	0.138	0.150	8.70	In^{3+}	3.22	1.507	1.688	12.01
Ca	161.282	0.081	0.114	40.74	La^{3+}	7.673	1.270	1.263	0.55
Sr	186.250	0.073	0.109	49.31	Tl^{3+}	5.857	1.481	1.382	6.68
Ba	267.903	0.088	0.097	10.23	C^{4+}	0.009	8.389	14.975	78.51
Zn	42.851	0.163	0.178	9.20	Si^{4+}	0.162	3.894	5.714	46.74
Cd	48.587	0.159	0.171	7.55	Ti^{4+}	1.482	2.618	2.732	4.35
Hg	38.465	0.180	0.185	2.78	Ge^{4+}	0.763	2.558	3.409	33.27
Li^+	0.192	1.489	2.160	45.06	Zr^{4+}	2.977	2.128	2.165	1.74
Na^+	1.002	0.963	1.245	29.28	Sn^{4+}	2.264	2.077	2.372	14.20
K^+	5.339	0.661	0.713	7.87	Pb^{4+}	4.170	2.042	1.935	5.24
Rb^+	9.076	0.579	0.597	3.11	N^{5+}	0.005	11.942	21.860	83.05
Cs^+	15.81	0.533	0.496	6.94	P^{5+}	0.106	5.429	7.898	45.48
Cu^+	5.36	0.515	0.712	38.25	V^{5+}	1.078	3.553	3.646	2.62
Ag^+	8.829	0.534	0.603	11.44	As^{5+}	0.510	3.495	4.679	33.88
Au^+	12.705	0.548	0.534	2.55	Nb^{5+}	2.275	2.814	2.842	0.99
B^+	11.3	0.615	0.555	9.76	Sb^{5+}	1.68	3.013	3.144	4.35
C^{2+}	3.9	1.328	1.187	10.62	Bi^{5+}	3.077	2.651	2.570	3.05
Be^{2+}	0.052	3.162	5.007	58.35	S^{6+}	0.072	6.780	10.483	54.62
Mg^{2+}	0.486	1.749	2.377	35.91	Se^{6+}	0.360	4.357	6.130	40.69
Ca^{2+}	3.193	1.153	1.269	10.06	Cr^{6+}	0.811	4.624	4.676	1.12
Sr^{2+}	5.813	1.003	1.039	3.59	Mo^{6+}	1.789	3.579	3.592	0.36
Zn^{2+}	2.296	1.060	1.417	33.68	Cl^{7+}	0.051	8.498	13.440	58.15
Cd^{2+}	4.971	1.000	1.095	9.50	Mn^{7+}	0.627	5.801	5.823	0.38
Hg^{2+}	8.401	0.974	0.919	5.65	Br^{7+}	0.266	5.435	7.750	42.59
B^{3+}	0.019	5.463	9.339	70.95	Ne	2.672	0.396	0.449	13.38
Al^{3+}	0.265	2.727	3.880	29.72	Ar	11.074	0.290	0.279	3.79
Sc^{3+}	2.129	1.805	1.937	7.31	Kr	16.762	0.257	0.243	5.45
Ga^{3+}	1.24	1.727	2.320	34.34	Xe	27.290	0.223	0.207	7.17

[a] Polarizability (α) and electronegativity (χ) values are given in au. Sources of data: α, refs 11 and 20−22; exptl χ, refs 14, 16, and 23. The average value of the % error is, with Ca, Sr, and the cations with $1s^2$, $2p^6$, and $3d^{10}$ configurations excluded, 5.8 (±3.7); with all included, 20.7 (±22.0).

via eq 6. This only means that the extra thermodynamic stability imparted to an atomic species by a closed shell configuration[11,31] is not reflected in its electronegativity. Such a conclusion is probably new.

It is imperative to compare our electronegativity values calculated by eq 8 with χ_{Allen} for the neutral atoms. For Hg and the first 56 elements (excluding He and Tc) of the Periodic Table where the χ_{Allen} values are available,[16] a strong linear correlation is obtained between the two (Figure 1) when H is not considered via eq 9 with a correlation coefficient of 0.974.

$$0.623(1/\alpha)^{1/3} = 0.026 + 0.384\chi_{Allen} \qquad (9)$$

As expected, eq 9 is numerically essentially similar to that described in ref 17.

We now try to justify Nagle's work[6] within the framework of our approach to the extent possible. We have observed that for some 33 main group elements (including the noble gases) there exists some sort of a linear correlation between $(1/\alpha)^{1/3}$ and $(n/\alpha)^{1/3}$ when H is excluded (eq 10; correlation coefficient = 0.943). Substitution of eq 10 in eq 8 leads to a relation

$$(1/\alpha)^{1/3} = 0.067 + 0.489(n/\alpha)^{1/3} \qquad (10)$$

between $(n/\alpha)^{1/3}$ and χ (eq 11). Thus, our approach shows that

$$\chi = [0.042 + 0.305(n/\alpha)^{1/3}](q + 1) \qquad (11)$$

at least for the main group elements $(n/\alpha)^{1/3}$ can be a measure of electronegativity. Equation 11 allows us to extend Nagle's definition, originally designed for the neutral atoms, to ionized atoms as well. However, the χ values produced by eq 11 for the main group atoms with $q \geq 0$ are less accurate than those obtained from eq 8. And in some of the open shell cations the choice of n is dubious (e.g., for Mg^+, $n = 9$ gives a result considerably better than $n = 1$), which seems to be a genuine problem in Nagle's approach. To highlight this problem, we mention that the transition elements do not conform to eq 10 at

