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may involve either tetrahedral or planar coordination to O-5, the former usually being preferred by approximately 1.1 kcal/mol. When a hydrogen bond was present between HO-4 and O-5, hydroxyl group HO-2 adopted an "anti-exo-anomeric"[39] orientation, thereby generating a chain of hydrogen bonds extending between HO-2 and O-3, HO-3 and O-4, and HO-4 and O-5. This hydrogen bond pattern led to the lowest energy structures. Alternatively, when HO-5 formed a hydrogen bond with O-4, a network of hydrogen bonds was generated between HO-5 and O-4, HO-4 and O-3, and HO-3 and O-2. This latter situation was less stable (by approximately 1 kcal/mol) than the former pattern and required that HO-2 adopt the "exo-anomeric" orientation.

In the high-energy structure **4n**, O-4 acted as a proton acceptor in hydrogen bonds with both HO-5 and HO-3, generating a three-center hydrogen bond.

Conclusions

The differences between the conformational preferences of **4** and **1**–**3** arise primarily from two factors. Firstly, replacement of O-6 by a methylene group subtly alters the ring geometry, and, secondly, the absence of the exo-anomeric effect changes the geometrical preferences of HO-2. In **4** the preference for HO-2 to adopt an "anti-exo-anomeric" orientation is attributable to the lack of an exo-anomeric effect as well as to the presence of an interaction between HO-2 and O-3.

In each of the sweet compounds, **1**, **3**, and **4**, low-energy conformations were found to exist in which HO-2 was hydrogen bonded to O-3. This anti-exo-anomeric orientation of HO-2 was less favored energetically in the case of the less sweet sugar **2**. While hydroxyl group HO-2 traditionally is believed to act as a proton donor in a hydrogen bond with the sweet receptor, previous work by us[13] has suggested that HO-2 may function as a proton acceptor (see also ref 40). As such, it must be capable of adopting orientations in which the hydroxyl proton is directed away from the proton-donor functionality of the receptor. On the basis of the geometry of the tripartite receptor,[41] HO-2 might act most effectively as a proton acceptor when it adopts an anti-exo-anomeric orientation. Thus, the ability of HO-2 to adopt an anti-exo-anomeric orientation may be related to the strength of the binding between the sweet molecule and the sweet receptor, and hence, may be pertinent to the sweetness of the molecule.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for the award of grants (to W.A.S. and V.H.S.) and a scholarship (to R.J.W.).

Registry No. **1**, 7660-25-5; **2**, 470-15-5; **3**, 82945-01-5; **4**, 115225-55-3.

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(39) In a pseudosugar there is no ring-oxygen atom, and the terms anti-exo-anomeric and exo-anomeric are used simply for ease of comparison between **4** and the other structures.

(40) Woods, R. J.; Khalil, M.; Pell, W.; Moffat, S. H.; Smith, V. H., Jr. *J. Comput. Chem.* **1990**, *11*, 297–310.

(41) (a) Kier, L. B. *J. Pharm. Sci.* **1972**, *61*, 1394–1397. (b) Shallenberger, R. S.; Lindley, M. G. *Food Chem.* **1977**, *2*, 145–153.

Atomic Polarizability and Electronegativity

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Abstract: A close relationship between atomic polarizability and electronegativity is demonstrated. It is shown how atomic polarizability can be used in conjunction with the number of s and p valence electrons to derive electronegativities interpreted as either valence electron densities or the electrostatic force exerted on valence electrons. This leads to a new set of electronegativities for every element in the periodic table that can be easily calculated and understood. Such values are in substantially better agreement with traditional Pauling values than those derived as the average of ionization energy and electron affinity. It is further demonstrated that traditional or chemical electronegativities are more closely related to the density functional definition of hardness than to the corresponding definition of electronegativity. This approach offers promise to ongoing theoretical efforts to delineate the role of electronegativity in chemical bonding.

The concept of electronegativity as first proposed by Pauling has become an indispensible tool for all chemists and is also used in physics, biology, and geology.[1] Despite the many variations and extensions of this basic idea, Pauling's original definition as "the power of an atom in a molecule to attract electrons to itself"[1f] continues to find widespread acceptance. Even the actual numerical values are still widely used and cited.[1]

This appeal reflects the continuing efforts of chemists to view matter from a discrete, atomic perspective.[2] To be able to understand properties and reactivities of not only isolated molecules but liquids and solids as well in terms of a single number characteristic of each element is unquestionably useful and attractive. The use of electronegativities to understand bond energy differences is widely appreciated.[1,3] However, there are many other important uses as well. For example, a striking dependence of the superconducting transition temperature on electronegativity is found for both solid elements[4] and the new high-temperature superconductors.[5] Further, the theoretical underpinning recently

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(1) (a) *Electronegativity*; Sen, K. D., Jorgensen, C. K., Eds.; Springer-Verlag: New York, 1987; Structure and Bonding, Vol. 66. (b) Pauling, L.; Herman, Z. S. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 1, Chapter 1. (c) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; 3rd ed.; Harper and Row: New York, 1983; pp 144–160, 845–848. (d) Moeller, T. C. *Inorganic Chemistry: A Modern Introduction*; Wiley: New York, 1982; pp 80–86. (e) Batsanov, S. S. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 684–697; *Usp. Khim.* **1982**, *51*, 1201–1224. (f) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960; Chapter 3. (g) Pauling, L. *General Chemistry*; W. H. Freeman and Company: San Francisco, 1970; pp 182–189. (h) Gordy, W.; Thomas, W. J. O. *J. Chem. Phys.* **1956**, *24*, 439–444. (i) Pritchard, H. O.; Skinner, H. A. *Chem. Rev.* **1955**, *55*, 745–786. (j) Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570–3582.

(2) Strong, L. E. *J. Chem. Educ.* **1971**, *48*, 562–565.

(3) (a) Reddy, R. R.; Rao, T. V. R.; Viswanath, R. *J. Am. Chem. Soc.* **1989**, *111*, 2914–2915. (b) Matcha, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4859–4862. (c) Bratsch, S. G. *Polyhedron* **1988**, *7*, 1677–1685. (d) Myers, R. T. *J. Chem. Educ.* **1979**, *56*, 711–712. (e) For the special case of metal cation solvation, see: Qureshi, P. M.; Varshney, R. K.; Singh, S. B. *J. Chem. Educ.* **1989**, *66*, 903–906.

