Absolute Electronegativity and Hardness: Application to Inorganic Chemistry

Ralph G. Pearson

The recent concepts of absolute electronegativity, χ, and absolute hardness, η, are briefly reviewed. The operational definitions, $\chi = (I + A)/2$ and $\eta = (I - A)/2$, are used to calculate experimental values for a large number of cations, atoms, radicals, and molecules. The resulting values are shown to be in good agreement with chemical behavior, both as to acid–base character and as to chemical hardness or softness. Anions are modeled by their corresponding radicals, and the importance of local softness, $\bar{\sigma}$, for delocalized anions is pointed out. Applications of the use of tabulated values of η, both for rank ordering and in numerical calculation, are given.

With density functional theory[1] as a starting point, two new concepts of potential importance to chemistry have been introduced. Any chemical system (atom, molecule, ion, radical) is characterized by its electronic chemical potential, μ,[2] and by its absolute hardness, η.[3] The exact definition of these quantities are

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v \qquad \eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \qquad (1)$$

where N is the number of electrons and v is the potential due to the nuclei, plus any external potential.

Operational and approximate definitions are

$$-\mu = (I + A)/2 = \chi \qquad \eta = (I - A)/2 \qquad (2)$$

where I is the ionization potential and A is the electron affinity.

Since $(I + A)/2$ is the Mulliken electronegativity for atoms, the value for any system, χ, is called the absolute electronegativity.[2] For an equilibrium system it must be constant everywhere. The hardness, η, need not be constant and can have local values, but $(I - A)/2$ is the average or global value. The softness, σ, is simply the inverse of the hardness, $\sigma = 1/\eta$.

If two systems, B and C, are brought together, electrons will flow from that of lower χ to that of higher χ, until the chemical potentials become equal. As a first approximation, the (fractional) number of electrons transferred, ΔN, will be given by

$$\Delta N = \frac{\chi_C - \chi_B}{2(\eta_C + \eta_B)} \qquad (3)$$

Obviously this is a convenient way of looking at generalized acid–base reactions

$$C + :B \rightarrow C:B \qquad (4)$$

where C is the Lewis acid. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance.

There is an energy lowering due to electrons being transferred to a lower chemical potential. But this is only a small part of the total energy change, which must also include covalent bonding and ionic interactions.[4] Even though (3) is incomplete, it is still useful because it measures the initial interaction between B and C using only properties of the isolated systems. Furthermore we can assume that the covalent bonding will show some proportionality to ΔN, since coordinate covalent bonding is involved. For neutral reactants the ionic binding will also depend on ΔN.

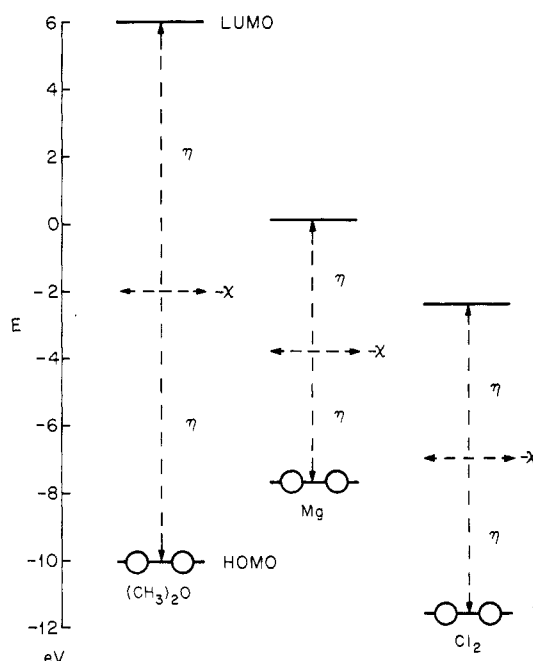The chemical potential and the hardness are molecular and not orbital properties. But the electrons will flow from a definite

Figure 1. Orbital energy diagram for several species, showing χ and η.

occupied orbital in B and will go into a definite empty orbital in C.[5] Usually, but not always, there can be electron flow in both directions, as in σ- plus π-bonding. The overlap between the exchanging orbitals will be critical in determining energy changes. There is no conflict with the frontier orbital theory of chemical reactivity.[6]

According to Koopmans' theorem, the frontier orbital energies are given by

$$-\epsilon_{HOMO} = I \qquad -\epsilon_{LUMO} = A \qquad (5)$$

Figure 1 shows the usual orbital energy diagrams for several molecules, where experimental values have been used for the frontier orbitals. The values of $\mu = -\chi$ are shown as dashed horizontal lines. The values of η are shown as dashed vertical lines. This shows very graphically what is meant by chemical hardness. *Hard molecules have a large HOMO–LUMO gap, and soft molecules have a small HOMO–LUMO gap.*[7]

The notion of chemical hardness was first introduced in connection with Lewis acids and bases.[8] Essentially, soft acids and bases were those of high polarizability. This definition is consistent with Figure 1, since a small energy gap leads to high polarizability, and a large gap means low polarizability.

(1) For an introduction, see: *Local Density Approximations in Quantum Chemistry and Solid State Physics*; Dahl, J. P., Avery, J., Eds; Plenum: New York, 1984.
(2) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978,** *68*, 3801–3807.
(3) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983,** *105*, 1503–1509.
(4) Pearson, R. G. *J. Am. Chem. Soc.* **1985,** *107*, 6801–6806.

(5) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984,** *106*, 4049–4050.
(6) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952,** *74*, 3341–3363. Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1968,** *41*, 1984–1997. Klopman, G.; Hudson, R. F. *Theor. Chim. Acta* **1967,** *8*, 165–174.
(7) Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1986,** *83*, 8440–8441.
(8) Pearson, R G. *J. Am. Chem. Soc.* **1963,** *85*, 3533–3539.

