charge. Eq. 5.68 allows us to quantify that effect: An iodine atom with a partial charge of about +0.4 is almost as electronegative as a neutral fluorine atom. The significance of the parameters a and b is clear. The *inherent* or *neutral atom electronegativity* is given by a. This is the electronegativity of an atom in a particular valence state as estimated by the Mulliken method and corresponds to similar estimates of electronegativity by Pauling (χ_P), Allred and Rochow (χ_{AR}), and others (see Table 5.6). It may be used alone ($\chi_{MJ} = a$) to say, for example, that in LiH the hydrogen atom ($a = 2.25$) is much more electronegative than is lithium ($a = 0.97$), and should be written Li$^{\delta+}$H$^{\delta-}$ or even Li$^+$H$^-$.

The parameter b is the *charge coefficient*. It measures the rate of change of electronegativity with charge. Mathematically, b is the second derivative of energy (first derivative of electronegativity) with respect to charge:

$$b = d^2E/d\delta^2 = d\chi/d\delta = IE_v - EA_v \qquad (5.69)$$

It thus defines the curvature of the energy–charge parabola. Chemically, it is the inverse of the charge capacity (κ) or polarizability:[31]

$$b = 1/\kappa \qquad (5.70)$$

Large, soft, polarizable atoms have low values of b, and small, hard, nonpolarizable atoms tend to have higher values. An atom with a large charge coefficient will change electronegativity much more rapidly than one with a lower value of b. Thus a small atom (low κ, large b) has only a limited ability to donate or absorb electron density before its electronegativity changes too much for further electron transfer to take place. One of the most important examples is the very electronegative but very small fluorine atom. Although initially very electronegative when neutral (note the steep slope at the origin of Fig. 5.32), it rapidly becomes "saturated" as it accepts electron density (note how quickly the slope flattens out between −0.4 and −0.6), and beyond ~0.7, it is necessary "to push" to get more electron density onto a fluorine atom. This is closely related to the comparatively low electron affinity of fluorine (Chapter 2).

The charge capacity effect is responsible for the well known inductive effect of alkyl groups (see page 196). It is also important in hard and soft acid–base theory (see Chapter 9), and causes several other unexpected effects.[32] It is basically a polarization effect in which larger atoms and groups can acquire or donate large amounts of electron density without unfavorable energy changes.[33]

Recent Advances in Electronegativity Theory

The advances in recent years have been more evolutionary than revolutionary. Increasingly, Mulliken's original idea of expressing electronegativity in terms of the energy of valence electrons has come into favor, and the other definitions in terms of resonance energy or algebraic relationships of size and charge have been viewed as useful approximations when orbital energies are not available. In addition, the relationship between electronegativity and acidity and basicity, always intimate, has been extended further (see Chapter 9).

[31] Politzer, P. *J. Chem. Phys.* **1987**, *86*, 1072–1073.

[32] Politzer, P.; Huheey, J. E.; Murray, J. S.; Grodzicki, M. *J. Mol. Structure (THEOCHEM)*, **1992**, *259*, 99–120.

[33] Huheey, J. E. *J. Org. Chem.* **1971**, *36*, 204–205. Politzer, P.; Murray, J. S.; Grices, J. E. In *Chemical Hardness*; Sen, K. D., Ed.; Springer-Verlag: Berlin, in press.

