

Atomic and molecular properties from the density-functional definition of electronegativity

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Density-functional theory allows a systematic theoretical approach for quantifying electronegativity of atoms. Here I compare electronegativities of elements from some popular definitions with the corresponding values within the density-functional framework. I propose three new formulae for calculation of binding energy, electric dipole moment and molecular hardness, and have calculated values for several diatomic molecules using density-functional definition of electronegativity. The values in the first two cases are better than those obtained from any other known prescription. I also report improved atomic-hardness values for several neutral atoms, and propose constancy of the ratio of hardness and electronegativity values for atoms belonging to the same group in the periodic table.

Of the various qualitative ideas in chemistry, the concept of electronegativity has been very popular. Although there have been several attempts to obtain electronegativity scales only three of them have been successful in estimating different molecular properties in terms of those electronegativities. These scales have been worked out by Pauling's thermochemical method^{1,2}, Mulliken's method³ of averaging ionization potential and electron affinity, and Allred and Rochow's⁴ scheme from classical Coulomb interactions. A spectroscopic scale has been proposed⁵ recently, in which electronegativity is defined as the average one-electron energy of the valence-shell electrons for the isolated atoms in their ground states. This scale is claimed⁵ to be 'the first quantitative quantum-mechanical realization of Pauling electronegativity scale'. However, most of the above methods are qualitative and empirical in nature. The first attempt at a systematic theoretical approach for calculating electronegativity was in density-functional theory (DFT), where electronegativity (χ) is defined as the negative of the chemical potential (μ)⁶ which is obtained from the Euler-Lagrange equation as^{7,8}

$$\delta E[\rho]/\delta\rho = \mu = -\chi. \quad (1)$$

In equation (1) ρ is the electron density and the energy functional is given by

$$E[\rho] = T[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho], \quad (2)$$

where $v(\mathbf{r})$ is the external potential, and $T[\rho]$ and $E_{xc}[\rho]$ are kinetic and exchange-correlation energy functionals respectively. Equation (1) would be a set of differential equations in the usual Kohn-Sham approach⁹ and may be a single differential¹⁰ or quadratic¹¹ equation depending on whether second- or first-gradient corrections to Thomas-Fermi functional are used for approximating $T[\rho]$ in equation (2).

Electronegativity can be obtained in four different ways: (a) by obtaining μ from a self-consistent solution of equation (1); (b) from the energies of the neutral atom and some of its cations and anions and numerically differentiating the E values with respect to the number of electrons for a constant external (nuclear) potential; (c) by calculating the ionization potential [$I = (E_{\text{cation}} - E_{\text{neutral atom}})$] and the electron affinity [$A = (E_{\text{neutral atom}} - E_{\text{anion}})$] and then applying Mulliken's definition³; and (d) by writing energy as a function of Z and N and analytically differentiating with respect to N , where Z and N are the numbers of protons and electrons respectively.

Considering the popularity of chemical concepts like electronegativity and hardness and their quantification within density-functional theory, what I would like to do in the present paper are the following: (i) to compare the χ values obtained from different methods; (ii) to correlate molecular properties like bond-dissociation energies and dipole moments with density-functional χ ; (iii) to analyse the assumed constancy of the proportionality between η and χ for the elements belonging to the same group in the periodic table; and (iv) to obtain molecular hardness in terms of atomic electronegativities rather than atomic-hardness values.

Method

The differences in electronegativities of the constituent atoms of a diatomic molecule provide estimates of different molecular properties, especially bond energy and dipole moment. There exist a number of relations correlating the bond-dissociation energy and the electronegativity difference. Some of them are the following:

(i) Pauling's geometric-mean relation¹

$$D_{AB} = \bar{D}_{AB} + 30(\Delta\chi)^2, \quad (3)$$

where D_{AB} is the bond-dissociation energy of the

molecule AB, and

$$\bar{D}_{AB} = (D_{AA} \cdot D_{BB})^{1/2} \text{ and } \Delta\chi = \chi_A - \chi_B;$$