Table I. Experimental Parameters[52] for Monatomic Cations (eV)

ion	I	A	χ	η
Li^+	75.64	5.39	40.52	35.12
Na^+	47.29	5.14	26.21	21.08
K^+	31.63	4.34	17.99	13.64
Rb^+	27.28	4.18	15.77	11.55
Cs^+	25.1	3.89	14.5	10.6
Cu^+	20.29	7.73	14.01	6.28
Ag^+	21.49	7.58	14.53	6.96
Au^+	20.5	9.23	14.9	5.6
Tl^+	20.43	6.11	13.27	7.16
Co^+	17.06	7.86	12.46	4.60
Rh^+	18.08	7.46	12.77	5.31
Ir^+	16.9[a]	9.1[a]	13.0	3.9
Cl^+	23.81	12.97	18.39	5.42
Br^+	21.8	11.81	16.8	5.0
I^+	19.13	10.45	14.79	4.34
Be^{2+}	153.89	18.21	86.05	67.84
Mg^{2+}	80.14	15.04	47.59	32.55
Ca^{2+}	50.91	11.87	31.39	19.52
Sr^{2+}	43.6	11.03	27.3	16.3
Sc^{2+}	24.76	12.80	18.78	5.98
Ti^{2+}	27.49	13.58	20.54	6.96
V^{2+}	29.31	14.65	21.98	7.33
Cr^{2+}	30.96	16.50	23.73	7.23
Mn^{2+}	33.67	15.64	24.66	9.02
Fe^{2+}	30.65	16.18	23.42	7.24
Co^{2+}	33.50	17.06	25.28	8.22
Ni^{2+}	35.17	18.17	26.67	8.50
Cu^{2+}	36.83	20.29	28.56	8.27
Zn^{2+}	39.72	17.96	28.84	10.88
Ge^{2+}	34.22	15.93	25.08	9.15
Y^{2+}	20.52	12.24	16.38	4.14
Zr^{2+}	22.99	13.13	18.06	4.93
Nb^{2+}	25.04	14.32	19.68	5.36
Mo^{2+}	27.16	16.15	21.60	5.51
Ru^{2+}	28.47	16.76	22.62	5.86
Rh^{2+}	31.06	18.08	24.57	6.49
Pd^{2+}	32.93	19.43	26.18	6.75
Ag^{2+}	34.8	21.5	28.2	6.7
Cd^{2+}	37.48	16.91	27.20	10.29
Sn^{2+}	30.50	14.63	22.57	7.94
Hf^{2+}	23.3	14.9	19.1	4.2
W^{2+}	25.4[a]	16.3[a]	20.9	4.5
Os^{2+}	27.7[a]	16.3[a]	22.3	5.7
Pt^{2+}	35.2[a]	19.2[a]	27.2	8.0
Hg^{2+}	34.2	18.76	26.5	7.7
Pb^{2+}	31.94	15.03	23.49	8.46
B^{3+}	259.37	37.93	148.65	110.72
Al^{3+}	119.99	28.45	74.22	45.77
Ga^{3+}	64.00	30.71	47	17
In^{3+}	54	28.03	41	13
Tl^{3+}	50.7	29.83	40.3	10.4
Sc^{3+}	73.47	24.76	49.11	24.36
Y^{3+}	61.8	20.52	41.2	20.6
La^{3+}	49.95	19.18	34.57	15.39
Ce^{3+}	36.76	20.20	28.48	8.28
Lu^{3+}	45.19	20.96	33.08	12.12
Ti^{3+}	43.27	27.49	35.38	7.89
V^{3+}	46.71	29.31	38.01	8.70
Cr^{3+}	49.1	30.96	40.0	9.1
Mn^{3+}	51.2	33.67	42.4	8.8
Fe^{3+}	54.8	30.65	42.73	12.08
Co^{3+}	51.3	33.50	42.4	8.9
Ni^{3+}	54.9	35.17	45.0	9.9
Zr^{3+}	34.34	22.99	28.65	5.68
Nb^{3+}	38.3	25.04	31.7	6.6
Mo^{3+}	46.4	27.16	36.8	9.6
Ru^{3+}	49.9[a]	28.5	39.2	10.7
Rh^{3+}	53.4[a]	31.1	42.2	11.2
Hf^{3+}	33.32	23.3	28.3	5.0
W^{3+}	39.3[a]	25.4[a]	32.4	7.0
Re^{3+}	41.5[a]	25.9[a]	33.7	7.8
Os^{3+}	42.7[a]	27.7[a]	35.2	7.5
Ir^{3+}	45.3[a]	29.5[a]	37.4	7.9
Au^{3+}	54.1[a]	37.4[a]	45.8	8.4

[a] Theoretical values: Carlson, T. A.; Nestor, C. W.; Wasserman, N.; McDowell, J. D. *At. Data Nucl. Data Tables,* **1970**, *2*, 63–78.

Table II. Experimental Parameters for Molecules (eV)

molecule	I^a	A^b	χ	η
SF_6	15.4	0.5	8.0	7.4
BF_3	15.81	-3.5[k]	6.2	9.7
SO_3	12.7[c]	1.7	7.2	5.5
Cl_2	11.6	2.4	7.0	4.6
H_2	15.4	-2.0[d]	6.7	8.7
SO_2	12.3	1.1	6.7	5.6
N_2	15.58	-2.2	6.70	8.9
Br_2	10.56	2.6	6.6	4.0
O_2	12.2	0.4[i]	6.3	5.9
CO	14.0	-1.8	6.1	7.9
I_2	9.4	2.6	6.0	3.4
BCl_3	11.60	0.33	5.97	5.64
CS	11.71	0.20	5.96	5.23
HNO_3	11.03	0.57	5.80	5.23
CH_3NO_2	11.13	0.45	5.79	5.34
PF_3	12.3	-1.0[e]	5.7	6.7
HCN	13.6	-2.3	5.7	8.0
BBr_3	10.51	0.82	5.67	4.85
PBr_3	9.9	1.6	5.6	4.2
S_2	9.36	1.66	5.51	3.85
$C_6H_5NO_2$	9.9	1.1	5.5	4.4
PCl_3	10.2	0.8	5.5	4.7
N_2O	12.9	-2.2	5.4	7.6
acrylonitrile	10.91	-0.21	5.35	5.56
CS_2	10.08	0.62	5.35	5.56
HI	10.5	0.0[b]	5.3	5.3
CO_2	13.8	-3.8[g]	5.0	8.8
HF	16.0	-6.0[h]	5.0	11.0
CH_3I	9.5	0.2	4.9	4.7
HCl	12.7	-3.3	4.7	8.0
CH_3CN	12.2	-2.8	4.7	7.5
CH_2O	10.9	-1.5	4.7	6.2
HCO_2CH_3	11.0	-1.8[k]	4.6	6.4
CH_3CHO	10.2	-1.2	4.5	5.7
C_2H_4	10.5	-1.8	4.4	6.2
C_5H_5N	9.3	-0.6	4.4	5.0
butadiene	9.1	-0.6	4.3	4.9
H_2S	10.5	-2.1	4.2	6.2
C_2H_2	11.4	-2.6	4.4	7.0
$HCONH_2$	10.3	-2.0	4.2	6.2
styrene	8.47	-0.25	4.11	4.36
CH_3COCH_3	9.7	-1.5	4.1	5.6
PH_3	10.0	-1.9	4.1	6.0
C_6H_6	9.3	-1.2	4.1	5.3
toluene	8.8	-1.1	3.9	5.0
propylene	9.74	-2.0	3.9	5.9
C_6H_5OH	8.5	-1.0	3.8	4.8
C_6H_5SH	8.3	-0.8[k]	3.8	4.6
CH_3Cl	11.2	-3.7	3.8	7.5
p-xylene	8.4	-1.1	3.7	4.8
1,2,5-trimethylbenzene	8.40	-1.03	3.69	4.72
cyclohexene	8.9	-2.1	3.4	5.5
DMF	9.1	-2.4[k]	3.4	5.8
$C_6H_5NH_2$	7.7	-1.1	3.3	4.4
$CH_3CH{=}C(CH_3)_2$	8.7	-2.2	3.3	5.5
CH_3F	12.5	-6.2[i]	3.2	9.4
H_2O	12.6	-6.4[j]	3.1	9.5
$(CH_3)_3As$	8.7	-2.7	3.0	5.7
$(CH_3)_3P$	8.6	-3.1	2.8	5.9
$(CH_3)_2S$	8.7	-3.3	2.7	6.0
NH_3	10.7	-5.6[k]	2.6	8.2
CH_4	12.7	-7.8[i]	2.5	10.3
$C(CH_3)_4$	10.4	-6.1	2.2	8.3
$(CH_3)_2O$	10.0	-6.0	2.0	8.0
$(CH_3)_3N$	7.8	-4.8	1.5	6.3