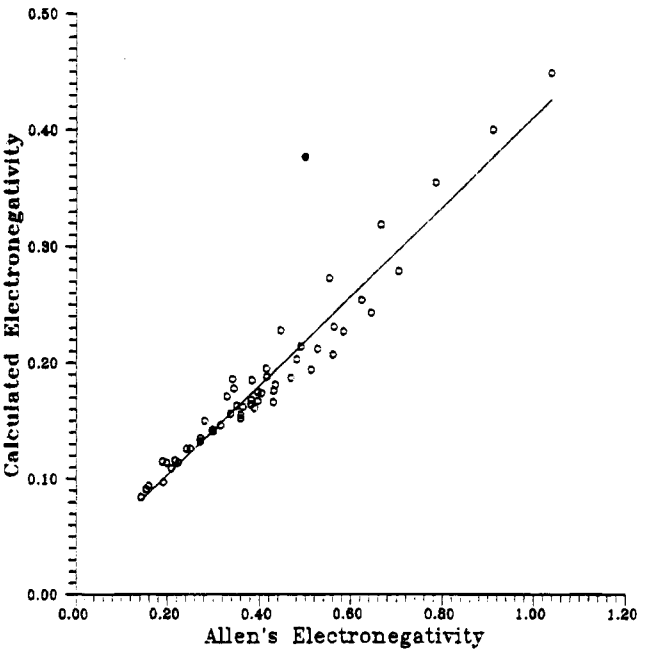

Figure 1. Correspondence between Allen's electronegativity (in au) and our calculated electronegativity (in au; by eq 8) for some 55 neutral atoms. Allen's values are taken from ref 16. For our values, see Tables 2a and 3. The H atom marked by a dark circle is not included in the least squares fit; the correlation coefficient is 0.974.

all with $n = 2$ as arbitrarily set by Nagle. However, for the same set of neutral atoms considered in Figure 1, χ_{Allen} (an experimental scale for the neutral atoms other than that of Mulliken) correlates somewhat better with $(n/\alpha)^{1/3}$ (correlation coefficient = 0.985; calculated by us) than $(1/\alpha)^{1/3}$. Consequently, the preceding discussion of ours on Nagle's scale seems to be valid only to the extent that Mulliken's definition is acceptable as the experimental electronegativity.

In the past, electronegativity of ions has seldom received any attention. This is presumably because with a molecule being electrically neutral with the constituent atoms bearing some amount of fractional charges, the conventional approach has been to start with the electronegativities of the neutral atoms and express them as some function of charge. Stress has been given on characterizing the electronegativity of a neutral atom in the appropriate valence state so that one can have a representation of the atom in a molecule. A widely accepted equation which describes the variation of electronegativity χ of a neutral species with charge q on it is eq 12

$$\chi = \chi^0 + 2\eta^0 q \tag{12}$$

where the superscript 0 specifies the neutral state.[25,32] It should be noted that with $q = \pm 1$, eq 12 does not yield the electronegativity of the corresponding ions. For example, the experimental χ^0 and η^0 of the free Li atom are respectively 0.111 and 0.088 au, and consequently eq 12 predicts the electronegativity of the free Li^+ ion as 0.287 au. while the experimental χ is 1.489 au. This is not at all unexpected. Equation 12, which is only an approximation, is actually derived from the Taylor series expansion around the neutral point $q = 0$.[32] Hence eq 12 is valid only for small values of q. The only method available so far to describe the electronegativity of an ion is the definition given by Mulliken.[33-36] Recently we have shown that the electronegativity of an ionic group can be estimated from the position of Bader's bond critical point in a similarly charged ion containing the group;[27] this approach, however, cannot be applied to a free ion. Here we have demonstrated that the quantity $(q + 1)(1/\alpha)^{1/3}$ can be used as an index of the electronegativity of a monoatomic cation. Obviously our index predicts zero electronegativity for a monovalent anion and negative electronegativity for the multivalent anions. While such predictions may not be chemically too unrealistic for the closed shell anionic atoms, open shell monovalent anions like O^-, S^-, etc. can have definite positive values.[27] Thus, it is not clear how far the proposed index is applicable to negatively charged atoms.

In conclusion, here we have shown that there exists a very simple relation (eq 8) between polarizability and electronegativity for an atomic species. Though the relation is developed specifically for an open shell species, it can be applied to closed shell cases also with some exceptions. Accordingly eq 8 is proposed to be general enough. A rather interesting incidental result obtained here is that theoretically one does expect a proportionality between η and χ at least for an atomic species. However, experimentally it is found to be valid more for the open shell atomic systems with the proportionality constant being numerically a bit different from that predicted theoretically. The most important result of our present study is that the quantity $(q + 1)(1/\alpha)^{1/3}$ can be used to describe the electronegativity of an atom with $q \geq 0$ quite effectively.

Acknowledgment. We are thankful to a reviewer for providing us a copy of ref 22a.

Supplementary Material Available: Table S contains electronegativities calculated by eq 3, the available polarizability data, and known experimental electronegativity values of some 133 atomic species with various charges (6 pages). Ordering information is given on any current masthead page.

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(18) Sources of polarizability data: neutral atoms, ref 11; open shell monoatomic cations, refs 8 and 19; Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}, ref 20; Au^+, Hg^{2+}, Tl^{3+}, Pb^{4+}, and Bi^{5+}, ref 21; B^+ and C^{2+}, ref 22a; other closed shell monoatomic cations, ref 22b.
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