(ii) Pauling's arithmetic-mean relation¹

$$D_{AB} = \bar{D}'_{AB} + 23(\Delta\chi)^2, \quad (4)$$

where $\bar{D}'_{AB} = \frac{1}{2}(D_{AA} + D_{BB})$;

(iii) Matcha's relation¹²

$$D_{AB} = \bar{D}_{AB} + 103(1 - \exp(-0.29(\Delta\chi)^2)); \quad (5)$$

(iv) Reddy *et al.*'s relation¹³

$$D_{AB} = \bar{D}_{AB} + 32.058|\Delta\chi|. \quad (6)$$

Equation (6) provides good bond energies using Pauling's electronegativities¹. However, none of the above relations gives satisfactory bond-dissociation energies if one uses the DFT-based electronegativity values⁸. It is worth noting that the Pauling scale of electronegativity has been defined within an atoms-in-a-molecule framework while the absolute electronegativity of density-functional theory is applicable to the overall species (atom, molecule, ion or radical). Although the density-functional definition has been criticized¹⁴ for creating unnecessary confusion it is believed¹⁵ that the confusion and misunderstanding can be avoided if one can keep track of which electronegativity measure is being considered. To get meaningful estimates for different physicochemical quantities using the DFT-based electronegativity values⁸ I propose a simple relation linear in $|\Delta\chi|$ for estimating bond energies:

$$D_{AB} = \bar{D}_{AB} + 13.28|\Delta\chi|, \quad (7)$$

where the number before $|\Delta\chi|$ includes a conversion factor (eV to kcal mol⁻¹) as in other equations.

An estimate for the electric dipole moment can be obtained from the knowledge of $|\Delta\chi|$ through either of the following relations

$$\mu_{el} = 1.36|\Delta\chi| \quad (8a)$$

$$\text{and } \mu_{el} = 2.76|\Delta\chi| - 0.21(\Delta\chi)^2. \quad (8b)$$

Both equation (7) and equation (8) are obtained through least-square fitting of the available data¹⁶⁻¹⁸. It is worth mentioning that these expressions may lead to erroneous results¹⁹ because they take care of only ionic-bond moments whereas the molecular dipole moment comprises two other important contributions, *viz.* moments arising out of hybridization of lone pairs and differences in size of the constituent atoms.

The chemical hardness (η) has been defined as²⁰

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v = -\frac{1}{2} \left(\frac{\partial \chi}{\partial N} \right)_v, \quad (9)$$

and has been calculated⁸ for several atoms and their ions from a self-interaction-corrected and correlated density-functional calculation and making use of the following three-point finite-difference approximation for the second derivative in equation (9) to get

$$\eta = \frac{E_{N+1} - 2E_N + E_{N-1}}{2(\Delta N)^2} = \frac{1}{2}(I - A). \quad (10)$$

In this paper I modify equation (10) by using a five-point central-difference formula to get

$$\begin{aligned} \eta^{\text{modified}} &= \left[-\frac{1}{12}(E_{N+2} + E_{N-2}) + \frac{4}{3}(E_{N+1} + E_{N-1}) - \right. \\ &\quad \left. \frac{5}{2}E_N \right] / 2(\Delta N)^2 \\ &= \frac{1}{12}[16\eta + \chi^- - \chi^+], \end{aligned} \quad (11)$$

where χ^+ and χ^- are χ values for monpositive and mononegative ions respectively⁸.

It ought to be emphasized that for the above numerical differentiation to be valid it has to be tacitly assumed that the E -vs- N curve is continuous although it is known²¹ to be a continuous series of straight-line segments. For a system with nonintegral number of electrons a linear interpolation has been prescribed²¹. The rationale for a continuous variation is that²² $E(N)$ is convex for atoms and molecules and accordingly the zero-temperature limit of grand-canonical-ensemble theory for these systems exists. Explicit drawing of the E -vs- N curve for oxygen shows²² that it can be legitimately assumed to be continuous, which validates the use of equation (11).

