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The Calculation of Atomic Charges by an Electronegativity Equalization Procedure

William L. Jolly* and Winfield B. Perry

Abstract

A procedure for calculating atomic charges based on the equalization of atomic orbital electronegativities has been extended to cover compounds containing any of the elements in the periodic table up to radon. Atomic charges calculated by this method correlate well with core electron binding energies of compounds of silicon, sulfur, chlorine, chromium, germanium, bromine, xenon, and tungsten.

Introduction

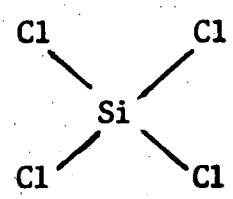
In a previous study, an electronegativity equalization procedure for calculating atomic charges of compounds of the first row of the periodic table was calibrated using experimental 1s electron binding energies for carbon, nitrogen, oxygen, and fluorine.[1] We now show that this method can be extended to the remainder of the periodic table, and that atomic charges calculated by this method may be used to correlate core electron binding energy data for volatile compounds of silicon, sulfur, chlorine, chromium, germanium, bromine, xenon, and tungsten. In our earlier paper, we discussed the theoretical justification of the general procedure. In this paper, we describe the method for making calculations, and discuss the theoretical aspects only of the novel features introduced to account for the heavier elements of the periodic table.

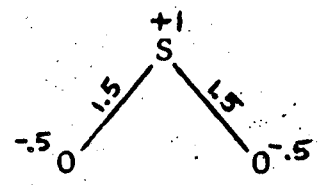
The Calculational Procedure

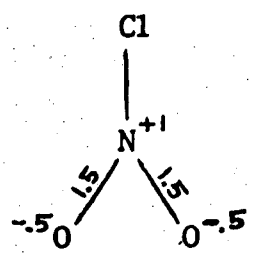
In this section we give detailed stepwise instructions, without justification or rationalization, for the calculation of atomic charges in molecules. The justification and rationalization of the procedures are discussed later.

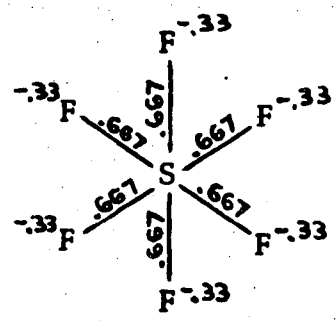
Step 1. A valence bond structure, or hybrid of several such structures, is drawn for the compound. If possible, each nontransition element atom heavier than helium should have just an octet of valence electrons; only s and p valence orbitals should be used for these atoms. Bond orders are assigned to the bonds, and formal charges[2] are assigned to the atoms. Several examples of valence bond structures for nontransition element compounds

follow. (In these and following examples, bond orders of unity and formal charges of zero are omitted.)



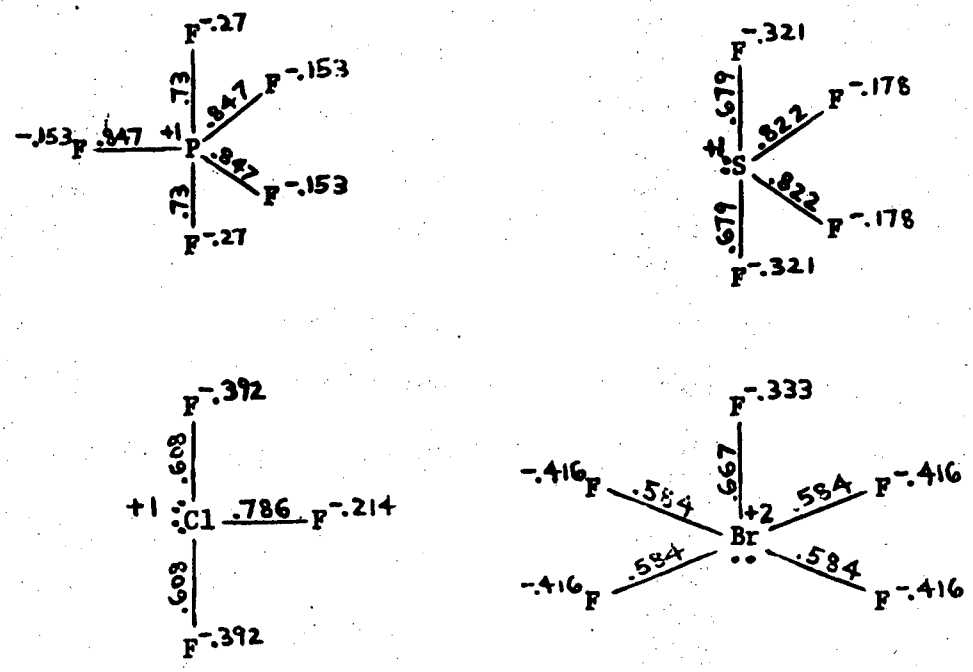






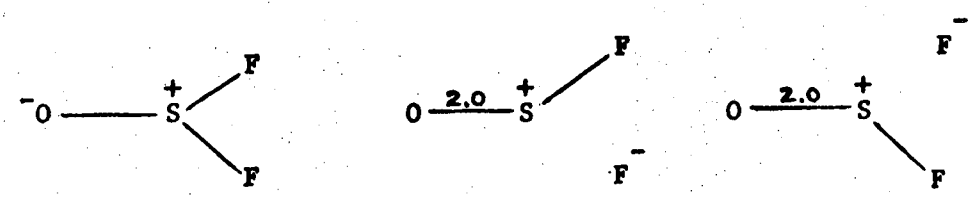
When nonequivalent resonance structures can be written for a molecule, these structures must be suitably weighted to permit the calculation of average bond orders and formal charges. Structures having adjacent atoms with finite formal charges of the same sign are forbidden, unless there is no acceptable alternative. Structures without formal charges are weighted much more than structures with formal charges. We can now offer no general rule for the relative weighting of such structures; in the absence of calibration data such as core electron binding energies, we recommend complete neglect of the formal-charged structures. Similarly, structures with widely distributed π bonding are weighted more than those with localized π bonding. Thus we have assigned relative weights of 2 and 1 to the structures $^{-}N{=}\overset{+}{N}{=}O$ and $N{\equiv}\overset{+}{N}{-}O^{-}$, respectively.[1]