[a] Data from ref 13, except as indicated. [b] Data from ref 14, 15 and 53, except as indicated. [c] Lloyd, D. R.; et al. *Mol. Phys.* **1976**, *31*, 1549. [d] Lowe, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5557. [e] Estimated. See; Xiao, S. X.; Trogler, W. c.; Ellis, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 7033. [f] Spence, D.; Chupka, W. A.; Stevens, C. M. *J. Chem. Phys.* **1982**, *76*, 2759. [g] Cadez, I.; et al. *J. Phys. B.* **1977**, *10*, 3821. [h] Theoretical value: Bondeybey, V.; Pearson, P. K.; Schaefer, H. F. *J. Chem. Phys.* **1972**, *57*, 1123. [i] Tossell, J. A.; et al. *Acc. Chem. Res.* **1986**, *19*, 281. [j] Melton, C. E. *J. Chem. Phys.* **1972**, *57*, 4218. [k] References in: Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557–588.

Table III. Experimental Parameters for Atoms (eV)

atom	I^a	A^b	χ	η
H	13.60	0.75	7.18	6.43
Li	5.39	0.62	3.01	2.39
Be	9.3	0.4	4.9	4.5
B	8.3	0.28	4.29	4.01
C	11.26	1.27	6.27	5.00
N	14.53	0.07	7.30	7.23
O	13.62	1.46	7.54	6.08
F	17.42	3.40	10.41	7.01
Na	5.14	0.55	2.85	2.30
Mg	7.65	−0.15	3.75	3.90
Al	5.99	0.46	3.23	2.77
Si	8.15	1.39	4.77	3.38
P	10.49	0.74	5.62	4.88
S	10.36	2.08	6.22	4.14
Cl	12.97	3.62	8.30	4.68
K	4.34	0.50	2.42	1.92
Ca	6.1	−1.8	2.2	4.0
Sc	6.54	0.14	3.34	3.20
Ti	6.82	0.08	3.45	3.37
V	6.7	0.5	3.6	3.1
Cr	6.77	0.66	3.72	3.06
Mn	7.44	0	3.72	3.72
Fe	7.87	0.25	4.06	3.81
Co	7.8	0.7	4.3	3.6
Ni	7.64	1.15	4.40	3.25
Cu	7.73	1.23	4.48	3.25
Zn	9.39	−0.49	4.45	4.94
Ga	6.0	0.3	3.2	2.9
Ge	7.9	1.2	4.6	3.4
As	9.8	0.8	5.3	4.5
Se	9.75	2.02	5.89	3.87
Br	11.81	3.36	7.59	4.22
Rb	4.18	0.49	2.34	1.85
Sr	5.7	−1.7	2.0	3.7
Y	6.38	0	3.19	3.19
Zr	6.84	0.43	3.64	3.21
Nb	6.9	1.0	4.0	3.0
Mo	7.10	0.75	3.9	3.1
Ru	7.4	1.5	4.5	3.0
Rh	7.46	1.14	4.30	3.16
Pd	8.34	0.56	4.45	3.89
Ag	7.58	1.30	4.44	3.14
Cd	8.99	−0.33	4.33	4.66
In	5.8	0.3	3.1	2.8
Sn	7.34	1.25	4.30	3.05
Sb	8.64	1.05	4.85	3.80
Te	9.01	1.97	5.49	3.52
I	10.45	3.06	6.76	3.69
Cs	3.89	0.47	2.18	1.71
Ba	5.2	−0.5	2.4	2.9
La	5.6	0.5	3.1	2.6
Hf	6.7	−0.8	3.8	3.0
Ta	7.89	0.32	4.11	3.79
W	7.98	0.82	4.40	3.58
Re	7.88	0.15	4.02	3.87
Os	8.7	1.1	4.9	3.8
Ir	9.1	1.6	5.4	3.8
Pt	9.0	2.1	5.6	3.5
Au	9.23	2.31	5.77	3.46
Hg	10.44	−0.63	4.91	5.54
Tl	6.1	0.3	3.2	2.9
Pb	7.42	0.37	3.90	3.53
Bi	8.42	0.95	4.69	3.74

a Reference 52. *b* Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731.

The HSAB principle, "hard acids prefer to coordinate to hard bases, and soft acids to soft bases", has been useful in a variety of contexts.[9] The explanation given by Klopman emphasized that soft acids and bases were largely covalently bound and hard acids and bases were ionically bound.[10] This explanation is completely consistent with Figure 1 and with (3).

The energy gap in Figure 1 is also related to vis–UV spectra. But we cannot simply equate the energy of the first absorption band of a molecule to $(I - A)$. In fact the latter will usually be about twice as large as the excitation energy. The difference comes from the extra electron–electron repulsion energy that results from adding an electron. Also the first absorption bands may involve excitation to orbitals such as Rydberg orbitals. If the initially and finally occupied MO's are not valence shell orbitals, the energies will contain little information on chemical reactivity.