(4) (a) Luo, Q. G.; Wang, R. Y. *J. Phys. Chem. Solids* **1987**, *48*, 425–430. (b) Ichikawa, S. *J. Phys. Chem. Solids* **1989**, *50*, 931. (c) Balasubramanian, S.; Rao, K. J. *Solid State Commun.* **1989**, *71*, 979–982.

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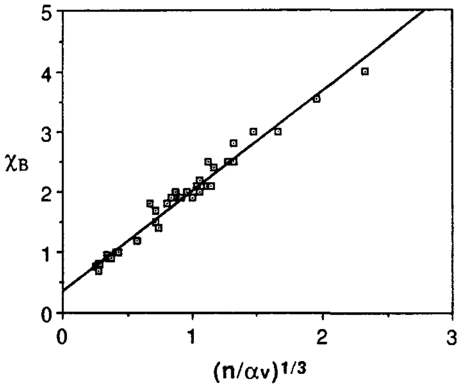

Figure 1. Plot of traditional electronegativities as recommended by Batsanov[1e] (χ_B) versus $(n/\alpha_v)^{1/3}$ (electrons Å^{-1}; see text) for s- and p-block elements.[24] The solid line through the data was calculated with eq 1.

provided by density functional theory in which electronegativity is identified as the negative of the chemical potential[6] has led to renewed interest in the concept.[1a]

Unfortunately, electronegativity—unlike atomic number, mass, ionization energy, or electron affinity—is not a directly measurable experimental property of an isolated atom.[7] In this respect it suffers from the same shortcomings as does the concept of atomic size. In fact, values for both electronegativity[1] and atomic size[8] are usually derived from *molecular* properties by using less than ideal procedures. In order to avoid being more than just elaborate parametrization schemes, more direct approaches based on measurable *atomic* properties would be desirable.

Some efforts to provide values based on experimental measures of atomic properties have been attempted. For example, the definition of electronegativity as the average of the ground-state ionization energy and electron affinity of an atom was first proposed by Mulliken[9] and, according to density functional theory,[6] provides a first approximation to estimating accurate values. Although rough agreement with Pauling's thermochemical values is found,[10] the use of ground-state ionization energies and electron affinities does not lead to the same smooth variation in electronegativies across a row in the periodic table.[10,11] Furthermore, the relative values for hydrogen, oxygen, chlorine, and a few other key elements are not in accord with Pauling's values.[10,11] Recent density functional calculations based on valence-state definitions[11a,12] have gone a long way toward resolving some of these discrepancies but further work needs to be done. And as pointed out elsewhere,[13] close agreement between Pauling and Mulliken values is not to be expected given that Pauling values incorporate "the average effects of hardness" as well as the chemical potential contribution[6] (see below).

Table I. Values of Polarizability Electronegativities (χ_α) Calculated by Using Eq 1 in the Text Along with Electronegativities Derived from Other Approaches for s- and p-Block Elements

Z	element	n^a	$\chi_B{}^b$	$\chi_{AR}{}^c$	$\chi_P{}^d$	$\chi_{spec}{}^e$	$\chi_Z{}^f$	χ_α
1	H	1	2.1	2.20	2.20	2.30	2.27	2.27
2	He	2		5.50		4.20		3.92
3	Li	1	0.95	0.97	0.98	0.91	0.94	0.94
4	Be	2	1.5	1.47	1.57	1.58	1.46	1.55
5	B	3	1.9	2.01	2.04	2.05	1.97	2.02
6	C	4	2.5	2.50	2.55	2.54	2.54	2.56
7	N	5	3.0	3.07	3.04	3.07	3.06	3.12
8	O	6	3.55	3.50	3.44	3.61	3.64	3.62
9	F	7	4.0	4.10	3.98	4.19	4.19	4.23
10	Ne	8		4.84		4.79		4.89
11	Na	1	0.9	1.01	0.93	0.87	0.96	0.95
12	Mg	2	1.2	1.23	1.31	1.29	1.21	1.32
13	Al	3	1.5	1.47	1.61	1.61	1.50	1.55
14	Si	4	1.9	1.74	1.90	1.92	1.77	1.87
15	P	5	2.1	2.06	2.19	2.25	2.13	2.22
16	S	6	2.5	2.44	2.58	2.59	2.48	2.49
17	Cl	7	3.0	2.83	3.16	2.87	2.84	2.82
18	Ar	8		3.20		3.24		3.18
19	K	1	0.8	0.91	0.82	0.73	0.90	0.84
20	Ca	2	1.0	1.04	1.00	1.03	1.03	1.11
31	Ga	3	1.7	1.82	1.81	1.76	1.56	1.56
32	Ge	4	2.0	2.02	2.01	1.99	1.80	1.81
33	As	5	2.0	2.20	2.18	2.21	2.04	2.12
34	Se	6	2.4	2.48	2.55	2.42	2.29	2.31
35	Br	7	2.8	2.74	2.96	2.69	2.53	2.56
36	Kr	8		2.94	3.00	2.97		2.82
37	Rb	1	0.8	0.89	0.82	0.71	0.89	0.83
38	Sr	2	1.0	0.99	0.95	0.96	1.00	1.06
49	In	3	1.8	1.49	1.78	1.66	1.45	1.52
50	Sn	4	1.8	1.72	1.80	1.82	1.58	1.70
51	Sb	5	1.9	1.82	2.05	1.98	1.76	1.88
52	Te	6	2.1	2.01	2.10	2.16	1.94	2.08
53	I	7	2.5	2.21	2.66	2.36	2.14	2.27
54	Xe	8		2.40	2.60	2.58		2.46
55	Cs	1	0.75	0.86	0.79		0.89	0.80
56	Ba	2	0.9	0.97	0.89		1.01	0.98
81	Tl	3	1.4	1.44	1.62		1.49	1.59
82	Pb	4	1.9	1.55	1.87		1.56	1.76
83	Bi	5	1.9	1.67	2.02		1.70	1.83
84	Po	6	2.0	1.76	2.00		1.91	1.96
85	At	7	2.2	1.90	2.20		2.05	2.12
86	Rn	8		2.06				2.28
87	Fr	1	0.7	0.86	0.70		0.88	0.83
88	Ra	2	0.9	0.97	0.90		0.96	0.99

[a] Number of s and p valence electrons. [b] Reference 1e. [c] References 1c, 26a. [d] References 1, 28. [e] Reference 25b. [f] Reference 26d.