In the case of "hypervalent" molecules in which the central atom is bonded to two sterically distinct types of ligands (as in PF_5, SF_4, ClF_3, and BrF_5), the bonding electrons must be appropriately apportioned between the two types of bonds. In the case of a trigonal bipyramidal molecule such as PF_5, we assign bond orders of 0.73 and 0.847 to the axial and equatorial bonds, respectively. We assume that nonbonding orbitals, such as those on the central atoms of SF_4 and ClF_3, are completely occupied by pairs of electrons. Thus, in the hypothetical conversion of PF_5 into SF_4 and ClF_3 by the replacement of equatorial fluorines by lone pairs, we must withdraw some electron density from the remaining bonds. Our recipe is to withdraw twice as much electron density from axial bonds as from equatorial bonds. In this way we obtain axial and equatorial bond orders of 0.679 and 0.822, respectively, for SF_4, and 0.608 and 0.786, respectively, for ClF_3. In SF_6, all the bond orders are 0.667. In the hypothetical conversion of SF_6 into BrF_5, we assume that the nonbonding orbital is filled by withdrawal of electron density only from the adjacent, basal, bonding orbitals. Thus we obtain apical and basal bond orders of 0.667 and 0.584, respectively, in BrF_5. The structures for these molecules are indicated below.

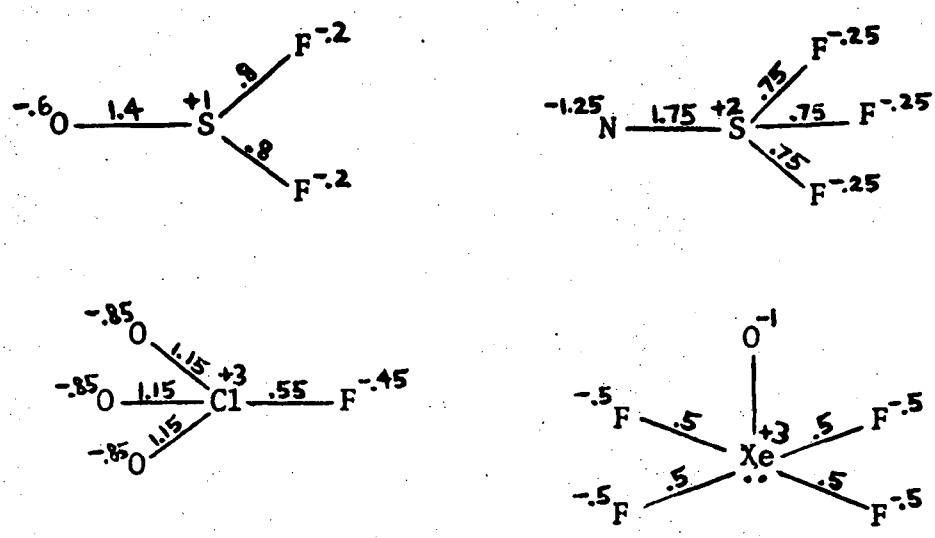


By analogous reasoning, we obtain bond orders of 0.5 in XeF_2, XeF_4, and XeF_6.

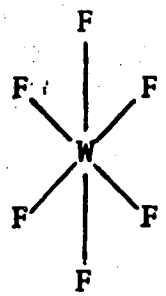
Hyperconjugated ("no-bond") resonance structures are given substantial weight when the only alternative structure requires an atom to be simultaneously bonded to an atom with a negative formal charge and a fluorine atom. For example, the following structures are written for thionyl fluoride.

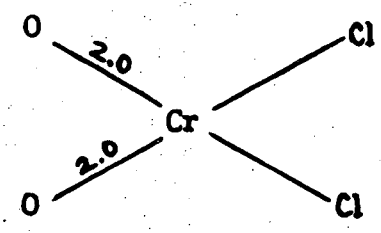


Similar resonance structures can be written for NSF_3, ClO_3F, and $XeOF_4$. The hybrid structures for those four molecules which fit the binding energy data and which can be used as models for other hyperconjugated molecules are shown below.

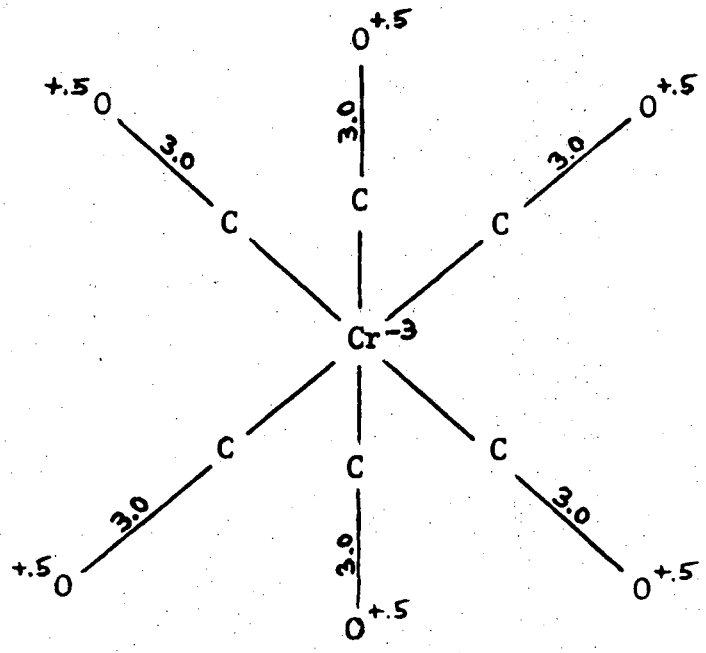


In the case of a transition metal atom or ion, we assume that the number of orbitals available to accept electrons from ligands is equal to the number of vacant s, p, and d valence orbitals. In general, the available s and p orbitals are completely involved in bonding. Vacant d orbitals of σ symmetry are used to the extent necessary to provide each ligand, as far as possible, with a full σ bond. Vacant d orbitals of π symmetry are used in $p\pi \rightarrow d\pi$ bonding only if a reduction in formal charges results. Thus, in WF_6 and CrO_2Cl_2, although the +6 metal ions each have nine available orbitals, we assume that only six of these are used, as shown by the following structures.