Table 5.6

Electronegativities of the elements

Element	Pauling χ_P^b	Sanderson χ_S^c	Allred–Rochow χ_{AR}^d	Allen χ_{spec}^e	Orbital or hybrid	Pauling scale^f (a)	Volts (a)	Volts/electron (b)
1. H	2.20	2.59	2.20	2.30	s	2.25	7.17	12.84
2. He				5.50^g	s	3.49^a	12.98^a	23.22
						4.86^g	15.08^g	
3. Li	0.98	0.89	0.97	0.91	s	0.97	3.00	4.77
4. Be	1.57	1.81	1.47	1.58	sp	1.54	4.65	6.58
5. B	2.04	2.28	2.01	2.05	sp^2	2.04	6.37	8.74
					sp^3	1.90	5.86	8.64
6. C	2.55	2.75	2.50	2.54	sp	2.99	10.42	11.70
					sp^2	2.66	8.91	11.50
					sp^3	2.48	8.15	11.39
7. N	3.04	3.19	3.07	3.07	sp	3.68	14.00	13.32
					sp^2	3.26	11.78	13.22
					sp^3	3.04	10.66	13.16
					20%s	2.90	10.00	13.13
					p	2.28	7.32	13.00
8. O	3.44	3.65	3.50	3.61	sp^2	3.94	15.48	15.62
					sp^3	3.68	14.02	15.55
					17%s	3.41	12.55	15.47
					p	2.82	9.63	15.33
9. F	3.98	4.00	4.10	4.19	sp^3	4.30	17.63	17.99
					14%s	3.91	15.30	17.81
					p	3.35	12.20	17.57
10. Ne		4.50^g	4.84^g	4.79	sp^3	4.49	18.86	18.92
					12%s	3.98	15.71	18.50
					p	3.41^a	12.56^a	18.08
						4.26^g	13.29^g	—
11. Na	0.93	0.56^h	1.01	0.87	s	0.91	2.84	4.59
12. Mg	1.31	1.32	1.23	1.29	sp	1.37	4.11	5.27
13. Al(I)		0.84			p	0.91	2.86	6.23
Al(III)	1.61	1.71	1.47	1.61	sp^2	1.83	5.61	6.12
					sp^3	1.71	5.21	5.92
14. Si	1.90	2.14^h	1.74	1.92	sp^3	2.28	7.30	7.13
15. P	2.19	2.52	2.06	2.25	sp^3	2.41	7.84	9.53
					20%s	2.30	7.41	9.39
					p	1.84	5.67	8.83
16. S	2.58	2.96	2.44	2.59	sp^3	2.86	9.84	10.36
					17%s	2.69	9.04	10.20
					p	2.31	7.44	10.12
17. Cl	3.16	3.48	2.83	2.87	14%s	3.10	12.15	11.55
					p	2.76	10.95	11.40
18. Ar		3.31^h	3.20^g	3.24	sp^3	3.49	12.98	12.38
					12%s	3.19	11.41	12.18
					p	2.86^a	9.83^a	11.98
						3.11^g	9.87^g	—
19. K	0.82	0.45	0.91	0.73	s	0.73	2.42	3.84
20. Ca	1.00	0.95	1.04	1.03	sp	1.08	3.29	1.08

Mulliken–Jaffé, χ_{MJ}^a

Table 5.6
Electronegativities of the elements (Continued)

Element	Pauling χ_P^b	Sanderson χ_S^c	Allred–Rochow χ_{AR}^d	Allen χ_{spec}^e	Orbital or hybrid	Mulliken–Jaffé, χ_{MJ}^a — a Pauling scale^f	Volts	b Volts/electron
21. Sc(III)	1.36	1.02	1.20					
22. Ti(II)	1.54	0.73						
Ti(III)		1.09						
Ti(IV)		1.50	1.32					
23. V(II)	1.63	0.69						
V(III)		1.39	1.45					
V(V)		2.51						
24. Cr(II)	1.66							
Cr(III)		1.66	1.56					
Cr(VI)		3.37						
25. Mn(II)	1.55	1.66	1.60					
Mn(III)		2.20						
Mn(IV)		2.74						
Mn(V)		3.28						
Mn(VI)		3.82						
Mn(VII)		4.36?						
26. Fe(II)	1.83	1.64	1.64					
Fe(III)	1.96	2.20						
27. Co(II)	1.88	1.96	1.7					
Co(III)		2.56						
28. Ni(II)	1.91	1.94	1.75					
29. Cu(I)	1.90	2.03	1.75		s	1.49	4.48	6.50
Cu(II)	2.00	1.98						
30. Zn	1.65	2.23	1.66		sp	1.65	4.99	5.91
					p	0.87	2.75	6.36
31. Ga(I)		0.86						
Ga(III)	1.81	2.42	1.82	1.76	sp²	2.01	6.28	6.22
					p	1.30	3.92	7.63
32. Ge(II)		0.56						
Ge(IV)	2.01	2.62	2.02	1.99	sp³	2.33	7.53	7.62
33. As(III)	2.18	2.82	2.20	2.21	sp³	2.38	7.70	8.98
					20%s	2.26	7.25	8.85
					p	1.68	5.45	8.34
34. Se	2.55	3.01	2.48	2.42	sp³	2.79	9.48	9.70
					17%s	2.60	8.65	9.59
					p	2.20	6.99	9.39
35. Br	2.96	3.22	2.74	2.68	14%s	2.95	10.25	10.41
					p	2.60	8.63	10.22
36. Kr	3.00g	2.91h	2.94g	2.97	sp³	3.31	12.03	11.02
					12%s	3.00	10.48	10.80
					p	2.66a	8.93a	10.58
						2.77g	8.86g	—
37. Rb	0.82	0.31	0.89	0.71	s	0.82	2.33	3.69
38. Sr	0.95	0.72	0.97	0.96	sp	1.00	3.07	4.17
39. Y(III)	1.22	0.65	1.11					
40. Zr(II)	1.33	0.52						
Zr(IV)		0.90	1.22					
41. Nb(II)		0.77						
Nb(V)	1.6	1.42	1.23					