The static electric dipole polarizability[14] (for convenience this will be referred to hereafter as simply polarizability) is an experimentally measurable and theoretically calculable property of an isolated atom. In fact, tabulations for virtually every atom in the periodic table are available.[15] Unfortunately, in contrast

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(6) (a) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801–3807. (b) Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631–656. (c) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford: New York, 1989.

(7) Sharpe, A. G. *Inorganic Chemistry*, 2nd ed.; Longman: New York, 1986; pp 128–131.

(8) Mason, J. *J. Chem. Educ.* **1988**, *65*, 17–20. Campbell, J. A. *J. Chem. Educ.* **1989**, *66*, 739–740.

(9) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782–793; **1935**, *3*, 573–585.

(10) (a) Lackner, K. S.; Zweig, G. *Phys. Rev. D* **1987**, *36*, 1562–1569. (b) Liebman, J. F.; Huheey, J. E. *Phys. Rev. D* **1987**, *36*, 1559–1561.

(11) (a) Bohm, M. C.; Schmidt, P. C. *Ber. Bunsenges. Phys. Chem.* **1986**, *90*, 913–919. (b) Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112–118.

(12) (a) Sen, K. D.; Bohm, M. C.; Schmidt, P. C. *Struct. Bond.* **1987**, *66*, 99–123. (b) Schmidt, P. C.; Bohm, M. C.; Weiss, A. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 1330–1340. (c) Schmidt, P. C.; Bohm, M. C. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 925–932. (d) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34–41.

(13) (a) Komorowski, L. *Z. Naturforsch. A* **1987**, *42*, 767–773. (b) Komorowski, L. *Chem. Phys. Lett.* **1983**, *103*, 201–204. (c) Komorowski, L. *Chem. Phys.* **1987**, *114*, 55–71. This reference also contains some important comments about the ambiguities inherent in Pauling's original definition of electronegativity and Sanderson's principle of electronegativity equalization.

(14) (a) Atkins, P. W. *Physical Chemistry*, 3rd ed.; W. H. Freeman and Company: New York, 1986; pp 579–583. (b) Adamson, A. W. *Physical Chemistry*, 3rd ed.; Wiley: New York, 1988; pp 82–85. (c) Barrow, G. M. *Physical Chemistry*, 5th ed.; McGraw-Hill: New York, 1988; pp 655–677. (d) Bowers, W. A. *Am. J. Phys.* **1986**, *54*, 347–350. (e) Ref 1g, pp 395–397. (f) Rich, R. *Periodic Correlations*; Benjamin: New York, 1965; Chapter 4. (g) Syrkin, Y. K.; Dyatkina, M. E. *Structure of Molecules and the Chemical Bond*; translated from the Russian and revised by Partridge, M. A., Jordan, D. O.; Butterworths Scientific Publications: London, 1950; pp 193–200. (h) Rice, O. K. *Electronic Structure and Chemical Bonding*; McGraw-Hill: New York, 1940; pp 171–178. (i) Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1988**, *25*, 37–60.

(15) Miller, T. M. In *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986–1987; pp E66–E70. This source lists both theoretical and experimental values. Empirical calculations with atomic ionization energies have also been helpful in establishing reliable polarizability values. See: Fricke, B. *J. Chem. Phys.* **1986**, *84*, 862–866; Dmitrieva, I. K.; Plindov, G. I. *J. Appl. Spectrosc.* (*Engl. Transl.*) **1986**, *44*, 4–9; *Zh. Prikl. Spekt.* **1985**, *44*, 11–16.

to the other measurable atomic properties mentioned above, these values have been greatly under-appreciated and under-utilized by chemists.[16] For example, discussions of atomic polarizabilities rarely appear in standard introductory or inorganic chemistry textbooks, although some mention of polarizability is found in many physical chemistry[14a-c] and solid state chemistry[17] textbooks. Pauling, recognizing that the dimensions of polarizability correspond to those of volume,[18] used the term "polarizability radius"[19] in referring to the cube root of polarizability. Similarly, Atkins uses the term "polarizability volume"[20] in referring to polarizability in the non-SI units of Å^3. Although polarizabilities can be anisotropic,[15] the values determined along different orientations are similar. In other words, atoms can be considered as approximately spherical in shape.

The use of polarizabilities as a direct experimental measure of atomic size should be encouraged. In fact it has already been shown how these values can be used in conjunction with experimental molar densities to predict the onset of metallic behavior in elements.[21] Briefly, when the ratio of refractivity (polarizability multiplied by $N_A/3\epsilon_0$) to molar volume (molar mass divided by mass density) is greater than one, the element will exhibit metallic properties. Thus the relative volume of an isolated atom compared to that in its condensed form is what determines metallic behavior (electron delocalization or itinerancy).

The primary concern here however is with electronegativity. Although it has been pointed out that there is an inverse relationship between polarizability and electronegativity,[13c,22] a quantitative relationship between the two quantities apparently has not been explored in detail. Since valence electron density[23] has been used successfully as a definition and measure of electronegativity, then some function of the number of valence electrons divided by polarizability, n/α, might be expected to provide a measure of electronegativity. A plot of the cube root of this ratio, $(n/\alpha)^{1/3}$, versus conventional electronegativity values[24] on the Pauling scale is shown in Figure 1 for all s- and p-block elements (except the noble gases). The correlation between the two sets of values is striking, and an unweighted, linear least-squares fit of the data yields the parameters given in eq 1 where χ_α represents electronegativities on the Pauling scale as derived from polarizabilities. A tabulation of χ_α values calculated from

$$\chi_\alpha = 1.66(n/\alpha)^{1/3} + 0.37 \qquad (1)$$

eq 1 along with electronegativity values from other sorces is given in Table I. Values for the noble gases obtained from eq 1 with $n = 8$ are in good agreement with previous estimates.[25] Although $(n/\alpha)^{1/3}$ could provide a set of absolute electronegativity values (see below), it is more appropriate at this point to convert these to the widely used Pauling scale.