When $d\pi \rightarrow p\pi$ back-bonding can occur in a transition metal complex, we assume that it occurs as far as possible, consistent with the number of metal $d\pi$ electrons and empty ligand $p\pi$ orbitals available. Formal charges are modified in accordance with the back-bonding, but bond orders are assumed to be the same as those in the structures without back-bonding. Thus for $Cr(CO)_6$ we write



Step 2. It is necessary to assign an orbital hybridization (i.e., the fractional s character) for each σ bond of each nontransition element in the compound. This assignment is necessary because the s and p electronegativities of such elements are different. However, for the transition elements, we have made no distinction between the valence s,p, and d electronegativities (an average electronegativity is used), and therefore it is unnecessary to assign hybridizations for such elements. We define S_{nm} as the fractional s character of the σ orbital used by atom n in the bond to atom m. For any atom for which the total ligancy (i.e., the number of complete lone pairs[3] plus the number of other atoms bonded to that atom) is four or less, we assume that S_{nm} is the same for each bond and equal to the reciprocal of the total ligancy. Thus $S_{nm} = 0.25$ for the central atoms in GeH_4, NSF_3, OSF_2, and H_2S, and $S = 0.33$ and 0.5, respectively, for the middle atoms in SO_2 and CO_2. When the total ligancy is five (trigonal bipyramid type molecules), one p orbital must be assigned to the two axial bonds, and two p orbitals must be assigned to the three equatorial orbitals. For the axial bonds, $S_{nm} = (N_{ax} - 0.5)/N_{ax}$, where N_{ax} is the axial bond order; for the equatorial bonds, $S_{nm} = (N_{eq} - 0.667)/N_{eq}$, where N_{eq} is the equatorial bond order. When the total ligancy is six (octahedral-type molecules), one p orbital must be assigned to the pair of orbitals along each axis. Thus for any bond, $S_{nm} = (N-0.5)/N$, where N is the bond order.

Step 3. For each bond (or each set of equivalent bonds) in the compound, an equation of the following type is set up.

$$\frac{7.3(h_m + h_n)}{(N_{nm})^{0.7}} q_{mn} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} =$$

$$x(p)_n - x(p)_m + \frac{S_{nm}}{(1 + \Pi_{nm})^{0.7}} \left[x(s)_n - x(p)_n \right]$$

$$- \frac{S_{mn}}{(1 + \Pi_{nm})^{0.7}} \left[x(s)_m - x(p)_m \right] + c_n h_n F_n - c_m h_m F_m$$

In this equation, the subscripts n and m refer to the two atoms of the bond. The parameters x(s), x(p), and h are listed in Table I for most of the elements in the periodic table. The parameter c has the value 3.1 for hydrogen, helium, and the elements of the first row of the periodic table. For second-row elements, c = 2.5, and for elements beyond the second row, c = 1.6. The terms N_{nm} and Π_{nm} stand for the bond order and the π bond order, respectively, and F stands for the atomic formal charge. It should be noted that, when $N_{nm} > 1$, $N_{nm} = 1 + \Pi_{nm}$. The quantity q_{nm} is the negative charge transferred from atom n to atom m. (Thus $q_{nm} = -q_{mn}$.) The term $\sum_{i \neq m} q_{ni}$ is the sum of the negative charges transferred from atom n to all the atoms bonded to atom n except atom m, and $\sum_{i \neq n} q_{mi}$ is the analogous term for atom m.

Upon completion of step 3 for a molecule containing j different types of bonds, one obtains j linear equations with j unknown q values.

Table I

Atomic Parameters Used in Electronegativity Equalization Calculations[a]

Atom	x(s)	x(p)	h
H	2.21		1.285
He	(2.75)		(1.50)
Li	0.84	0.47	0.46
Be	2.15	0.82	0.63
B	3.25	1.26	0.84
C	4.84	1.75	1.12
N	6.70	2.65	1.21
O	8.98	3.49	1.53
F	10.31	3.90	1.70
Ne	(11.44)	(4.40)	(1.90)
Na	0.74	0.32	0.467
Mg	1.77	0.56	0.53
Al	2.69	1.11	0.585
Si	3.88	1.82	0.737
P	4.62	2.23	1.075
S	5.12	2.63	0.982
Cl	6.26	2.95	1.11
Ar	(9.00)	(4.20)	(1.50)
K	0.77	0.38	0.288
Ca	1.36	0.42	0.452
Sc	1.20		(0.50)
Ti	1.32		(0.50)

Table I, contd.

Atom	x(s)	x(p)	h
V	1.45		(0.50)
Cr	1.56		(0.50)
Mn	1.60		(0.50)
Fe	1.64		(0.50)
Co	1.70		(0.50)
Ni	1.75		(0.50)
Cu	1.75		(0.50)
Zn	1.66		(0.50)
Ga	3.18	1.22	0.632
Ge	4.06	2.09	0.680
As	3.84	2.40	0.868
Se	4.97	2.56	1.240
Br	5.94	2.62	0.940
Kr	(8.00)	(4.00)	(1.40)
Rb	0.50	0.54	0.418
Sr	1.26	0.34	0.424
Y	1.11		(0.50)
Zr	1.22		(0.50)
Nb	1.23		(0.50)
Mo	1.30		(0.50)
Tc	1.36		(0.50)
Ru	1.42		(0.50)
Rh	1.45		(0.50)
Pd	1.35		(0.50)

Table I, contd.