Table 5.6
Electronegativities of the elements (Continued)

Element	Pauling χ_P^b	Sanderson χ_S^c	Allred–Rochow χ_{AR}^d	Allen χ_{spec}^e	Orbital or hybrid	Mulliken–Jaffé, χ_{MJ}^a — a Pauling scale^f	Volts	b Volts/electron
42. Mo(II)	2.16	0.90						
Mo(III)	2.19	1.15						
Mo(IV)	2.24	1.40	1.30					
Mo(V)	2.27	1.73						
Mo(VI)	2.35	2.20						
43. Tc	1.9		1.36					
44. Ru	2.2		1.42					
45. Rh	2.28		1.45					
46. Pd	2.20		1.35					
47. Ag(I)	1.93	1.83	1.42		s	1.47	4.44	6.27
					sp			
48. Cd(II)	1.69	1.98	1.46		sp	1.53	4.62	5.91
					p	1.12	3.40	6.11
49. In(I)					sp²	1.76	5.39	6.63
In(III)	1.78	2.14	1.49	1.66	30%s	1.85	6.09	6.97
50. Sn(II)	1.80	1.49			sp³	2.21	7.05	5.04
Sn(IV)	1.96		1.72	1.82	sp³	2.22	7.09	8.16
51. Sb	2.05	2.46h	1.82	1.98	20%s	2.12	6.68	8.02
					p	1.67	5.08	7.45
52. Te	2.1	2.62	2.01	2.16	sp³	2.57	8.52	8.74
					17%s	2.41	7.83	8.64
					p	2.06	6.46	8.44
53. I	2.66	2.78	2.21	2.36	sp³	2.95	10.26	9.38
					14%s	2.74	9.29	9.33
					p	2.45	8.00	9.25
54. Xe	2.60g	2.34h	2.40g	2.58	sp³	3.01	10.52	9.52
					12%s	2.73	9.24	9.36
					p	2.44a	7.96a	9.21
						2.40g	7.76g	—
55. Cs	0.79	0.22	0.86		s	0.62	2.18	3.42
56. Ba	0.89	0.68	0.97		sp	0.88	2.79	3.93
57. La	1.10		1.08					
58. Ce	1.12		1.08					
59. Pr	1.13		1.07					
60. Nd	1.14		1.07					
61. Pm			1.07					
62. Sm	1.17		1.07					
63. Eu			1.01					
64. Gd	1.20		1.11					
65. Tb			1.10					
66. Dy	1.22		1.10					
67. Ho	1.23		1.10					
68. Er	1.24		1.11					
69. Tm	1.25		1.11					
70. Yb			1.06					
71. Lu	1.27		1.14					
72. Hf	1.3		1.23					

Table 5.6

Electronegativities of the elements (Continued)

Element	Pauling χ_P^b	Sanderson χ_S^c	Allred–Rochow $\chi_{AR}{}^d$	Allen $\chi_{spec}{}^e$	Orbital or hybrid	Mulliken–Jaffé, $\chi_{MJ}{}^a$ a — Pauling scale^f	a — Volts	b — Volts/electron
73. Ta	1.5		1.33					
74. W(II)	2.36	0.73						
W(III)		0.98	1.40					
W(VI)		1.67						
75. Re	1.9		1.46					
76. Os	2.2		1.52					
77. Ir	2.20		1.55					
78. Pt	2.28		1.44					
79. Au	2.54		1.41		s	1.87	5.77	6.92
80. Hg	2.00	2.20	1.44		sp	1.81	5.55	5.81
81. Tl(I)	1.62	0.99			p	0.76	2.50	5.92
Tl(III)	2.04	2.25	1.44		sp²	1.96	6.08	6.40
82. Pb(II)	1.87	1.92	1.5		p	1.16	3.52	7.47
Pb(IV)	2.33	2.29^h			sp³	2.41	7.82	5.32
83. Bi	2.02	2.34	1.67		20%s	2.15	6.81	8.09
84. Po	2.0		1.76		17%s	2.48	8.14	8.81
85. At	2.2		1.90		14%s	2.85	9.76	10.03
					p	2.55		
86. Rn			2.06^g		p	2.12^g	6.92^g	—
87. Fr	0.7		0.86		s	0.68	2.30	3.40
88. Ra	0.9		0.97		sp	0.92	2.88	3.69
89. Ac	1.1		1.00					
90. Th	1.3		1.11					
91. Pa	1.5		1.14					
92. U	1.38		1.22					
93. Np	1.36		1.22					
94. Pu	1.28		1.22					
95. Am	1.3		(1.2)					
96. Cm	1.3		(1.2)					
97. Bk	1.3		(1.2)					
98. Cf	1.3		(1.2)					
99. Es	1.3		(1.2)					
100. Fm	1.3		(1.2)					
101. Md	1.3		(1.2)					
102. No	1.3		(1.2)					