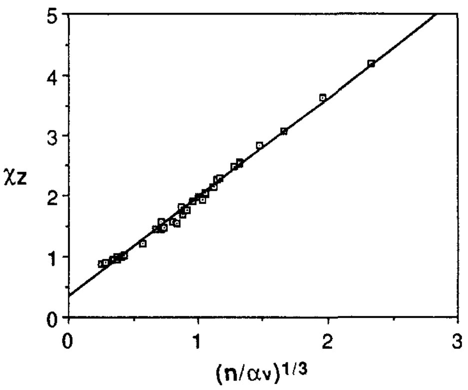

Figure 2. Plot of electronegativities as determined by an electrostatic approach[26d] (χ_Z) versus $(n/\alpha_v)^{1/3}$ for s- and p-block elements (where values for more than one oxidation state of an element are listed in ref 26d, the value for the *lowest* oxidation state is shown in the figure). The solid line through the data was collected by using the equation $\chi_Z = 1.63(n/\alpha)^{1/3} + 0.35$. This equation was determined by a least-squares fit of the data.

A complication arises in determining the number of valence electrons for d- and f-block elements. For example, should all fifteen valence electrons of cadmium or all fifteen of thulium be used in determining valence electron density? A tentative answer comes both from a consideration of common oxidation states and a comparison with values of electronegativity derived for these elements from other approaches.[1,11b,23,26,27] That answer is that for all d- and f-block elements two electrons (i.e. the number of electrons in or easily promoted to the valence s-orbital) can be used for purposes of calculating valence electron densities and (from eq 1) electronegativities on the Pauling scale. This provides good numerical agreement with existing electronegativity values for these elements, although detailed comparisons are difficult

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(16) This comment does not apply to *ionic* polarizabilities (Atkins, P. W. *General Chemistry*; Scientific American Books: New York, 1989. Puddephatt, R. J.; Monaghan, P. K. *The Periodic Table of the Elements*, 2nd ed.; Oxford University Press: New York, 1986; pp 30–31), for which reliable values are now also becoming available: Fowler, P. W.; Tole, P. *Chem. Phys. Lett.* **1988**, *149*, 273–277. Fowler, P. W.; Pyper, N. C. *Proc. R. Soc. London, A* **1985**, *398*, 377–393. Bogdanovich, P.; Vaitiekunas, P. *Sov. Phys. Collect.* (*Engl. Transl.*) **1985**, *25*, 15–23. Johnson, W. R.; Kolb, D.; Huang, K.-N. *At. Data Nucl. Data Tables* **1983**, *28*, 333–340.

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(18) The SI units of atomic polarizability are C^2 m^2 J^{-1} atom^{-1} = F m^2 atom^{-1} as a result of the inclusion of the factor $4\pi\epsilon_0$. See ref 15; ref 14a, p 579; and Forbes (Forbes, R. G. *Surf. Sci.* **1977**, *64*, 367–371) for a discussion of the relationship between SI and non-SI units of polarizability.

(19) Reference 1g, p 395.

(20) Reference 14a, p 579. Actually refractivity, $\alpha/3\epsilon_0$, is more appropriate as a representation of atomic polarizability volume (ref 14a, p 581).

(21) Edwards, P. P.; Sienko, M. J. *J. Chem. Educ.* **1983**, *60*, 691–696; *Int. Rev. Phys. Chem.* **1983**, *3*, 83–137.

(22) (a) Poluektov, N. S.; Meshkova, S. B.; Topilova, Z. M. *Dokl. Chem.* (*Engl. Transl.*) **1986**, *288*, 192–195; *Dokl. Akad. Nauk SSSR* **1986**, *288*, 1125–1129. (b) van Genechten, K. A.; Mortier, W. J.; Geerlings, P. *J. Chem. Phys.* **1987**, *86*, 5063–5071. (c) Murthy, V. R. *Acta Cienc. Indica, Phys.* **1985**, *11*, 94–97.

(23) (a) Gorbunov, A. I.; Kaganyuk, D. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1986**, *60*, 1406–1407; *Zh. Fiz. Khim.* **1986**, *60*, 2336–2338. Gorbunov, A. I.; Filippov, G. G. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1988**, *62*, 974–976; *Zh. Fiz. Khim.* **1988**, *62*, 1909–1912. (b) Sanderson has used the concept of "stability ratio" to devise a scale of electronegativities. Stability ratio is defined as a relative "average electron density" where electron density is determined as a function of Z/r^3 where Z is the nuclear charge and r is a covalent or ionic radius: Sanderson, R. T. *Science* **1951**, *114*, 670–672; *J. Am. Chem. Soc.* **1952**, *74*, 4792–3; *J. Chem. Educ.* **1952**, *29*, 539–544; *J. Chem. Educ.* **1954**, *31*, 2–7, 238–245. *Chemical Bonds and Bond Energy*, 2nd ed.; Academic Press: New York, 1976. *Polar Covalence*; Academic Press: New York, 1983. Sanderson, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 2259–2261; *Inorg. Chem.* **1986**, *25*, 3518–3522; *Inorg. Chem.* **1986**, *25*, 1856–1868; *J. Chem. Educ.* **1988**, *65*, 227–231. A recent attempt has been made to improve upon Sanderson's method: Batsanov, S. S. *Zh. Strukt. Khim.* **1988**, *29*, 167–171. (c) Electronegativity has been defined also as the ratio of the number of valence electrons to Sanderson's covalent radius, and a linear relationship to Pauling's values was found: Yuan, H. C. *Acta Chim. Sin.* **1964**, *30*, 341–347. Recent applications of this definition are discussed in: Luo, Y. R.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 7333–7335 and references therein.

(24) The electronegativity values used in the plot are a set of "best" values from ref 1e. For those elements for which different values for different oxidation states are given in ref 1e, the value for the lowest oxidation was used in the plot, as these best correspond to traditional Pauling values.

(25) (a) The exception is the value derived here for He of 3.9, which is less than that for F. Allen and Huheey give an average of 5.5 for He. Since no stable compounds of He are known it is difficult, if not impossible, to say which value makes most chemical sense. Allen, L. C.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1523–1524. (b) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003–9014.