It has been proposed²³ that η is proportional to χ with the same proportionality constant λ for all atoms. This assumption has a bearing on the concepts of the arithmetic-mean principle for molecular softness²³ and the geometric-mean principle for electronegativity^{24,25}. I have calculated λ values for atoms using η^{modified} from equation (11) and χ values from Goycoolea *et al.*⁸ Making use of the mean principles²³⁻²⁵ and the modified η values from equation (11) molecular hardness can be obtained. I, however, calculate molecular hardness for a number of diatomic molecules (AB) from atomic electronegativities rather than the atomic-hardness values. The following new approximate relation has been used for this purpose:

$$\eta_{AB} = \frac{1.64 \chi_A \chi_B}{\chi_A + \chi_B}, \quad (12)$$

which has been obtained from the consideration of a mean λ value (averaged over the λ values calculated above) for all atoms and the arithmetic average for molecular softness.

Results and discussion

Figure 1 depicts the electronegativities for the elements with atomic numbers 1 through 54 (whatever available) according to various scales discussed above. It is important to note that Pauling's scale is relative because it considers the atoms in molecular environment, whereas Mulliken's scale or density-functional electronegativity values are for free atoms and hence absolute. Accordingly the qualitative trend is similar but the numbers may have large deviations. The sources of errors are also different in different scales. Apart from numerical errors in all calculations there may be intrinsic errors in absolute scales associated with the sources of I and A values in the Mulliken scale and approximations for $E_{xc}[\rho]$ in DFT-based calculations.

Table 1 allows a comparison of estimated bond energies obtained from the above relations using DFT-based electronegativities⁸ (for H atom χ is taken from ref. 24). Values obtained from equation (7) are in good agreement with the experimental bond-dissociation energies¹⁶. The regression coefficients (r^2) and the root-mean-square deviations (σ) from the available experimental results¹⁶ for different equations are respectively as follows. Equation (3): 0.02, 842.00; equation (4): 0.03, 637.08; equation (5): 0.35, 41.95; equation (6): 0.17, 90.35; equation (7): 0.45, 28.60. Although equation (7) produces by far the best results among the popular