Atom	x(s)	x(p)	h
Ag	1.42		(0.50)
Cd	1.46		(0.50)
In	2.83	0.92	0.602
Sn	3.80	2.08	0.435
Sb	4.22	2.36	0.871
Te	4.81	2.77	1.187
I	5.06	2.52	0.915
Xe	(7.60)	(3.80)	(1.20)
Cs	(0.40)	(0.40)	(0.40)
Ba	(1.15)	(0.25)	(0.40)
La	1.08		(0.50)
Ce	1.06		(0.50)
Pr-Sm	1.07		(0.50)
Eu	1.01		(0.50)
Gd	1.11		(0.50)
Tb-Ho	1.10		(0.50)
Er,Tm	1.11		(0.50)
Yb	1.06		(0.50)
Lu	1.14		(0.50)
Hf	1.23		(0.50)
Ta	1.33		(0.50)
W	1.40		(0.50)
Re	1.46		(0.50)
Os	1.52		(0.50)

Table I, contd.

Atom	x(s)	x(p)	h
Ir	1.55		(0.50)
Pt	1.44		(0.50)
Au	1.42		(0.50)
Hg	1.44		(0.50)
Tl	(2.44)	(0.94)	(0.60)
Pb	(2.35)	(1.28)	(0.50)
Bi	(2.58)	(1.44)	(0.80)
Po	(3.06)	(1.76)	(1.00)
At	(3.90)	(1.96)	(0.90)
Rn	(6.00)	(3.00)	(1.00)

[a]Values were taken from Refs. 6 and 7; parenthesized values are estimates.

Step 4. The equations are solved for the q values, and the charge Q on each atom is calculated using the general relation

$$Q_n = F_n + \Sigma q_{ni}$$

We shall illustrate the method of calculation with two examples, OSF_2 and WF_6, for which we have already given the valence bond structures. In OSF_2 both the sulfur and fluorine atoms have total ligancies of 4, corresponding to a value of 0.25 for S_{FS}, S_{SF}, and S_{SO}. The oxygen atom has a total ligancy of 3, corresponding to $S_{OS} = 1.3$. Thus for OSF_2 we obtain the following equations.

$$\frac{7.3(1.53 + 0.982)}{1.4^{0.7}} q_{OS} + 1.53 \times 0 - 0.982 \times 2q_{SF} =$$

$$2.63 - 3.49 + \frac{0.25}{1.4^{0.7}}(5.12 - 2.63) - \frac{1/3}{1.4^{0.7}}(8.98 - 3.49)$$

$$+ 2.5 \times 0.982 \times 1 - 3.1 \times 1.53(-0.6)$$

$$\frac{7.3(1.70 + 0.982)}{0.8^{0.7}} q_{FS} + 1.70 \times 0 - 0.982(q_{SF} + q_{SO}) =$$

$$2.63 - 3.90 + \frac{0.25}{1^{0.7}}(5.12 - 2.63) - \frac{0.25}{1^{0.7}}(10.31 - 3.90)$$

$$+ 2.5 \times 0.982 \times 1 - 3.1 \times 1.70(-0.2)$$

These reduce to the following pair of equations

$$14.490\, q_{OS} - 1.964\, q_{SF} = 3.487$$

$$0.982\, q_{OS} - 23.871\, q_{SF} = 1.259$$

From these we readily calculate $q_{OS} = 0.2348$ and $q_{SF} = -0.0431$, and then $Q_S = +0.6790$, $Q_O = -0.3652$, and $Q_F = -0.1569$.

In WF_6, the fluorine atoms have total ligancies of 4, corresponding to $S_{FW} = 0.25$. An average electronegativity value is used for tungsten, and therefore it is unnecessary to evaluate S_{WF}. (In effect, we assume $x(s) = s(p)$.) Thus we obtain the following equation.

$$\frac{7.3(1.70 + 0.50)}{1^{0.7}} q_{FW} + 1.70 \times 0 - 0.50 \times 5q_{WF} =$$

$$1.40 - 3.90 - \frac{0.25}{1^{0.7}} (10.31 - 3.90) + 1.6 \times 0.50 \times 0$$

$$-3.1 \times 1.70 \times 0$$

From this equation we readily calculate $q_{WF} = 0.2210$, $Q_W = +1.326$, and $Q_F = -0.2210$.

We have written a Fortran IV computer program, CHELEQ, for making these atomic charge calculations; a printout of the program will be sent upon request.

Correlation of Core Binding Energies

Atomic charges calculated by the procedure which we have outlined can be used to correlate core binding energies by the point charge potential model equation.[4]

$$E_B = kQ + V + \ell$$

In this equation, E_B is the binding energy for a particular core level in a particular atom (the "ionized" atom), Q is the charge of the ionized atom, V is the coulomb potential energy at the site of the ionized atom due to the other charged atoms of the molecule, and k and ℓ are empirical constants, determined by least-squares fitting of the binding energies for a given element to the calculated Q and V values.

We have correlated 101 core binding energies for 56 different gaseous compounds containing elements heavier than neon. These binding energies include 11 silicon 2p binding energies, 11 sulfur $2p_{3/2}$ binding energies, 15 chlorine $2p_{3/2}$ binding energies, 3 chromium $2p_{3/2}$ binding energies, 8 germanium $3p_{3/2}$ binding energies, 10 bromine $3d_{5/2}$ binding energies, 5 xenon $3d_{5/2}$ binding energies, 2 tungsten $4f_{7/2}$ binding energies, 20 fluorine 1s binding energies, 10 oxygen 1s binding energies, 1 nitrogen 1s binding energy, and 5 carbon 1s binding energies. The compounds were

selected to cover a wide range of types of bonding and atomic charges.

The compounds, the appropriate atomic charges, and the experimental and calculated binding energies are listed in Table II. The least-squares evaluated parameters, k and ℓ, and the corresponding standard deviations and correlation coefficients for various elements are listed in Table III. The data for sulfur and chlorine are presented graphically in Figures 1 and 2, respectively, as plots of E_B (expt) vs E_B (calc). All in all, the correlations, as measured by the standard deviations and the correlation coefficients, are quite good and attest the usefulness of the charge calculation method. By a simple interpretation of the potential model equation it can be shown that the empirical k values should be inversely proportional to the radii of the valence electron shells.[4] One might expect that valence shell radii would be proportional to the corresponding covalent radii, and, indeed, we have found that the k values obtained from our binding energy correlations are fairly well represented by the expression $17.5/r_{cov}$, where r_{cov} stands for the covalent radius taken from the table given by Huheey.[5] The empirical k values may be compared with the values calculated from this expression in Table III. It should be noted that the multiplicative constant 17.5 is not much greater than the value 14.4, which would be expected if the valence sheel radius were the same as the covalent radius.