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Table II. Values of Various Atomic Properties Derived from Polarizabilities[a]

Z	element	α_v	V_α	r_α	n	$\sigma_\alpha \times 10^{21}$	$\eta_\alpha \times 10^{-18}$	μ_α	χ_α
1	H	0.666793	2.793	0.87	1	9.72	102.9	16.48	2.27
2	He	0.204956	0.859	0.59	2	5.21	192.1	30.77	3.92
3	Li	24.3	101.8	2.90	1	32.23	31.0	4.97	0.94
4	Be	5.60	23.5	1.78	2	15.68	63.8	10.22	1.55
5	B	3.03	12.7	1.45	3	11.16	89.6	14.35	2.02
6	C	1.76	7.37	1.21	4	8.46	118.2	18.93	2.55
7	N	1.10	4.61	1.03	5	6.72	148.9	23.85	3.12
8	O	0.802	3.36	0.93	6	5.69	175.8	28.16	3.62
9	F	0.557	2.33	0.82	7	4.79	209.0	33.48	4.23
10	Ne	0.3956	1.66	0.73	8	4.08	244.9	39.23	4.89
11	Na	23.6	98.9	2.87	1	31.92	31.3	5.02	0.95
12	Mg	10.6	44.4	2.20	2	19.40	51.5	8.26	1.32
13	Al	8.34	34.9	2.03	3	15.64	63.9	10.24	1.55
14	Si	5.38	22.5	1.75	4	12.28	81.4	13.05	1.87
15	P	3.63	15.2	1.54	5	10.00	100.0	16.02	2.22
16	S	2.90	12.1	1.43	6	8.73	114.5	18.35	2.49
17	Cl	2.18	9.13	1.30	7	7.54	132.6	21.24	2.82
18	Ar	1.6411	6.87	1.18	8	6.56	152.4	24.42	3.18
19	K	43.4	181.8	3.51	1	39.10	25.6	4.10	0.84
20	Ca	22.8	95.5	2.84	2	25.04	39.9	6.40	1.11
21	Sc	17.8	74.6	2.61	2	23.06	43.4	6.95	1.17
22	Ti	14.6	61.2	2.44	2	21.58	46.3	7.42	1.23
23	V	12.4	51.9	2.31	2	20.44	48.9	7.84	1.27
24	Cr	11.6	48.6	2.26	2	19.99	50.0	8.01	1.29
25	Mn	9.4	39.4	2.11	2	18.64	53.7	8.60	1.36
26	Fe	8.4	35.2	2.03	2	17.95	55.7	8.92	1.40
27	Co	7.5	31.4	1.96	2	17.29	57.8	9.27	1.44
28	Ni	6.8	28.5	1.89	2	16.73	59.8	9.58	1.47
29	Cu	6.1	25.6	1.83	2	16.14	62.0	9.93	1.51
30	Zn	7.1	29.7	1.92	2	16.97	58.9	9.44	1.46
31	Ga	8.12	34.0	2.01	3	15.51	64.5	10.33	1.56
32	Ge	6.07	25.4	1.82	4	12.79	78.2	12.53	1.81
33	As	4.31	18.1	1.63	5	10.59	94.4	15.13	2.11
34	Se	3.77	15.8	1.56	6	9.53	104.9	16.81	2.31
35	Br	3.05	12.8	1.45	7	8.44	118.6	18.99	2.56
36	Kr	2.4844	10.4	1.35	8	7.53	132.7	21.26	2.82
37	Rb	47.3	198.1	3.62	1	40.24	24.9	3.98	0.83
38	Sr	27.6	115.6	3.02	2	26.69	37.5	6.00	1.06
39	Y	22.7	95.1	2.83	2	25.00	40.0	6.41	1.11
40	Zr	17.9	75.0	2.62	2	23.10	43.3	6.94	1.17
41	Nb	15.7	65.8	2.50	2	22.11	45.2	7.25	1.21
42	Mo	12.8	53.6	2.34	2	20.66	48.4	7.76	1.26
43	Tc	11.4	47.8	2.25	2	19.88	50.3	8.06	1.30
44	Ru	9.6	40.2	2.13	2	18.77	53.3	8.54	1.35
45	Rh	8.6	36.0	2.05	2	18.09	55.3	8.86	1.39
46	Pd	4.8	20.1	1.69	2	14.90	67.1	10.76	1.61
47	Ag	7.2	30.2	1.93	2	17.05	58.6	9.40	1.45
48	Cd	7.2	30.2	1.93	2	17.05	58.6	9.40	1.45
49	In	9.1	38.1	2.09	3	16.11	62.1	9.95	1.52
50	Sn	7.7	32.3	1.97	4	13.84	72.2	11.58	1.70
51	Sb	6.6	27.6	1.88	5	12.21	81.9	13.13	1.88
52	Te	5.5	23.0	1.77	6	10.81	92.5	14.82	2.08
53	I	4.7	19.7	1.68	7	9.74	102.6	16.44	2.27
54	Xe	4.044	16.9	1.59	8	8.86	112.8	18.08	2.45
55	Cs	59.6	249.7	3.91	1	43.46	23.0	3.69	0.79
56	Ba	39.7	166.3	3.41	2	30.13	33.2	5.32	0.98
57	La	31.1	130.3	3.14	2	27.77	36.0	5.77	1.04
58	Ce	29.6	124.0	3.09	2	27.32	36.6	5.86	1.05
59	Pr	28.2	118.1	3.04	2	26.88	37.2	5.96	1.06
60	Nd	31.4	131.5	3.15	2	27.86	35.9	5.75	1.03
61	Pm	30.1	126.1	3.11	2	27.47	36.4	5.83	1.04
62	Sm	28.8	120.6	3.07	2	27.07	36.9	5.92	1.05
63	Eu	27.7	116.0	3.03	2	26.72	37.4	6.00	1.06
64	Gd	23.5	98.4	2.86	2	25.30	39.5	6.33	1.10
65	Tb	25.5	106.8	2.94	2	25.99	38.5	6.16	1.08
66	Dy	24.5	102.6	2.90	2	25.65	39.0	6.25	1.09
67	Ho	23.6	98.9	2.87	2	25.33	39.5	6.32	1.10
68	Er	22.7	95.1	2.83	2	25.00	40.0	6.41	1.11
69	Tm	21.8	91.3	2.79	2	24.67	40.5	6.49	1.12
70	Yb	21.0	88.0	2.76	2	24.36	41.0	6.58	1.13
71	Lu	21.9	91.7	2.80	2	24.71	40.5	6.48	1.12
72	Hf	16.2	67.9	2.53	2	22.35	44.8	7.17	1.20
73	Ta	13.1	54.9	2.36	2	20.82	48.0	7.70	1.26
74	W	11.1	46.5	2.23	2	19.70	50.8	8.13	1.31
75	Re	9.7	40.6	2.13	2	18.83	53.1	8.51	1.35
76	Os	8.5	35.6	2.04	2	18.02	55.5	8.89	1.39
77	Ir	7.6	31.8	1.97	2	17.36	57.6	9.23	1.43

Table II (Continued)