For the systems shown in Figure 1, the direction of spontaneous electron flow will be from dimethyl ether to magnesium and from magnesium to chlorine. Since $(CH_3)_2O$ is a hard molecule, there will be little electron transfer and little bonding to magnesium. The chlorine molecule is quite soft and the magnesium atom is softer still, so that ΔN will be large. Neutral metal atoms are all soft, but bulk metals are softer still. In fact $I = A$ for metals, so that the softness $\sigma = 1/\eta$, is infinite.[11]

Results for Cations

It is necessary to show that $(I - A)$ indeed does correlate with earlier assignments of hardness and softness for various systems. At the same time $(I + A)$ must correlate with behavior as Lewis acids or bases. Large values of χ characterize Lewis acids, and small values apply to bases.

Table I lists the experimental values of I, A, χ, and η for all the important monatomic cations in their common oxidation states. For the heaviest metals some experimental ionization potentials are still not available. It can be seen that, with one exception, the values of η calculated for these ions agree very well with their known chemical hardness.

In addition to the expected effects of ionic charge and size, the influence of d electrons is very clear. That the d subshell is very important in promoting soft behavior has been emphasized by Ahrland.[12] The role of the d electrons in chemical bonding is usually attributed to π-back-bonding and/or polarization in the field of the ligands. However ligand field stabilization is also important, and it is interesting to point out that this is also a polarizability effect. Localizing the d electrons in certain favored orbitals is a special kind of polarization.

The only cases where the values of η are not a reliable guide to chemical softness occur for Ce^{3+} and the other trivalent lanthanide ions. These have low values of η compared to that for La^{3+}, but they are all typical hard Lewis acids. Clearly the f electrons are responsible for the low values of η, since they can be ionized rather easily, so that I is small. However f electrons are chemically quite inert. Because they are well screened and because of their spatial distribution, covalent bonding, ligand field effects, and chemical polarizability are all small for 4f electrons.

The effect of unshared p electrons in the valence shell is similar to that for d electrons. While only the halonium ions are listed, similar low values of η are expected for ions such as RO^+, RS^+, RSe^+, R_2N^+, and R_2P^+. Carbonium ions are expected to be much harder, through it is difficult to measure the second ionization potentials of these ions to prove this point.

Results for Neutral Molecules

Table II gives the values of I, A, χ, and η for most of the neutral molecules that are of interest to inorganic chemistry, where the data are available. While many values of I are known,[13] values of A are still scarce, though there are now methods for measuring both positive and negative values.[14,15] The negative values of A

(9) *Hard and Soft Acids and Bases*; Pearson, R. G., Ed; Dowden, Hutchinson and Ross: Stroudsville, PA, 1973. Ho, T. L. *Hard and Soft Acids and Bases in Organic Chemistry*; Academic: New York, 1977.
(10) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–234.

(11) A more detailed analysis shows that for metals σ is equal to the density of states at the Fermi level, a large but finite number. Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6223–6277.
(12) Ahrland, S. *Struct. Bonding (Berlin)* **1966**, *1*, 207–220.
(13) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. No. 1.
(14) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557–588.
(15) Fukuda, S. K.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 2291–2296. Grimsrud, S. A.; Caldwell, G.; Chowdhury, S.; Kebarle, P. *Ibid.* **1985**, *107*, 4627–4634. Tossell, J. A.; Moore, J. H.; Giordan, J. C. *Inorg. Chem.* **1985**, *24*, 1100–1109; *J. Am. Chem. Soc.* **1985**, *107*, 5600–5604.

correspond to vertical electron affinities, i.e., no change in nuclear positions. These are the ones that density functional theory requires and also the ones that are most appropriate for discussing partial transfer of electrons between molecules. While vertical values of the ionization potential would also be preferred, no attempt has been made to correct, or to select, such values of I.

The molecules are arranged in order of decreasing χ, so that Lewis acids start the list and Lewis bases are at the bottom. Generally, the ordering is very reasonable, though there are some surprises, with SF_6, CO, N_2, and H_2 shown as Lewis acids of high electronegativity. However, the order shown must *not* be taken as an order of acid strength but of inherent tendency to give up or take up electrons. The acid strength depends strongly on two other characteristics: the charge of dipole moment of the acid and the nature of the orbital that accepts the electron density. The same properties of each base must also be considered.

For example, SF_6 is essentially inert. Being neutral, and nonpolar, it must accept electrons to interact with a base. But the accepting orbital is an antibonding one, which is physically inaccessible. If filled, if would form unstable products such as $BF^+SF_5^-$, where B is the base. Both CO and N_2 are nonpolar and have accepting orbitals of π-type. Bonding to σ-donors, such as NH_3, would be weak. Only π-bases of low electronegativity will bind well. Note that H_2 and N_2 are both very hard, which helps account for their low reactivity. But acids such as Cl_2 and I_2 are much softer.

Among the bases, the most significant feature is that molecules where the donor atom is F, O, or N are all very hard. This results from large negative values of the electron affinity. For similar molecules where the donor atom is Cl, S, or P, there is always a large drop in η. A further, smaller drop occurs for Br, I, Se, and As.

The second feature to note in Table II is the softening effect of unsaturation. Compare C_6H_6 and C_2H_4 with CH_4, $C_6H_5NH_2$ with NH_3, and CH_3COCH_3 with $(CH_3)_2O$. This effect is consistent with the increased polarizability due to unsaturation.

Table III contains the values for χ and η for the elements, where known. These represent monatomic, neutral molecules. The Mulliken χ values are roughly linear with Pauling (and other) electronegativities, but some deviations exist. The hydrogen atom is considerably more electronegative and oxygen somewhat less electronegative than on the Pauling scale. These discrepancies are not alarming since both the definition and the uses of the two scales are quite different. The original Pauling definition was[16] "the power of an atom in a molecule to attract electrons to itself."

The chief use of the Pauling scale is to estimate the polarity of each chemical bond and the net charge on each atom in the molecule. It does this very successfully. The absolute scale also can be used in a similar way.[17] The principle of electronegativity equalization is the usual basis for such calculations.