Table II

Experimental and Calculated Core Binding Energies

Compound	Q	E_B, eV[a]	
		Exptl	Calcd[m]
Silicon			
$Si(CH_3)_4$	0.035	105.82[b]	107.05
Si_2H_6	-0.023	106.56[c]	106.65
SiH_3CH_3	-0.013	106.68[b]	106.70
SiH_4	-0.029	107.14[b]	106.64
$(SiH_3)_2O$	0.099	107.67[b]	107.16
SiH_3Br	0.057	107.94[b]	107.53
SiH_3Cl	0.071	107.97[b]	107.62
$SiCl_3CH_3$	0.284	109.11[c]	109.42
$SiBr_4$	0.308	109.59[b]	109.92
$SiCl_4$	0.368	110.25[b]	110.29
SiF_4	0.633	111.65[b]	111.40
Sulfur			
CS_2	-0.042	169.80[d]	170.47
C_4H_4S	-0.063	169.90[e]	169.74
H_2S	-0.119	170.20[d]	169.82
OCS	-0.028	170.60[f]	171.00
S_2Cl_2	0.034	171.40[g]	171.04
SO_2	0.565	174.80[d]	174.77
OSF_2	0.679	176.20[d]	175.90

Table II, contd.

Compound	Q	E_B, eV Exptl.	E_B, eV Calcd.
Sulfur (contd.)			
NSF_3	0.824	176.80[g]	176.95
SF_4	0.788	177.60[h]	177.18
SF_5Cl	1.072	179.10[g]	179.85
SF_6	1.143	180.40[d]	180.07
Chlorine			
GeH_3Cl	-0.096	205.50[b]	205.76
SiH_3Cl	-0.109	206.05[b]	205.75
CH_3Cl	-0.081	206.07[b]	206.06
CrO_2Cl_2	-0.156	206.07[c]	206.93
$GeCl_4$	-0.079	206.42[b]	206.75
S_2Cl_2	-0.034	206.64[g]	206.65
ICl	-0.042	206.68[i]	206.49
$SiCl_4$	-0.092	206.77[b]	206.77
CCl_4	-0.064	206.84[b]	206.97
HCl	-0.090	207.22[b]	206.40
SF_5Cl	-0.105	207.27[g]	207.74
Cl_2	0.000	207.64[b]	206.97
ClF	0.084	208.21[i]	207.71
ClF_3	0.746	213.02[i]	213.74
ClO_3F	1.147	216.02[j]	215.70

Table II, contd.

Compound	Q	E_B, eV Exptl.	E_B, eV Calcd.
Chromium			
$Cr(CO)_5C(OCH_3)CH_3$	-0.970	581.40[k]	581.53
$Cr(CO)_6$	-1.004	582.22[k]	582.10
CrO_2Cl_2	0.916	587.64[k]	587.64
Germanium			
$Ge(CH_3)_4$	-0.030	127.90[b]	128.82
GeH_3CH_3	-0.076	128.78[b]	128.80
GeH_4	-0.091	129.19[b]	128.78
GeH_3Br	-0.003	129.90[b]	129.55
GeH_3Cl	0.012	130.09[b]	129.66
$GeBr_4$	0.250	131.21[b]	131.61
$GeCl_4$	0.316	131.98[b]	132.03
GeF_4	0.602	133.61[b]	133.41
Bromine			
GeH_3Br	-0.078	75.82[b]	76.07
IBr	-0.022	76.16[i]	76.58
CH_3Br	-0.066	76.25[b]	76.26
SiH_3Br	-0.093	76.30[b]	76.06
$GeBr_4$	-0.062	76.41[b]	76.77
$SiBr_4$	-0.077	76.64[b]	76.84
CBr_4	-0.050	76.74[b]	76.89

Table II, contd.

Compound	Q	E_B, eV Exptl.	E_B, eV Calcd.
Bromine (contd.)			
HBr	-0.076	77.19[b]	76.52
Br_2	0.000	77.23[b]	76.74
BrF_5	1.556	84.58[i]	84.58
Xenon			
Xe	0.000	0.00[1]	-0.34
XeF_2	0.840	2.87[1]	3.32
XeF_4	1.498	5.41[1]	5.91
$XeOF_4$	1.824	7.07[1]	6.54
XeF_6	2.006	7.64[1]	7.56
Tungsten			
$W(CO)_6$	-0.937	37.06[c]	
WF_6	1.326	46.38[c]	
Fluorine			
XeF_2	-0.420	690.72[1]	689.05
XeF_4	-0.374	691.60[1]	691.43
ClF_3(axial)	-0.299	691.74[h]	691.71
BrF_5(basal)	-0.328	692.31[i]	692.92
SF_4(axial)	-0.251	692.37[h]	692.74
$XeOF_4$	-0.341	692.58[1]	692.80

Table II, contd.

Compound	Q	E_B, eV Exptl.	E_B, eV Calcd.
<u>Fluorine</u> (contd.)			
XeF_6	-0.334	692.82[l]	693.46
OSF_2	-0.157	693.60[d]	694.13
PF_5(axial)	-0.212	693.70[h]	693.65
WF_6	-0.221	693.98[c]	694.17
ClF	-0.084	694.04[i]	693.70
BrF_5(apical)	-0.240	694.14[i]	694.66
ClF_3(equat.)	-0.146	694.27[h]	694.43
GeF_4	-0.150	694.38[b]	694.23
ClO_3F	-0.220	694.60[j]	694.14
SF_4(equat.)	-0.142	694.75[h]	694.74
SiF_4	-0.158	694.87[b]	694.45
PF_5(equat.)	-0.129	694.90[h]	695.28
SF_5Cl	-0.193	695.13[g]	694.72
NSF_3	-0.127	695.70[g]	695.55
<u>Oxygen</u>			
$(SiH_3)_2O$	-0.283	-4.64[b]	-5.82
CrO_2Cl_2	-0.301	-3.96[c]	-3.22
$Cr(C\overset{*}{O})_5C(OCH_3)CH_3$	-0.081	-3.91[k]	-2.60
$Cr(CO)_5C(\overset{*}{O}CH_3)CH_3$	-0.113	-3.91[k]	-2.96
OSF_2	-0.365	-3.70[d]	-4.68
$XeOF_4$	-0.470	-3.29[l]	-4.06

Table II cont.