Z	element	α_v	V_α	r_α	n	$\sigma_\alpha \times 10^{21}$	$\eta_\alpha \times 10^{-18}$	μ_α	χ_α
78	Pt	6.5	27.2	1.87	2	16.48	60.7	9.72	1.49
79	Au	5.8	24.3	1.80	2	15.87	63.0	10.10	1.53
80	Hg	5.7	23.9	1.79	2	15.78	63.4	10.16	1.54
81	Tl	7.5	31.4	1.96	3	15.10	66.2	10.61	1.59
82	Pb	6.8	28.5	1.89	4	13.28	75.3	12.07	1.76
83	Bi	7.4	31.0	1.95	5	12.68	78.9	12.64	1.83
84	Po	6.8	28.5	1.89	6	11.60	86.2	13.81	1.96
85	At	6.0	25.1	1.82	7	10.57	94.6	15.16	2.12
86	Rn	5.3	22.2	1.74	8	9.70	103.1	16.52	2.27
87	Fr	48.7	204.0	3.65	1	40.63	24.6	3.94	0.82
88	Ra	38.3	160.4	3.37	2	29.77	33.6	5.38	0.99
89	Ac	32.1	134.5	3.18	2	28.07	35.6	5.71	1.03
90	Th	32.1	134.5	3.18	2	28.07	35.6	5.71	1.03
91	Pa	25.4	106.4	2.94	2	25.96	38.5	6.17	1.08
92	U	27.4	114.8	3.01	2	26.62	37.6	6.02	1.06
93	Np	24.8	103.9	2.92	2	25.75	38.8	6.22	1.09
94	Pu	24.5	102.6	2.90	2	25.65	39.0	6.25	1.09
95	Am	23.3	97.6	2.86	2	25.22	39.6	6.35	1.10
96	Cm	23.0	96.3	2.84	2	25.11	39.8	6.38	1.11
97	Bk	22.7	95.1	2.83	2	25.00	40.0	6.41	1.11
98	Cf	20.5	85.9	2.74	2	24.17	41.4	6.63	1.13
99	Es	19.7	82.5	2.70	2	23.85	41.9	6.72	1.14
100	Fm	23.8	99.7	2.88	2	25.40	38.4	6.31	1.10
101	Md	18.2	76.2	2.63	2	23.23	43.0	6.90	1.17
102	No	17.5	73.3	2.60	2	22.93	43.6	6.99	1.18

[a] The symbols and units used are from Table II.

owing to the poor agreement among the existing values.[1,11b,23,26,27] Thus the values of χ_α for the d- and f-block elements calculated from eq 1 and listed in Table II should be considered provisional. It is likely that a better measure of the number of "valence" electrons for these elements could be determined from a careful analysis of their atomic spectra. Encouragingly, the expected ordering[26c,d] of electronegativities as Mn < Fe < Co < Ni < Cu (Table II) is found by using a constant value of $n = 2$ in eq 1 for these elements.

Related to this difficulty with d- and f-block elements is the use of different electronegativity values for different oxidation states of an atom.[1,23,26,27] To illustrate, values of 1.62 for Tl(I) and 2.04 for Tl(III) have been used to account for the fact that TlCl, for example, is much more ionic than $TlCl_3$.[28] While it would be possible to derive values of $1.66(1/\alpha)^{1/3} + 0.37 = 1.21$ for Tl(I) and $1.66(3/\alpha)^{1/3} + 0.37 = 1.59$ for Tl(III), such an approach[1c,23,27a,28,29] loses the original simplicity and attraction of having a single number for each atom to account for such differences. An alternative approach is to use group negativities.[11a,23c,30] For example, the ionic character of the bond in TlCl would be related to the difference between the atomic electronegativities of Tl and Cl. For $TlCl_3$ on the other hand it would be related to the difference between the group electronegativity of $TlCl_2$ and the atomic electronegativity of Cl. Since the group electronegativity of $TlCl_2$ would have some value between the atomic values for Tl and Cl (a result of the electronegativity equalization principle[1c,11a,23b,30e,31]), it would yield a smaller ionic contribution to the Tl–Cl bonding in $TlCl_3$ as compared to TlCl.

Note how the polarizability approach to electronegativity can be interpreted not only in terms of valence electron density but also in terms of the electrostatic force exerted by a nucleus on its valence electrons, Z_{eff}/r^2, where Z_{eff} is the effective nuclear charge of an atom and r is its radius.[1,26,27g] Since polarizability is a measure of size, and since the number of valence electrons for s- and p-block elements also happens to equal the core charge of an atom, the two approaches are seen to be conceptually similar. In fact, excellent correlations between $(n/\alpha)^{1/3}$ and electronegativities derived from this electrostatic approach[1h,26] are found and illustrated in Figure 2.[32] Furthermore, a good correlation between Pauling electronegativities and $(Z_{eff}/\alpha)^{1/3}$ is observed when theoretical Z_{eff} values[33] are used. Further work along these lines would be helpful. It is gratifying though that even "controversial" cases like the C–Si–Ge–Sn–Pb electronegativity alternations[34] (as well as the absolute values) are reproduced in a sensible way through the use of polarizabilities and simple assumptions about the number of valence electrons.

What is it about polarizability that leads to such good agreement with Pauling electronegativities? Density functional theory[6] points to electron density as the key parameter from which all other properties are (at least in principle) derived, and this is surely an indication that electron density is somehow related to empirical measures of electronegativity. Further insight into this question is possible if it is assumed that, as mentioned above, Pauling electronegativities as derived thermochemically[3c,28] include not only a chemical potential contribution (as defined by the density functional approach[6]) but the "average effects of hardness"[13a] as well. Polarizability is a very sensitive measure of the accessibility of low-lying, vacant orbitals to population by electrons in filled or partially filled orbitals[14f,35] (and is therefore closely related to

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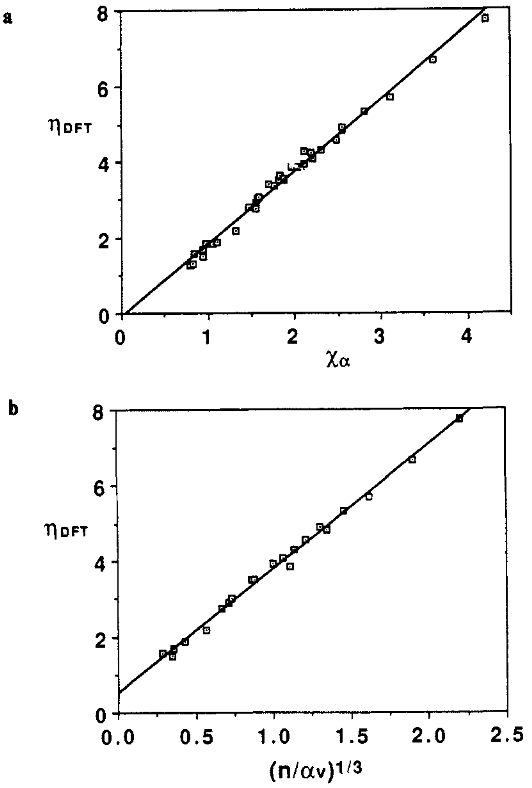