The absolute scale can also be used to answer the question of bond polarity in a unique way. Consider a molecule X–Y. Does the polarity of the bond mean that the molecule acts as X^+, Y^- or as X^-, Y^+? The hypothetical reaction

$$X(g)^- + Y(g)^+ = X–Y(g) = X(g)^+ + Y(g)^- \qquad (6)$$
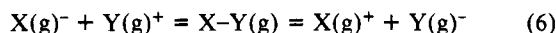
answers this question unambiguously. The difference in energy between the products on the right and those on the left is

$$\Delta E = (I_x - A_y) - (I_y - A_x) = 2(\chi_x - \chi_y) \qquad (7)$$

If $\chi_x > \chi_y$, then the molecule acts as X^-, Y^+.

While (6) is in the gas phase, the effect of the solvent can often be included.[18] It is usually small, unless X or Y is the hydrogen atom. The much larger heat of hydration of H^+ (-269 kcal/mol) than of H^- (-108 kcal/mol) has the effect of greatly reducing the apparent electronegativity of hydrogen.

(16) Pauling L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 88.
(17) Mortier, W. J.; Ghosh, S. I.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315–4320.
(18) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41–49.

Table IV. Experimental Values for Radicals (Also Models for Corresponding Anions)

radical	I^a	A^b	χ	η
F	17.42	3.40	10.41	7.01
OH	13.17	1.83	7.50	5.67
NH_2	11.40	0.74	6.07	5.33
CH_3	9.82	0.08	4.96	4.87
Cl	13.01	3.62	8.31	4.70
SH	10.41	2.3	6.4	4.1
PH_2	9.83	1.25	5.54	4.29
SiH_3	8.14	1.41^e	4.78	3.37
Br	11.84	3.36	7.60	4.24
SeH	9.80^c	2.2	6.0	3.8
I	10.45	3.06	6.76	3.70
H	13.59	0.74	7.17	6.42
HO_2	11.53	1.19	6.36	5.17
NO_2	>10.1	2.3	>6.2	>3.9
CN	14.02	3.82	8.92	5.10
CH_3S	8.06	1.9	5.0	3.1
C_6H_5S	8.63	2.47	5.50	3.08
C_6H_5O	8.85	2.35	5.60	3.25
C_2H_5	8.38	−0.39	4.00	4.39
i-C_3H_7	7.57	−0.48	3.55	4.03
t-C_4H_9	6.93	−0.30	3.31	3.61
C_6H_5	9.20	1.1	5.2	4.1
C_2H_3	8.95	0.74	4.85	4.10
CF_3	9.25	>1.1	>5.18	<4.08
$Mn(CO)_5$	8.44^d	2^f	5.2	3.2

^{a} References 13 and 52. ^{b} References 53 and 54, except as indicated. ^{c} Interpolated from H_2Se and Se. ^{d} Bidinosti, D. R.; McIntyre, N. S., *Chem. Commun.* **1966**, 555–556. ^{e} Nimlos, M. R.; Ellis, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522–6529. ^{f} Beauchamp, J. L.; Stevens, A. E., private communication.

The Anion Problem, Local Softness

Anions pose a special problem since we do not know, nor are we likely to know, the electron affinity of any anion. At any rate such numbers would have little chemical significance. What would be important for anions would be the size of the HOMO–LUMO gap in Figure 1, in the absence of added interelectronic repulsion. This would enable us to rate anions in the order of increasing chemical polarizability.

For practical reasons, it is difficult to obtain this information from either vis–UV spectra or optical polarizabilities. As an approximation, however, it seems reasonable to use I and A values for the corresponding radicals, X, to evaluate η for the anions, X^-. Consider the classical charging energy of a conducting sphere of radius R and charge q, $E = q^2/2R$. Now increase q by one unit, and decrease q by one unit, and calculate the changes in energy, which are I and A.

$$I = \frac{2q + 1}{2R} \qquad A = \frac{2q - 1}{2R} \qquad \chi = \frac{q}{R} \qquad \eta = \frac{1}{2R} \qquad (8)$$

The hardness is seen to be independent of the charge, and inversely proportional to the radius.

This classical result closely matches the actual results for atoms and free radicals. In these cases $(I - A)$ is usually due to the mean interelectronic repulsion of two electrons in the same orbital.[4] Larger orbitals mean less repulsion. For closed-shell systems $(I - A)$ is a combination of mean electron repulsions and the energy gap between the HOMO and LUMO in the absence of such repulsions. But even these energy differences would be a function of atom size. A large atom, such as iodine, has smaller intervals between successive orbitals than a small atom like fluorine. This follows from both experimental and quantum mechanical results.

Table IV lists the parameters for most of the radicals where the data are available. The assumption seems to be generally reasonable, since we find hardness orders $F^- > Cl^- > Br^- > I^-$, $OH^- > SH^- > SeH^-$, $NH_2^- > PH_2^-$, $CH_3^- > SiH_3^-$, and $F^- > OH^- > NH_2^- > CH_3^-$. However, H^- is definitely out of line, since chemically it is very soft.

Table IV includes some large, delocalized anions, which are

soft, as expected, but all parts are not equally soft. Unlike the chemical potential, μ, η is a local property.[19] Furthermore the local hardness, $\bar{\eta}$, is different for adding electrons to, or removing electrons from, each part of the molecule.

Fortunately these rather complex results have a simple theoretical expression, if couched in terms of local softness, $\bar{\sigma}$.[11]

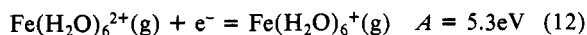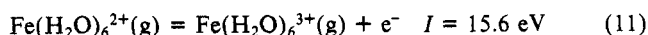$$\bar{\sigma} = \sigma\rho_{HOMO} \text{ as nucleophile} \qquad (9)$$

$$\bar{\sigma} = \sigma\rho_{LUMO} \text{ as electrophile} \qquad (10)$$

Here ρ_{HOMO} and ρ_{LUMO} are the normalized electron densities of the frontier orbitals. For the easiest transfer of charge density, reaction should occur at that part of the molecule where $\bar{\sigma}$ is the largest.[5]

To summarize: we cannot hope to evaluate η for anions on the same basis as for cations and neutrals; to rank order anions, we may use the corresponding radicals or make estimates based on ion size. Delocalized anions have large effective sizes. For localized anions, the softness is concentrated on the donor atom. For delocalized anions, we need the wave functions for the frontier orbitals to find where the softness is concentrated.