Compounds	Q	E_B, eV Exptl.	E_B, eV Calcd.
Oxygen (contd)			
$W(CO)_6$	-0.064	-3.23[c]	-1.94
$Mo(CO)_6$	-0.064	-3.19[c]	-2.00
$Cr(CO)_6$	-0.062	-3.14[k]	-1.95
$FClO_3$	-0.309	-1.61[j]	-1.83
Nitrogen			
NSF_3	-0.443	406.20[g]	401.93
Carbon			
$Cr(CO)_6$	0.230	0.0[k]	0.0
$Cr(\overset{*}{C}O)_5C(OCH_3)CH_3$	0.212	-0.7[k]	-1.0
$Cr(CO)_5C(\overset{*}{O}CH)_3CH_3$	0.109	-1.4[k]	-0.3
$Cr(CO)_5C(OCH_3)\overset{*}{C}H_3$	0.043	-1.4[k]	-1.4
$Cr(CO)_5\overset{*}{C}(OCH_3)CH_3$	0.131	-2.7[k]	-1.8

[a]The listed binding energies are absolute values except in the case of the compounds of xenon, oxygen and carbon, for which relative values are listed. [b]W.B. Perry and W.L. Jolly, Inorg. Chem., 13, 000 (1974). [c]W.B. Perry and W.L. Jolly, unpublished data, 1973. [d]Ref. 4. [e]U. Gelius, C.J. Allan, G. Johansson, H. Siegbahn, D.A. Allison and K. Siegbahn, Phys. Scr., 3, 237 (1971). [f]C.J. Allan, U. Gelius, D. A. Allison, G. Johansson, H. Siegbahn and K. Siegbahn, J. Electron Spectr., 1, 131 (1972).

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Table III

Parameters of Potential Model Correlations

Element	k empirical	k calcd[c]	ℓ	Std. dev.	Correl. Coeff.
Si	16.54	14.8	106.84	0.51	0.957
S	17.43	17.2	170.61	0.43	0.994
Cl	17.63	17.7	206.97	0.48	0.986
Cr	11.34	12.5	584.90	0.12	0.999
Ge	15.42	14.3	129.32	0.47	0.968
Br	13.18	15.4	76.74	0.36	0.990
Xe	11.56	13.5	-0.34	0.46	0.989
W	12.05	11.7	40.86	-	-
F[a]	25.14	24.6	695.07	0.47	0.918
O[b]	20.60	24.0	-2.18	1.04	0.688

[a]The parameters correspond to a correlation of the 20 F 1s binding energies listed in Table II and 24 F 1s binding energies for compounds of the first row of the periodic table, listed in Ref. 1.

[b]The parameters correspond to a correlation of the 10 O1s binding energies listed in Table II and 21 O1s binding energies for compounds of the first row of the periodic table, listed in Ref. 1.

[c]Calculated from the empirical relation $k = 17.5/r_{cov}$.

Parameterization

The parameters x(s), x(p), and h, given in Table I, were obtained as far as possible from the orbital electronegativity tabulations of Hinze and Jaffé.[6] Corresponding electronegativity data for transition metals are either lacking or difficult to use because of uncertainties regarding orbital hybridizations in transition metal compounds. For these compounds we have chosen to ignore hybridization of the transition metal orbitals and to use an average zero-charge electronegativity value for all the bonding orbitals of a given transition metal. The transition metal electronegativities listed in Table I were calculated by the Allred-Rochow formula;[7] like the Hinze-Jaffé electronegativities, they are similar in magnitude to the Pauling values.[8] The parameters for the nontransition elements heavier than iodine are estimates; those for the rare gases are partly based on data of Fung.[9]

An increase in the formal charge of an atom by one unit causes the electronegativities of the atomic orbitals to increase by an amount proportional to the factor c. The increase in formal charge is always caused by the bonding of a Lewis acid to the atom, with conversion of a lone pair into a bonding pair. Thus the increase in electronegativity is caused, at least partly, by an increased positive field due to the polarization of a lone pair by

a Lewis acid. One would expect the electronegativity increase to be smaller the farther the atomic orbitals are from the lone pair, i.e., the larger the atom. Hence it is understandable that we found it necessary to use smaller values of c for elements of higher atomic number.

Rationale for the Treatment of Bonding

The procedure described in this paper for calculating atomic charges yields exactly the same results for compounds of the first row of the periodic table as were obtained by our earlier, more restricted procedure.[1] Special methods were introduced to account for bonding characteristics peculiar to the heavier elements and to give atomic charges which correlate well with core electron binding energies of the heavier elements by use of the potential equation. In a sense, these special methods are *ad hoc* inasmuch as they were introduced to fit the binding energies. However it happens that each method has a simple theoretical rationale and has, in most cases, considerable precedent. In the following paragraphs we discuss the rationale of the special methods.