Figure 3. (a) Plot of hardness (eV) as defined and calculated from density functional theory (η_{DFT}; ref 12a) for s- and p-block elements versus values of χ_α calculated from eq 1. (b) Plot of hardness (eV) versus $(n/\alpha_v)^{1/3}$ (electrons Å^{-1}) where both α_v and η_{DFT} are calculated from density functional theory (ref 12a).

chemical hardness in the density functional approach[36,37]. It is just this population of vacant or partially filled orbitals that often occurs when atoms join to form a chemical bond. Thus, in contrast to the Mulliken–Jaffe–Hinze approach,[38] no prior knowledge of, or assumptions about, the valence state of an atom in a molecule is required.

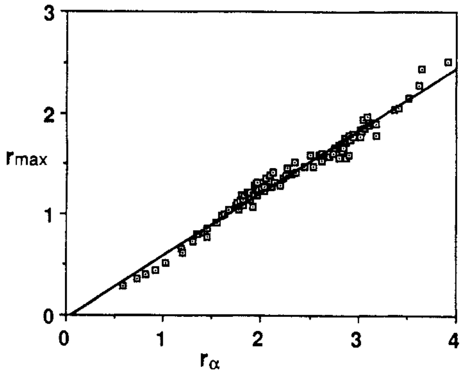

Figure 4. Plot of the maximum in the probability distribution function for the outermost orbital r_{max} (Å atom^{-1}) as calculated from a relativistic SCF approach (ref 39) versus polarizability radius $r_\alpha = \alpha_v^{1/3}$ (Å atom^{-1}).

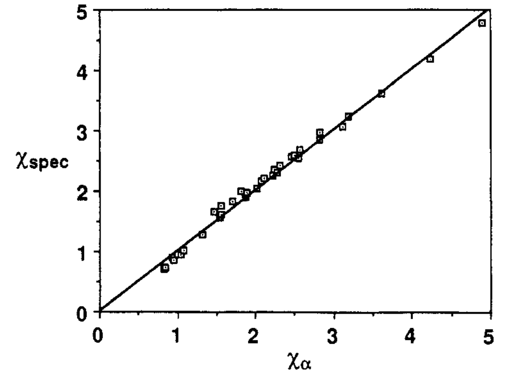

Figure 5. Plot of electronegativities as derived from ionization energies (χ_{spec}; ref 25b) versus polarizability electronegativities (χ_α) calculated from eq 1.

Table III. Relationship between Atomic Polarizability and Properties Derived from It

term	symbol and defining equation	units[a]
polarizability (SI units)	α	F m^2 atom^{-1}
polarizability (vol units)	$\alpha_v = 10^{30}\alpha/4\pi\epsilon_0$	Å^3 atom^{-1}
volume	$V_\alpha = 10^{30}\alpha/3\epsilon_0 = 4\pi\alpha_v/3$	Å^3 atom^{-1}
radius	$r_\alpha = (10^{30}\alpha/4\pi\epsilon_0)^{1/3} = \alpha_v{}^{1/3}$	Å atom^{-1}
softness (electron capacitance)	$\sigma_\alpha = 4\pi\epsilon_0(\alpha/4\pi\epsilon_0 n)^{1/3}$	F electron^{-1}
hardness	$\eta_\alpha = (4\pi\epsilon_0 n/\alpha)^{1/3}/4\pi\epsilon_0 = \sigma_\alpha{}^{-1}$	electrons F^{-1}
potential	$\mu_\alpha = (4\pi\epsilon_0 n/\alpha)^{1/3}e/4\pi\epsilon_0 = n\eta_\alpha$	V
electronegativity	$\chi_\alpha = 1.66(n/\alpha_v)^{1/3} + 0.37$	

[a] The descriptive units atom and electron are included for clarity. See the following for discussions of descriptive units: Wadlinger, R. L. *J. Chem. Educ.* **1983**, *60*, 942–945. Strobel, P. *J. Chem. Educ.* **1989**, *66*, 270–271. Wadlinger, R. L. *J. Chem. Educ.* **1989**, *66*, 271.

This interpretation is supported by the excellent correlation (Figure 3a) between χ_α and values of atomic hardness as defined by and calculated with (within the local density approximation) density functional theory.[12a] As pointed out in that study, hardness is much less sensitive than electronegativity (as defined by density functional theory) to the change from ground-state to valence-state electron configurations.[12a]

Fortunately, reliable atomic polarizabilities, ionization energies, electron affinities, and density functionally defined electronegativities and average hardnesses for both ground and valence states can and have been calculated theoretically by using a common approach.[11a,12] As shown in Figure 3b there is an excellent cor-

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(35) For example, $ns \rightarrow np$ transitions in alkali metal atoms are responsible for the relatively large values of the polarizabilities of these elements since excited-state polarizability values are generally substantially larger than ground-state values. See: Persson, B. N. J.; Dubois, L. H. *Phys. Rev. B* **1989**, *39*, 8220–8235; Christiansen, P. A.; Pitzer, K. S. *Chem. Phys. Lett.* **1982**, *85*, 434–436. This effect is most pronounced for Li which has an even lower lying *n*p orbital than the other alkali metals since there are no filled 1p orbitals to shield the empty 2p orbitals (Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *23*, 272–295). Hence, contrary to expected trends, Li has a larger polarizability and therefore a smaller electronegativity than Na (see Table I). Alternatively, the Li 2s electron can be considered as being relatively loosely held compared to the analogous 3s electron in Na since Li has no filled p orbitals incompletely shielding its valence electron from the nucleus. See ref 26d for related comments on the effects of incomplete shielding on electronegativities.