Effect of Ligands

Table I shows χ and η for bare cations, but of course in chemistry we must deal with metal ions surrounded by various ligands. Some of the examples in Table II show that neutralizing the cationic charge by anionic ligands greatly reduces both χ and η. This is an expected result, and neutral ligands will have a similar, but smaller, effect. Data for this are hard to obtain since we need to know ligand bonding energies to a metal in three different oxidation states. For water as a ligand there is enough information to calculate the following:[20]

$$Fe(H_2O)_6^{2+}(g) = Fe(H_2O)_6^{3+}(g) + e^- \quad I = 15.6 \text{ eV} \qquad (11)$$

$$Fe(H_2O)_6^{2+}(g) + e^- = Fe(H_2O)_6^+(g) \quad A = 5.3 \text{eV} \qquad (12)$$

Thus χ is 10.4 and η is 5.15, compared to 23.4 and 7.24 for Fe^{2+}.

The rather small lowering of η due to water ligands is probably the minimum effect of any neutral ligands, since water is the hardest ligand of this kind. The basis for this statement is the "symbiotic effect" of Klixbüll Jørgensen.[21] Soft ligands make the central atom soft, and hard ligands make the central atom hard. One sees this rule operating in the cases of PF_3, PCl_3, and PBr_3, and also BF_3, BCl_3, and BBr_3 (Table II).

For neutral ligands, the following general argument can be made: hard ligands are usually innocent, and soft ligands are usually noninnocent.[22] An innocent ligand allows an unambiguous assignment of the oxidation states of the central ion. Noninnocent ligands offer the possibility that they have been oxidized or reduced and not the central ion. Famous examples are the dithiolate ions,[23] such as mnt^{2-}, $(CN)_2C_2S_2^{2-}$.

What noninnocent ligands do, at the very least, is delocalize changes in charge over the entire complex, rather than concentrate such changes on the metal ion. The effective size of the ion becomes large, and η becomes small, according to eq 8. Alternatively, we can say that I is reduced and A is increased, because delocalization lowers the energy for changes in charge. Thus $(I - A)$ becomes smaller for soft ligands, as predicted.

For octahedral complexes we might expect the values of $10Dq$, or Δ_{oct}, to be a measure of $(I - A)$, as suggested by Figure 1. Hard ligands should then give a large value of $10Dq$, and soft ligands a small value, to agree with the symbiotic effect. But typically soft ligands are found at both ends of the spectrochemical series.[24]

Table V. Electron Transfer in Reactions of X–Y with Ground-State Iron Atoms

X–Y	ΔN^a	X–Y	ΔN^a
F_2	0.26	HF	0.030
Cl_2	0.17	HCl	0.027
Br_2	0.15	H_2S	0.007
I_2	0.12	C_2H_2	0.004
H_2	0.11	CH_3Cl	-0.013
O_2	0.11	CH_3F	-0.035
HI	0.072	H_2O	-0.036
HCN	0.066	CH_4	-0.060
CH_3I	0.048	NH_3	-0.065

^{a}Calculated from eq 3.

This is also a result of their ability to delocalize charge. The net responses would be quite different for actually changing the charges, as in I and A, and in redistributing charge, as in $10Dq$.

The effect of the ligands on χ and η for metal ions is related to, but not the same as, solvent effects. The latter refers to the variation of the properties of $Fe(H_2O)_6^{2+}$ and other complex ions, on being transferred from the gas phase to solutions. The solution values, I' and A', can be calculated in many cases.[25] However, they are not as fundamental as the gas-phase numbers.

Application of the Tables

Tables I–IV can be used in two possible ways: as a rank ordering of similar acids or bases to predict relative properties or as a source of numbers to use in relevant equations such as (3). Table I will be useful only for rank ordering, for two reasons. The first is that we rarely deal with isolated gaseous ions but rather deal with a central metal ion plus ligands. The second is that it is unlikely that numbers such as the fourth ionization potential of aluminum will appear in chemically useful equations. In fact, the semiempirical MO theory of the bonding of Al^{3+} with Cl^- will contain only the first three ionization potentials of Al.[26]

As an example of rank ordering, consider the divalent cations of the first transition series. There is a pronounced increase in hardness at Mn^{2+} and Zn^{2+}. The reason for this is clearly the spectral stability of half-filled and filled d shells. But the results correlate nicely with chemical behavior. The sequence of stability constants for high-spin complexes in water is almost always the Irving–Williams order[27] $V^{2+} < Cr^{2+} > Mn^{2+} < Fe^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. While this order is sometimes attributed to ligand field effects, the drops in stability at Mn^{2+} and Zn^{2+} are greatest for polarizable ligands.[28] In other words, hard Mn^{2+} and Zn^{2+} prefer to remain coordinated to hard H_2O ligands rather than softer ones. The ferric ion shows a similar increased value for η amongst the trivalent ions, connsistent with its affinity for oxygen donor ligands.

The numbers in Tables II and III can be used for both rank ordering and numerical calculations. The same is true for Table IV for the reactions of the neutral atoms and radicals. However ions are indirectly included, since the empirical MO theory of bonding between Ag^+ and Br^- is the same as that for Ag and Br. Also, rank ordering of the anions may be done from Table IV, with some reservations.

For many reactions of neutral molecules, or radicals, eq 3 may be used for numerical calculations. The assumption is usually that a large value of ΔN is favorable for a reaction. But caution is needed since it is quite possible that two systems of equal electronegativity could react to yield strong bonds, even though ΔN would be zero.

Cases where (3) could be useful are those where extensive electron transfer in one direction is mandated. Since strong ionic bonding would result, we cannot estimate the final bond strengths. But eq 3, being an initial driving force, should be related to energy barriers to reaction. A large positive value for ΔN would lower

(19) Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811–6814.
(20) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; pp 60–65.
(21) Jørgensen, C. K. *Inorg. Chem.* **1964**, *3*, 1201–1202.
(22) Jørgensen, C. K. *Struct. Bonding (Berlin)* **1966**, *3*, 234–248.
(23) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49–213.
(24) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*, North-Holland/American Elsevier: Amsterdam/New York, 1971; p 347.

(25) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109–6114.
(26) Pearson, R. G.; Gray, H. B. *Inorg. Chem.* **1963**, *2*, 358–363.
(27) Irving, H.; Williams, R. J. P. *Nature (London)* **1948**, *162*, 146–148.
(28) Williams, R. J. P. *Discuss. Faraday Soc.* **1958**, *26*, 123–128.

the barrier, and a negative value would mean a contribution to the barrier.