^{a} Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34–41. See text for definitions of *a* and *b*.

^{b} Values to two decimal places are by Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215, unless otherwise noted. Values to one decimal place are from Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 93.

^{c} Sanderson, R. T. *Simple Inorganic Substances*; Krieger: Malabar, FL, 1989; p 23, unless otherwise noted.

^{d} Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264, except for italicized values from Little, E. J., Jr.; Jones, M. M. *J. Chem. Educ.* **1960**, *37*, 231, or otherwise noted. Values in parentheses are estimates.

^{e} Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003–9014.

^{f} $\chi_P = 1.35(\chi_{MJ})^{1/2} - 1.37$ (from ref. *a*).

^{g} Allen, L. C.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1523–1524.

^{h} Sanderson, R. T. *Polar Covalence*; Academic: New York, 1983; p 41.

Two recent approaches should be mentioned. In one, Parr and others[34] have followed Mulliken by defining electronegativity in terms of ionization energy and electron affinity. They have also advanced the idea of electronegativity in terms of density functional theory. This is a close parallel to the Mulliken–Jaffé system in its emphasis upon the first and second derivatives of the ionization potential–electron affinity energy curves. In addition, it provides quantum mechanical support for the intuitively appealing idea of electronegativity equalization (see page 198). It differs only to the extent that those using this method have tended to use *ground state values* instead of *valence state values*.

More recently Allen[35] has proposed that electronegativity be defined in terms of the average one-electron energy of valence shell electrons in ground-state free atoms which may be obtained spectroscopically. This quantity is termed the configuration energy:

$$CE = \frac{m\varepsilon_p + n\varepsilon_s}{m + n} \tag{5.71}$$

where ε_p and ε_s, m and n are the energies and numbers of electrons in the p and s orbitals of the valence shell, respectively. The result is another strong argument for defining electronegativity (χ_{spec}) in terms of orbital energy. This system of electronegativity has been successfully applied to periodic properties of the elements such as covalent, metallic, and ionic bonding; atomic radii; multiple bonding; oxidation states; and the unique properties of carbon and hydrogen. Note, however, that these energies are not valence state energies, nor does the calculation include electron affinities.[36] This prevents application to the effect of charge capacity (hardness and softness) as related to electronegativity or to the variability of electronegativity with hybridization (see below). On the other hand it presents an unambiguous measure of an atom's average electronegativity. Further efforts to apply the method to transition metals and to changes in oxidation states will probably be forthcoming.

The articles by Allen cited above are also recommended as the most recent review of various aspects of electronegativity theories and for the idea that electronegativity is "the third dimension of the periodic chart."

Variation of Electronegativity

Although electronegativity is often treated as though it were an invariant property of an atom, we have seen that it depends on two properties: valence state (hybridization) and atomic charge. Hybridization affects electronegativity because of the lower energy and hence greater electron-attracting power of *s* orbitals. We might expect the electronegativity of an atom to vary slightly with hybridization, with those orbitals having greater *s* character being more electronegative. Some results of the variation in

[34] Parr, R. G. *Ann. Rev. Phys. Chem.* **1983**, *34*, 631–656. Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *71*, 4218–4220. Van Genechten, K. A.; Mortier, W. J. *Zeolites* **1988**, *8*, 273–283. Pearson, R. G. *Acc. Chem. Res.* **1990**, *23*, 1–2.

[35] Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003–9014; *Acc. Chem. Res.* **1990**, *23*, 175–176; *J. Am. Chem. Soc.* **1992**, *114*, 1510–1511; *Can. J. Chem.* **1992**, *70*, 631–635. Note that Allen's spectroscopic electronegativity, like Mulliken's, will normally be expressed in terms of electron volts, but can be converted to the Pauling scale if desired.

[36] It should be noted that inasmuch as the ionization energy of most atoms is an order of magnitude larger than the electron affinity, electronegativity methods which are fundamentally related *only* to ionization energies are still successful.