Bond Order and Hybridization. We shall first discuss PF_5. Because of the trigonal bipyramidal symmetry of this molecule, no more than one phosphorus σp orbital can be involved in bonding the axial ligands, and no more than

two phosphorus σp orbitals can be involved in bonding the equatorial ligands. The only restrictions on the phosphorus s orbital are that it must be equally involved in the two axial bonds and equally involved in the three equatorial bonds. If there were complete participation of the s and p orbitals in bonding, with equal participation of the s orbital in all five bonds, the bond orders would be 0.7 and 0.867. Our assignment of 0.73 and 0.847 corresponds to a slight favoring of the axial orbitals by the s orbital. Such relative enhancement of s character in the digonal orbitals is consistent with the fact that the overlap integral of a pair of sp hybrid orbitals is greater than that of a pair of sp^2 hybrid orbitals.[10]

When an equatorial atom in a trigonal bipyramidal molecule is replaced by a nonbonding electron pair, it is necessary that bonding electrons be withdrawn from the other bonds to the central atom. Inasmuch as an s orbital is of lower energy than a p orbital, it is reasonable to assume that only s orbital density is removed from these bonds to fill the nonbonding orbital. And because an equatorial lone pair is repelled more strongly by axial bonding electrons than by equatorial bonding electrons,[11] it is reasonable to assume that twice as much electron density is withdrawn from the axial bonds as from the equatorial bonds. In the case of a molecule such as BrF_5, we assume that there is negligible repulsion between the lone pair and the axial bonding electrons and that all of the required electron density is withdrawn from the basal bonds.

Although there has been considerable speculation about the importance of valence-shell d orbitals in the bonding of second- and third-row nontransition elements, we ignore these orbitals for the following reasons: (a) there appears to be no strong evidence for the participation of valence-shell d orbitals in bonding,[12] (b) there are no reliable electronegativity values available for these orbitals, and (c) we have obtained good binding energy correlations with neglect of these orbitals.

Hyperconjugation. Hyperconjugation, or "no-bond" resonance, is justifiable when it effects a shift in negative formal charge from an atom of lower electronegativity to an atom of high electronegativity. Therefore it is reasonable to give significant weight to hyperconjugated structures in molecules such as OSF_2, NSF_3, ClO_3F, and $XeOF_4$. The formal charge distributions of the hybrid structures which fit the binding energy data suggest that the extent of hyperconjugation (a) is greater when the electronegativity difference between the atoms whose formal charges are changed is greater and (b) is proportional to the number of "donor" atoms and inversely proportional to the sum of the number of "donor" atoms and "acceptor" atoms. Althougth these results are reasonable, data for more molecules of this type must be examined before any firm rules can be established.

Transition Metal Compounds. There is abundant evidence that d orbitals are involved in the σ bonding of hexacoordinate transition metal complexes and that the metal-ligand bond order in such complexes is at least unity when the metal atom has two or more vacant d orbitals. Therefore

the assignment of a unit σ bond order to a complex such as WF_6 is justified. However the question of pπ→dπ bonding is somewhat problematical. There seems to be little doubt that π bonding is important in a complex such as CrO_4^{2-} in which the ligand atoms would otherwise have full -1 formal charges.[13] However there is some question as to the importance of π bonding in a complex such as WF_6 in which the ligand atoms would otherwise have no formal charge.[14] We have chosen to ignore π bonding in the latter case because of what seems to be a general tendency for the stability of structures in which formal charges are minimized and because of the structure of CrO_2F_2.[15] In the latter molecule, ∠O-Cr-O = 102.1° and ∠F-Cr-F = 118.9°. We interpret the difference in the angles as evidence for relatively great pπ→dπ bonding in the Cr-O bonds compared to the Cr-F bonds. (The bond angle corresponding to maximum pπ→dπ overlap is 90°). Our recipe for bond order yields bond order of 2 and 1 for the Cr-O and Cr-F bonds, respectively.

The main justification of our method for accounting for dπ→pπ back-bonding is that it gives reasonably good results in correlating the carbon and oxygen binding energies of metal carbonyl complexes. When further binding energy data become available for other types of complexes, it may be necessary to modify the method. The fact that our present method ignores the changes in bond order that accompany back-bonding is at least consistent with the fact that the average C-O bond distance in metal carbonyls is only about 0.01 Å longer than it is in free CO.[16]

Acknowledgment

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(2) The formal charge is the charge which the atom would have if the bonding electrons in each bond were equally apportioned between the pair of bonded atoms.

(3) A fractional number of lone pairs is associated with any atom for which the sum of the bond orders is nonintegral. For example, each fluorine atom in XeF_2 (with Xe-F bond orders of 0.5) has 3.5 lone pairs.

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Figure Captions

Figure 1. Plot of sulfur $2p_{3/2}$ binding energies vs. $kQ + V + \ell$ for sulfur compounds.

Figure 2. Plot of chlorine $2p_{3/2}$ binding energies vs. $kQ + V + \ell$ for chlorine compounds.