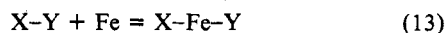A suitable example is the oxidative-addition reaction of transition-metal atoms. For iron as the metal

$$X-Y + Fe = X-Fe-Y \qquad (13)$$

Table V shows the values of ΔN calculated, from eq 3 and the data in Tables II and III, for the reaction of an iron atom with a number of common X–Y molecules. The results are in remarkable agreement with expectations. Large positive values of ΔN are calculated for facile, fast reactions and negative values for slow or unobservable reactions. These statements are based upon experimental results for iron atoms in low-temperature matrices,[29,30] and on rate studies of various X–Y molecules with suitable low-valent metal complexes.[31]

Naturally other factors that influence rates of reaction cannot be ignored. For example, the rate of addition of HX molecules is some 10^7 times faster than the addition of CH_3X. This refers to the concerted addition of molecular HX to $IrCl(CO)[P(C_6H_5)_3]_2$ in solvents such as toluene.[32] Clearly steric hindrance is much greater in CH_3X than in HX and accounts for the slower reaction in great part.

In addition to changing the substrate, we can also change the metal atom. Metals of lower electronegativity than iron should be more reactive, and metals of higher χ should be less reactive, up to a point. If χ for the metal becomes comparable to χ for the atoms or radicals X and Y, then electron transfer in one direction is not required, and eq 3 is no longer a good criterion.

The experimental results are in good agreement, though not complete. For example, in very low temperature matrice, Sc, Ti, and V react with H_2O, whereas Fe, Cu, and Ni do not react.[30] At 77 K Cr reacts, but Mo and W do not.[33] At 77 K, Ti and Zr react with i-C_4H_{10}, but Fe, Cr, Mn, Ni, Co, Cu, and Mo do not react.[34] Both V and W show some reactivity.

In oxidative addition of alkyl bromides and iodides to metal complexes, the complexes of the third transition series are usually the most reactive.[35] These are examples of the case where the electronegativity of the metal is nearly equal to that of X and Y. Hence, the bonds are not ionic, and electron transfer in one direction is not needed.

The addition of H_2 occurs more readily for the third transition series than for the second. The rates are predicted to be in the order Ni $\sim$ Pt $\gg$ Pd.[36] Similar behavior is expected for oxidative cleavage of hydrocarbons. There is a special reason for strong thermodynamic bonding of H^- and R^-, which will be discussed later.

Equation 3 may also be used to predict trends in bond energies, if certain conditions are met. Electron transfer in one direction should dominate, but ΔN should be small. Also a series of ligands or of metals should be compared where the interacting orbitals remain nearly constant or change in a systematic manner. One example is the binding of CO to neutral transition-metal atoms in their low-spin states.[37] Invariably CO is more electronegative than the metal atom, and therefore π-bonding is predominant. The value of ΔN from (3) measures the excess of π-bonding over σ-bonding. Good agreement is found between ΔN values for

Table VI. Electron Transfer in Reactions of Olefins with Low-Spin Nickel Atoms

olefin	$K_{eq}{}^a$	χ	η	ΔN^b
maleic anhydride	4×10^8	6.3	4.7	0.20
trans-NCCH=CHCN	1.6×10^8	6.2^c	5.6	0.17
CH_2=CHCN	4.0×10^4	5.4	5.6	0.12
C_2H_4	250	4.4	6.2	0.053
CH_2=CHF	90	4.2	6.1	0.042
styrene	10	4.1	4.4	0.045
CH_3CH=CH_2	0.5	3.9	5.9	0.024
trans-2-butene	2.7×10^{-3}	3.5	5.6	0.000
cyclohexene	3.5×10^{-4}	3.4	5.5	−0.006
$(CH_3)_2C$=$CHCH_3$	3.0×10^{-4}	3.3	5.5	−0.013
$Ni(d^{10})$		3.5	2.3	
$Pd(d^{10})$		4.8	3.5	
$Pt(d^{10})$		5.3	2.9	

^{a} Reference 41. ^{b} Calculated from eq 3. $^c I$ from: Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 5453–5459.

different metals and the mean bond strength of the metal carbonyls.

BF_3 is invariably found to be a weaker Lewis acid than either BCl_3 or BBr_3, a somewhat surprising result.[38] Consider the reactions with trimethylamine, for which some estimated bond energy data exist.[39]

$$(CH_3)_3N + BX_3 = (CH_3)_3N:BX_3 \qquad (14)$$
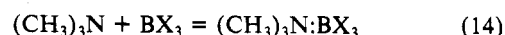
| BX_3	$-\Delta H$, kcal mol	ΔN
BF_3	19	0.15
BCl_3	37	0.19
BBr_3	45	0.19

The calculated values of ΔN show there is some reluctance to adding electrons to planar BF_3. But the difference is too small to account for the large change in ΔH. Therefore the energy needed to pyramidalize the acceptor molecule must also play some role. The two factors are related, since strong π-bonding in planar BF_3 leads to both the negative electron affinity and a reluctance toward becoming nonplanar.[40]

Tolman has used frontier orbital theory to rationalize the bonding of various olefins to Ni(0).[41] The data are the equilibrium constants in benzene for

$$NiL_3 + \text{olefin} \rightleftharpoons NiL_2(\text{olefin}) + L \quad K_{eq} \qquad (15)$$

where L is a phosphite ligand.

Table VI shows values of K_{eq} for various olefins, together with their χ and η values. Assuming that χ and η for NiL_2 are the same as for low-spin Ni, the values of ΔN have also been calculated by using (3) and are shown in Table VI. These are for

$$NiL_2 + \text{olefin} \rightleftharpoons NiL_2(\text{olefin}) \qquad (16)$$
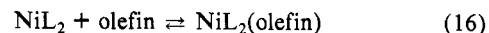
which is related to (15) by a constant factor.

The calculated ΔN's correlate very well with the equilibrium constants. Large positive values mean strong bonding, with π-bonding from metal to olefin dominating. Negative values mean that σ-bonding to the metal is greater than π-bonding. Clearly σ-bonding is less effective than π-bonding.

Ethylene has more π- than σ-bonding, in agreement with theoretical calculations for the reaction of $Ni(PH_3)_2$ with C_2H_4.[42]

(29) Parker, S. F.; Peden, C. F. H.; Barrett, P. H.; Pearson, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1304–1308.

(30) Kaufman, J. W. Ph.D. Thesis, Rice University, 1982.

(31) Halpern, J.; Chock, P. B. *J. Am. Chem. Soc.* **1966**, *88*, 3511–3513. Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577–7585. Collman, J. P.; McLaury, M. R. *Ibid.* **1974**, *96*, 3019–3020.

(32) Walper, W.; Kelm, H. *Z. Phys. Chem. (Munich)* **1978**, *113*, 207–217.