(36) (a) Hardness has been related to the energy difference between the highest occupied and lowest unoccupied molecular orbitals in the one-electron approximation: Pearson, R. G. *J. Phys. Chem.* **1989**, *54*, 1423–1430; *Inorg. Chem.* **1988**, *27*, 734–740; *J. Chem. Educ.* **1987**, *64*, 561–567. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8440–8441; *J. Am. Chem. Soc.* **1985**, *107*, 6801–6806; *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516. (b) Guo, Y.; Whitehead, M. A. *Phys. Rev. A* **1989**, *39*, 2317–2323. (c) Orsky, A. R.; Whitehead, M. A. *Can. J. Chem.* **1987**, *65*, 1970–1979. (d) Nalewjaski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944–945. (e) Komorowski, L. *Chem. Phys. Lett.* **1987**, *134*, 536–540. (f) Giambiagi, M.; De Giambiagi, M. S.; Pires, J. M. *Chem. Phys. Lett.* **1988**, *152*, 222–226. (g) Datta, D. *J. Phys. Chem.* **1986**, *90*, 4216–4217. (h) Yang, W.; Lee, C.; Ghosh, S. W. *J. Phys. Chem.* **1985**, *89*, 5212–5214. (i) Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811–6814. (j) Sen, K. D.; Schmidt, P. C.; Bohm, M. C. *J. Phys. B: At. Mol. Phys.* **1985**, *18*, L35–L38. (k) Vinayagam, S. C.; Sen, K. D. *Chem. Phys. Lett.* **1988**, *144*, 178–179.

(37) The correlation between hardness (and its inverse—softness or charge capacity) and polarizability is well-known (refs 11a, 12a, 14f (p 60), and: Politzer, P. *J. Chem. Phys.* **1987**, *86*, 1072–1073). Therefore α provides a convenient measure of both hardness and softness. A connection between hardness and aromaticity has recently been postulated (Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371–7379; *Tetrahedron Lett.* **1988**, *29*, 4843–4846).

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relation between $(n/\alpha)^{1/3}$ and hardness with use of values of α calculated in the same way as hardness.[12a] In fact the correlation is so good that calculated values for the d- and f-block elements could be used to determine optimal values of n (and hence electronegativities) for these elements. Further insight into the relationships between electronegativity, hardness, size, and polarizability should emerge from this type of approach.

Since hardness is generally considered to be related to the inverse of radius,[13c] it is of interest to determine what relationship exists between polarizabilities and calculated orbital radii. Figure 4 shows an excellent correlation between polarizability radius ($[10^{30}\alpha/4\pi\epsilon_0]^{1/3}$ in units of Å per atom) and the calculated maximum density in the outermost ground state orbital radii with use of an SCF approach that includes relativistic effects.[39]

Table III provides a summary of various atomic quantities that can be derived from polarizability, the units given following previous suggestions.[13c] Although hardness, η_α, has the units of electrons per farad, these values multiplied by the electron charge e yield valence potentials, μ_α, in volts. Or, if hardness is to be related to the gap between the highest occupied and lowest unoccupied orbitals in the one-electron approach to atomic and molecular electronic structure, then μ_α multiplied by Faraday's constant F yields values in the SI units kJ per mol of atoms. Table II lists values of the various properties defined in Table III for elements of atomic number 1–102.

In conclusion, the use of atomic polarizability values provides a simple and reliable way of calculating Pauling electronegativities for every element based on a measurable atomic property. Since this approach is so simple and is closely related to existing concepts, it should play an important role in discussions of electronegativity at the introductory level. The excellent agreement between the values determined here and the recently published[25b] and publicized[40] values based on multiplet-averaged ionization energies (Figure 5) is encouraging and should provide theoreticians with a guide to further explore the role played by electronegativity in chemical bonding and reactivity. An extension of this work to molecular bond distances[41] and molecular[13c,42] and excited-state[43] polarizabilities is in progress.

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Ab Initio IGLO Studies of the Conformational Dependencies of α-, β-, and γ-Substituent Effects in the ^{13}C NMR Spectra of Aliphatic and Alicyclic Hydrocarbons

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Abstract: Ab initio IGLO (individual gauge for localized molecular orbital) methods of SCF-MO theory are used to study and analyze the mathematical form of the angular dependence of α-, β-, and γ-substituent effects in the ^{13}C NMR spectra of aliphatic and alicyclic hydrocarbons. The conformational dependencies of the isotropic ^{13}C shielding are investigated for all of the carbons in the series of aliphatic hydrocarbons: ethane, propane, *n*-butane, 2-methylbutane, and 2,2-dimethylbutane. The last three of these serve as model compounds for α-, β-, and γ-effects. In contrast to variation in the absolute ^{13}C shielding data, the shifts due to changes in dihedral angles are not sensitive to the size of the MO basis sets. In addition to providing a trigonometric form for the orientational dependence of the γ-effects, from these results it can be concluded that *α- and β-effects are strongly dependent on conformation* even for the usual situation in which the groups are trans and gauche. Each of these substituent effects is analyzed in terms of the variations in the IGLO C–H and C–C bond paramagnetic contributions. In contrast to a steric compression model for ^{13}C γ-substituent effects, *the torsional dependence of the calculated C1 shielding in n-butane is dominated by the changes in the paramagnetic contributions for the C1–C2 bond and for the C1–H bond which is directed away from the C4 methyl group.* The calculated shielding data for 2-methyl- and 2,2-dimethylbutanes results are quite consistent with additivity of the trigonometric forms for the γ-substituent effect in *n*-butane. To investigate α-, β-, and γ-substituent effects in cyclic molecules, shielding calculations at the double-ζ level were performed for methyl-substituted cyclohexanes and bicyclo[2.2.1]heptanes. Except for the carbons directly bonded to the methyl groups, these results are in reasonable agreement with the experimental data.

The α-, β-, and γ-substituent effects[1] in the ^{13}C NMR spectra of aliphatic and alicyclic compounds are of major importance in the application of NMR techniques to structural and conformational studies.[2] In these applications extensive use has been made of *empirical additivity relationships*. It was noted in ref 1 that ^{13}C chemical shifts for aliphatic and alicyclic hydrocarbons could be described by an empirical equation of which a typical form is[3,4]

$$\delta_C = n_\alpha A_\alpha + n_\beta B_\beta + n_\gamma C_\gamma + n_\delta D_\delta + S \qquad (1)$$

where n_α, n_β, n_γ, and n_δ denote the number of α-, β-, γ-, and δ-substituents having additivity increments A_α, B_β, C_γ, and D_δ,

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