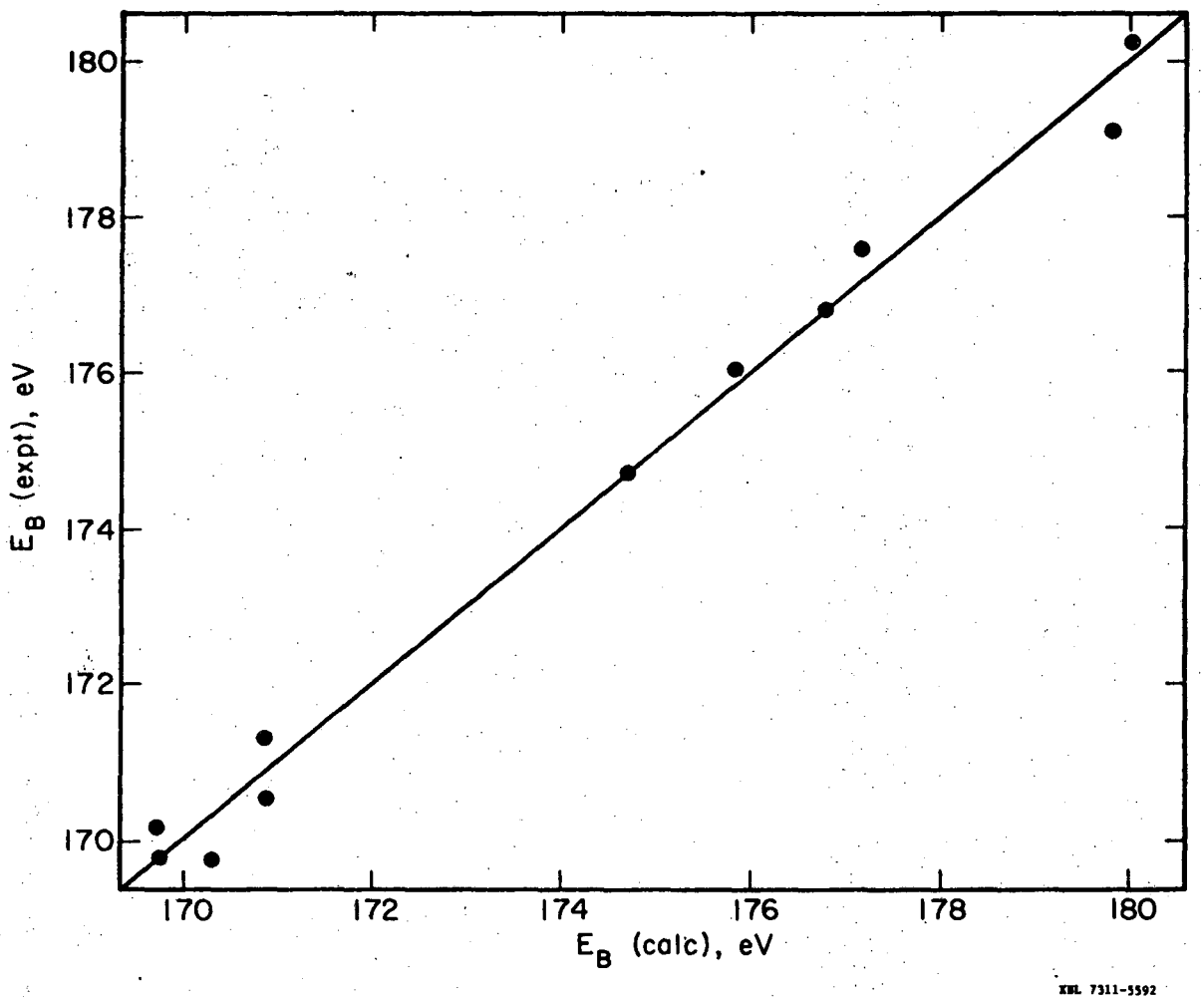
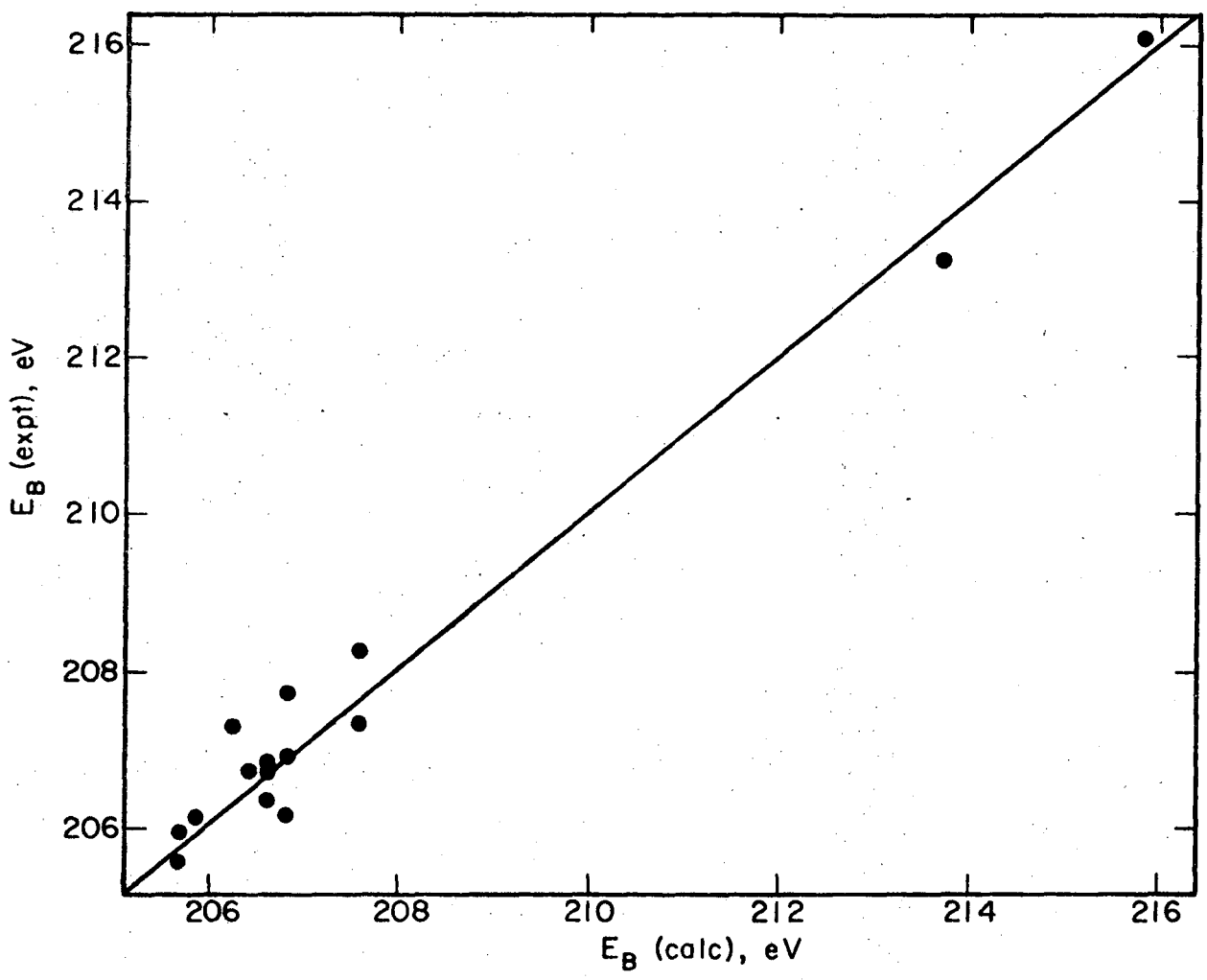

180
178
176
174
172
170
E_B (expt), eV
170
172
174
176
178
180
E_B (calc), eV
XBL 7311-5592

Fig. 1



XBL 7312-6758

Fig. 2

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