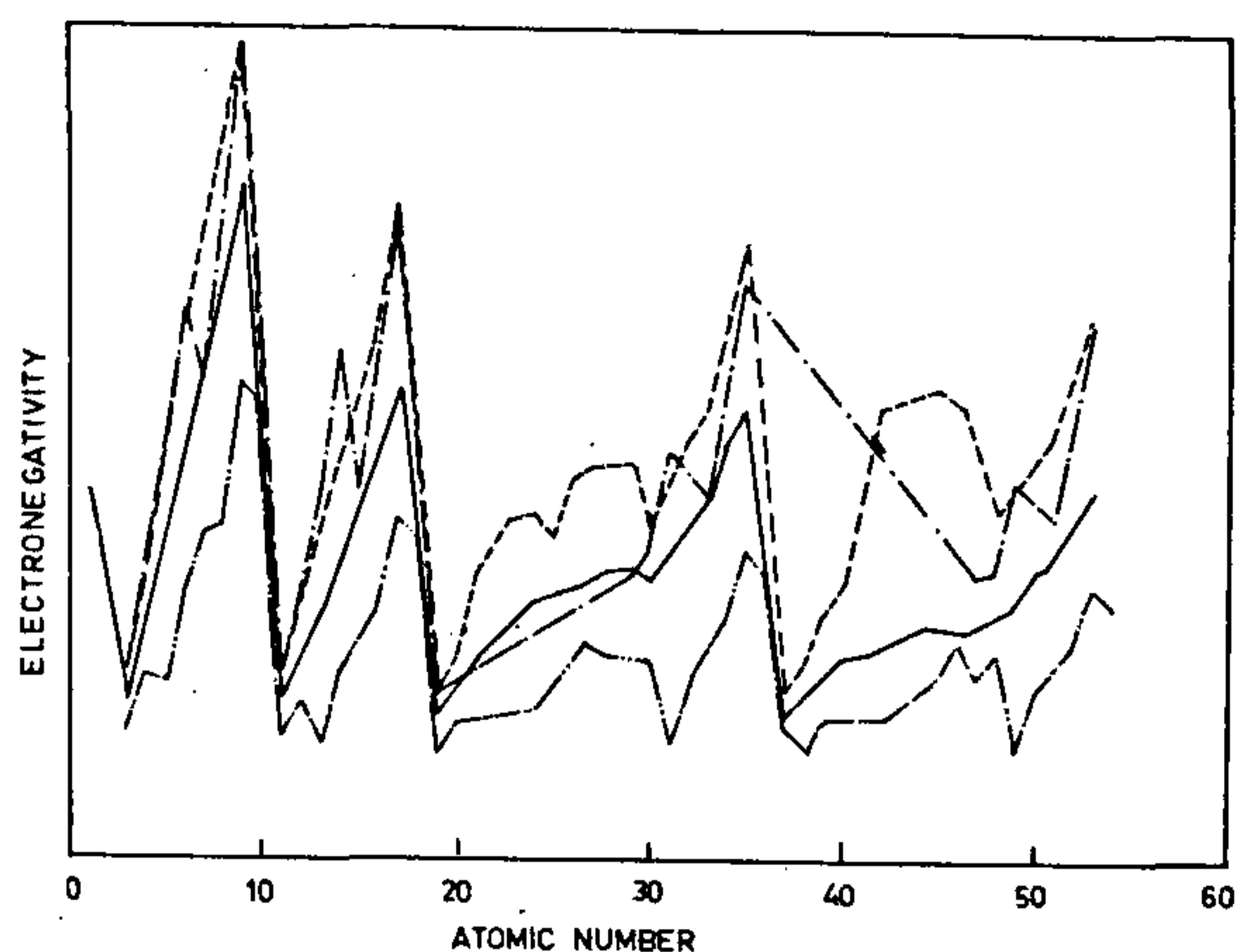


Figure 1. Electronegativity plots for elements with atomic numbers 1 through 54. ----, Pauling values; - · - · - ·, Mulliken values; —, Allred-Rochow values; - - - -, density-functional values. The maximum electronegativity values for the different plots are 3.98 for Pauling, 3.91 for Mulliken, 4.10 for Allred-Rochow and 11.31 for density-functional ($3 \leq Z \leq 54$ is the range for this plot).

prescriptions, it is not very satisfactory, implying that altogether different types of equations are necessary in case one uses the density-functional χ . The electric dipole moment values for several diatomic molecules have also been presented in Table 1. The quadratic fit is marginally better than the linear one. The r^2 and σ

Table 1. Dissociation energies and electric dipole moments for diatomic molecules.

Molecule	D_{AB} (kcal mol ⁻¹)						μ_{el} (Debye)		
	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Ref. 16	Eq. (8a)	Eq. (8b)	Refs. 17, 18
CF	795.99	644.56	175.65	230.15	137.95	130.75	6.68	8.49	-
CO	209.70	191.70	185.33	182.25	151.64	255.79	2.22	3.94	0.117
HBr	70.87	76.16	70.83	77.49	72.23	86.66	0.38	0.76	0.80
HCl	107.46	103.68	103.23	109.23	90.26	102.25	1.37	2.57	1.08
HF	575.96	464.32	164.06	194.50	116.75	135.34	5.63	7.83	1.91
HI	66.96	74.28	66.75	75.36	66.72	70.43	0.63	1.23	0.42
KBr	737.64	576.38	126.11	179.66	88.02	90.17	6.64	8.47	10.62
KCl	970.20	758.37	129.03	205.88	100.54	100.08	7.63	8.87	10.27
KF	2312.56	1781.31	123.93	301.12	137.00	116.92	11.89	8.08	8.59
KI	534.72	417.92	122.82	153.26	75.52	76.33	5.63	7.83	11.05
LiBr	590.40	462.03	135.64	171.28	90.35	99.85	5.86	7.99	7.27
LiCl	799.19	624.88	140.08	198.71	104.07	111.61	6.85	8.57	7.13
LiF	2032.32	1565.76	132.86	291.77	138.35	136.29	11.11	8.53	6.32
LiI	411.64	322.98	129.74	143.74	76.70	81.63	4.86	7.18	6.25
NaBr	603.01	472.27	130.08	167.89	85.64	86.25	5.96	8.06	9.12
NaCl	814.18	637.47	133.76	194.63	98.68	97.55	6.95	8.62	9.00
NaF	2061.70	1588.42	127.77	288.93	134.20	122.91	11.21	8.48	8.16
NaI	421.79	330.83	125.10	141.00	72.64	69.18	4.95	7.26	9.24
RbBr	519.61	409.37	124.82	153.14	76.71	89.94	5.54	7.75	-
RbCl	716.62	564.16	128.29	179.30	89.17	100.08	6.53	8.41	10.52
RbF	1906.98	1470.47	123.43	274.65	125.74	115.30	10.78	8.68	8.55
RbI	352.72	278.48	118.92	126.80	64.27	76.10	4.53	6.86	-
SiC	211.28	191.64	169.82	163.89	128.21	107.00	2.58	4.49	-
SiH	301.31	252.61	177.41	173.04	122.90	70.56	3.63	5.87	-
SiO	167.29	382.60	193.69	206.63	140.34	190.48	4.80	7.13	-
SH	138.32	129.84	132.50	137.28	116.63	81.86	1.50	2.78	-
OH	132.58	127.63	130.27	137.96	121.81	101.28	1.17	2.22	-
CH	139.41	136.87	137.90	146.31	131.85	79.90	1.05	2.00	-