(33) Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *4*, 195–198.

(34) Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* **1979**, *101*, 1320–1322.

(35) Pearson, R. G. *Adv. Chem. Series* **1987**, *No. 215*, 233–234. Gold may be an exception.

(36) Blomberg, M. R. A.; Siegbahn, P. E. M. *J. Chem. Phys.* **1983**, *78*, 986–987 & 5682–5692. Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609–622.

(37) Pearson, R. G. *Inorg. Chem.* **1982**, *23*, 1675–1679.

(38) Shriver, D. F.; Swanson, B. *Inorg. Chem.* **1971**, *10*, 1354–1366.

(39) Rothe, E. W.; Mathews, B. P.; Reck, G. P. *Inorg. Chem.* **1980**, *19*, 829–834.

(40) Tossell, J. A.; Moore, J. H.; Olthoff, J. K. *Int. J. Quantum Chem.* **1986**, *29*, 1117–1124.

(41) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780–2789. Since the electron affinities of the olefins were not known at that time, Tolman estimated their relative values from the $\pi \rightarrow \pi^*$ UV spectra of the olefins. His estimates are in good agreement with the A values in Table VI.

(42) (a) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292–2297. (b) Ziegler, T. *Ibid.* **1985**, *24*, 1547–1552.
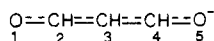
The calculated values of ΔN for the reactions of low-spin Pt and Pd are −0.0495 and −0.0206, compared with that for Ni, +0.053. This agrees with the theoretical results[42b] for binding energies, Ni > Pt > Pd, especially if π-bonding is stronger than σ-bonding.

If we change to more electrongative molecules, such as Br_2 or $Hg(CF_3CO_2)_2$, the situation is reversed.[43] Now σ-bonding is more important than π-bonding. The effect of substituents on the stability of ethylene complexes is just the opposite of that seen in Table VI.

Thermodynamically, the third transition series binds most ligands more strongly than the second.[44] For the ligands H^- and R^-, the binding is also stronger than that for the first transition series.[45] The reason for this is clear: these ligands are pure σ-bonders, and Pt has the advantage over Ni, and so on. The advantage must lie largely in the special stability of the 6s orbital, which in turn is due to relativistic effects.[46]

For polyatomic anion ligands, it is usually more important to know the local softness, $\bar{\sigma}$, than the global softness, σ. Equation 10 shows that we need to know the wave function of the anion, or at least of the HOMO. While this may appear daunting, there are two factors that help considerably. One is that wave functions have already been calculated for thousands of molecules and ions, and the results are available in tabulations and bibliographies.[47] The second is that usually only approximate wave functions are needed, such as the results of a Huckel calculation.[48]

For example, consider the anion of malonaldehyde, a model for β-diketone anions.

$$\underset{1}{O} \doteq \underset{2}{CH} \doteq \underset{3}{CH} \doteq \underset{4}{CH} \doteq \underset{5}{O}^-$$

The HOMO is a π-type orbital, for which a Huckel calculation gives[49]

$$\phi = 0.435\psi_1 - 0.286\psi_2 - 0.677\psi_3 - 0.2869\psi_4 + 0.435\psi_5 \quad (17)$$

Squaring this to obtain ρ, we find 0.458 for C_3^2, and 0.184 for C_1^2 and C_5^2. Thus the central carbon is the soft site, and the oxygen atoms are much harder. Overall, the oxygens are more negative than the carbon. Hard acids such as H^+, Al^{3+}, and Mg^{2+} will bind to oxygen, as will most transitions-metal ions. But Pt^{2+}, Pd^{2+}, and Hg^{2+} may bind to carbon, as will Br^+ and HO^+.

Even without calculation, we can often make reasonable predictions. In Table IV we see that $C_6H_5O^-$ and $C_6H_5S^-$ are not very different in their values for σ, though the latter is softer. But the HOMO of $C_6H_5O^-$ is known, and has coefficients at the *ortho* and *para* ring carbons that are almost as large as that an oxygen.[50] This delocalization is conventionally shown by resonance structures such as
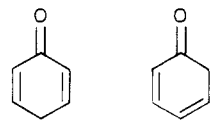
Since sulfur is less efficient at π-bonding to carbon than oxygen is, we can be fairly sure that $C_6H_5S^-$ has a HOMO that is more concentrated on S. Therefore it is locally very soft at sulfur, whereas $C_6H_5O^-$ is locally much harder at oxygen.

The assumption that attack by reagents occurs at sites where the electron density is large (HOMO) or at sites where the hole density is large (LUMO) is also part of the general frontier orbital theory of chemical reactivity.[51] But the reasons are quite different. In frontier orbital theory, these sites give the best overlap between interacting orbitals. In density functional theory, these sites are those where the original electron density can be changed with the least expediture of energy. Fortunately, both explanations arrive at the same conclusion.

(43) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240–7252; **1982**, *104*, 7599–7609.
(44) Johnston, R. D.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1973**, *10*, 247–251. Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905–3912.
(45) Pearson, R. G. *Chem. Revs.* **1985**, *85*, 41–49. Norton, J. R.; Sullivan, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263.
(46) See: Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271–276.
(47) Richards, W. G.; Walker, T. E. H.; Hinkley, R. K. *A Bibliography of ab initio Molecular Wave Functions*; Clarendon: Oxford, England, 1971. Supplements published in 1974, 1978, and 1981. Ohno, K.; Morokuma; K. *Quantum Chemistry, Literature Data Base*, Elsevier: Amsterdam, 1982. Supplements published annually in *J. Mol. Struct.* Streitwieser, A.; Brauman, J. I. *Supplementary Tables of Molecular Orbital Calculations*, Pergamon: Oxford, England, 1965; Vol. I and II; Snyder, L. C.; Basch, H. *Molecular Wave Functions and Properties*, Wiley: New York, 1972; Jorgensen, W. L., Salem, L. *The Organic Chemists Book of Orbitals*; Academic: New York, 1973.
(48) For example, see: Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

(49) Haddon, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 1807–1811.
(50) Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 818–820.
(51) Klopman, G. *Chemical Reactivity and Reaction Paths*; Wiley: New York, 1974; Chapter 4.
(52) Moore, C. E. "Ionization Potentials and Ionization Limits"; Natl. *Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*); 1970, NSRDS-NBS 34.
(53) Drzaic, P. S.; Marks, J.; Brauman, J. S. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1984; Vol. 3, Chapter 21.
(54) De Puy, C. H.; Bierbaum, V. M.; Darmrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053.