values for equations (8a) and (8b) are respectively as follows: 0.43, 3.00; 0.69, 2.15.

Table 2 presents the modified hardness values for 53 atoms while Figure 2 depicts the plot of λ for different atoms ($1 \leq Z \leq 56$). It is clear that λ remains more or less constant for atoms in the same group in the periodic table. For example, the λ values for Ne, Ar, Kr and Xe are respectively 1.02, 1.04, 1.05 and 1.05, for F, Cl, Br and I 0.57, 0.52, 0.52 and 0.51, and for N, P, As and Sb 0.83, 0.87, 0.85 and 0.80. There are two important consequences of this observation. Constancy of λ [$\equiv (\partial^2 E/\partial N^2)/(\partial E/\partial N)$] implies that the atomic

Table 2. Improved hardness values (eV) for neutral atoms.

Atom	Hardness (eV)		Atom	Hardness (eV)	
	Ref. 8	Eq. 11		Ref. 8	Eq. 11
Li	2.53	2.51	Zn	4.64	4.80
Be	4.51	4.69	Ga	2.54	2.44
B	3.74	3.52	Ge	3.01	2.90
C	4.69	4.43	As	4.22	4.25
N	6.54	6.42	Se	3.52	3.44
O	5.69	5.46	Br	3.98	3.90
F	6.72	6.43	Kr	6.76	7.07
Ne	11.01	11.22	Rb	0.94	0.76
Na	2.38	2.35	Sr	2.93	3.08
Mg	3.79	3.97	Y	2.53	2.56
Al	2.45	2.33	Zr	2.85	2.90
Si	3.03	2.89	Nb	3.01	3.06
P	4.53	4.54	Mo	3.12	3.17
S	3.81	3.70	Tc	3.02	3.04
Cl	4.41	4.28	Ru	3.19	3.22
Ar	7.62	7.93	Rh	3.33	3.38
K	1.98	1.98	Ag	3.12	3.12
Ca	2.80	2.90	Cd	3.69	3.74
Sc	3.12	3.23	In	2.35	2.26
Ti	3.11	3.19	Sn	2.74	2.65
V	3.26	3.33	Sb	3.72	3.75
Cr	3.40	3.47	Te	3.12	3.06
Mn	3.37	3.43	I	3.48	3.42
Fe	2.74	2.68	Xe	5.93	6.23
Co	2.92	2.85	Cs	1.72	1.71
Ni	3.78	3.92	Ba	2.50	2.59
Cu	4.22	4.44			

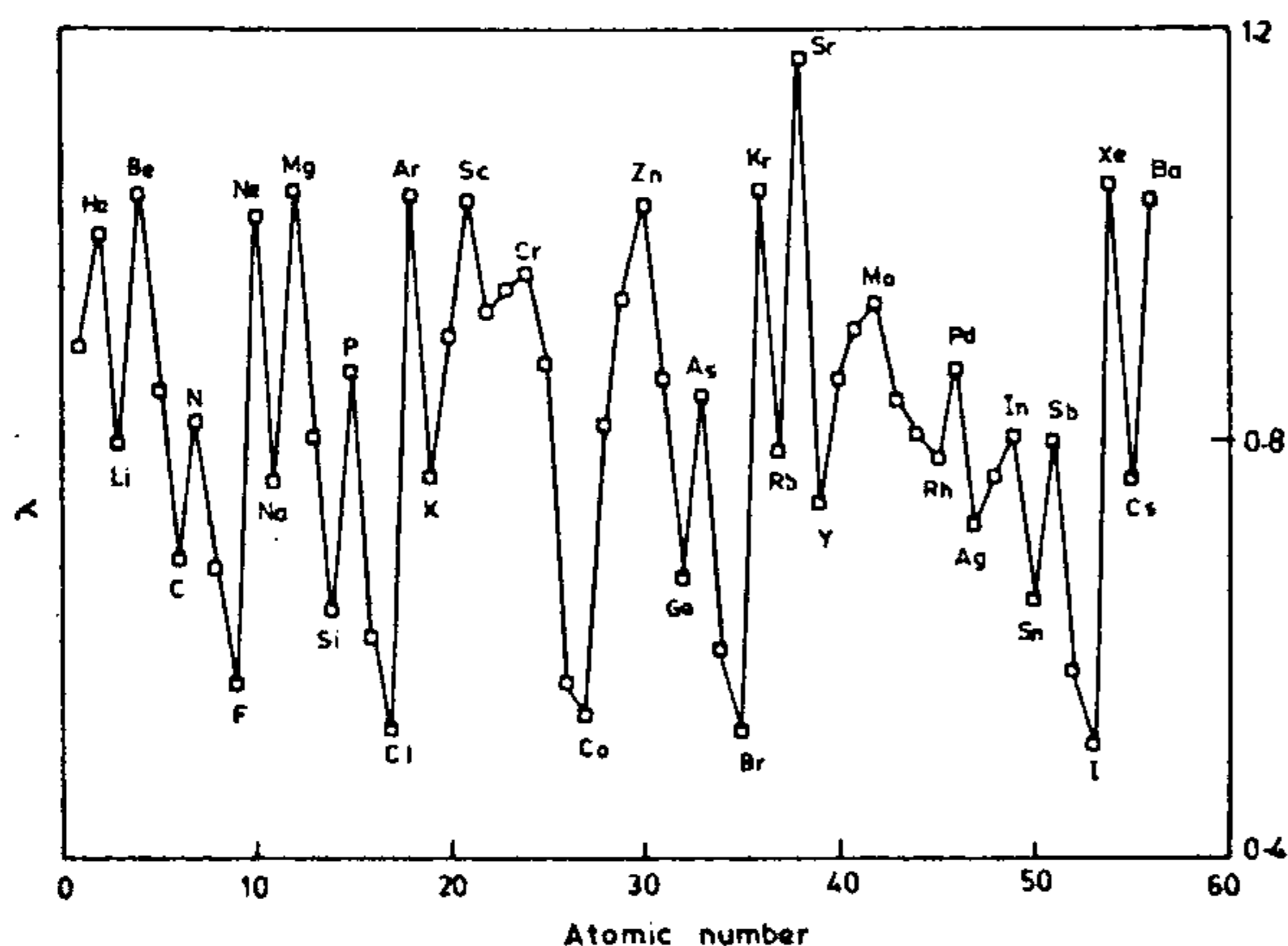


Figure 2. Plot of λ values vs atomic numbers ($1 \leq Z \leq 56$).

energy can be approximated as an exponentially decaying function of the number of electrons, with different exponents for different groups in the periodic table. This would be important for a better understanding of the electronegativity equalization principle. On the other hand, a simple componendo and dividendo argument with a constant λ [$\equiv (I-A)/(I+A)$] implies the corresponding constancy for the (I/A) ratio. Leaving the first-group elements and considering the problems associated with the determination of A values it is gratifying to note the near-constancy of the (I/A) values; e.g., for F, Cl, Br, I, the values are 5.12, 3.58, 3.51, 3.42; for O, S, Se, Te 9.31, 4.99, 4.82, 4.57; and for Li, Na, K, Rb, Cs 8.69, 9.34, 8.68, 8.53, 8.28.

Electropositive and electronegative elements will have different λ values, which is in conformity with chemical intuition. Another, counter-intuitive fact is that the average principles²³ for molecular χ and η dictate the same molecular chemical potential and hardness values for all the isomers of a molecule with the same molecular formula. However, one can use an average λ value for 'estimating' molecular hardness. An apparently unphysical λ value for the Rb atom indicates that there may be something wrong in the evaluation⁸ of χ for this atom. Values for the Rb atom and for other atoms not reported in ref. 8 have been taken from Parr and Bartolotti²⁴. The average λ value refers to

Table 3. Molecular hardness values for diatomic molecules.

Molecule	η (eV)	
	Eq. (12)	Ref. 23
CF	6.70	
CO	5.84	
HBr	5.99	
HCl	6.27	
HF	7.20	
HI	5.68	
KBr	3.13	
KCl	3.21	
KF	3.43	
KI	3.05	
LiBr	3.62	
LiCl	3.72	
LiF	4.03	
LiI	3.51	
NaBr	3.57	
NaCl	3.66	
NaF	3.96	
NaI	3.45	
RbBr	3.81	
RbCl	3.92	
RbF	4.27	
RbI	3.69	
SiC	4.33	
SiH	4.53	
SiO	4.73	
SH	5.39	
OH	6.21	6.24
CH	5.55	5.62

expression (12) for the hardness of diatomic molecules in terms of the electronegativities of the constituent atoms rather than their hardness values. The molecular-hardness values for several diatomic molecules (considered in Table 1) have been calculated using equation (12) and have been reported in Table 3. It provides a new method for calculating the η values for diatomic molecules, and the values compare favourably with other calculated values available²³.

In conclusion, I have attempted estimation of different molecular properties from electronegativities, a widely shared goal of chemists, with better electronegativity values, and these show good agreement. I have also reported improved atomic hardness values, which may be used for calculation of other related properties and in developing²⁶ the chemical concept of hardness from a more rigorous footing. The near-constancy of λ values for elements of the same group in the periodic table may lend additional insight into the chemical-structure theory of elements.

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Do objects in friezes of Somnathpur temple (1268 AD) in South India represent maize ears?

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Spindle-shaped structures in the hands of human figures in friezes in the Somnathpur temple (1268 AD) and other Hoysala temples (eleventh to thirteenth centuries AD) of South India have a striking similarity to maize ears, and hence have been viewed as evidence of cultivation of maize in India in pre-Columbian (before 1492 AD) times. This interpretation has implications for the existence of trans-oceanic trade contacts between the Old World and the New World before Columbus. But the basic assumption that maize ears served as the model for

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sculpturing these 'maize-like structures' (MLS) has frequently been questioned. We have compared qualitative and measurable features of MLS of Somnathpur temple with those of maize ears. Our data suggest that MLS at Somnathpur temple do not represent maize ears.

MAIZE is known to have originated in Mexico^{1,2} and then to have spread to the Old World following Columbus' voyage to America in 1492 AD. Nevertheless, a few reports propose that maize was being cultivated in the Old World before Columbus³⁻⁸. These reports have served as a source of the long-standing controversy and 'emotionally charged vehement arguments'² regarding the origin and spread of maize. After a critical analysis, Mangelsdorf² argued that these evidences were not unequivocal and 'there is no tangible evidence of any kind—botanical, archaeological, ethnographic, linguistic, ideographic, pictorial or historical—of the existence of maize in any part of the Old World before 1492 AD'.