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Publication Date

1972-12-01

LBL-1417 c.2

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December 1972

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

LBL-1417 c.2

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A METHOD FOR ESTIMATING ATOMIC CHARGES BASED ON ELECTRONEGATIVITY PARAMETERS *

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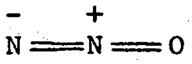
Introduction

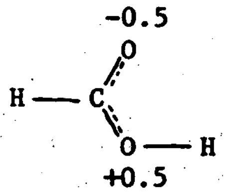
The value of X-ray photoelectron spectroscopy to chemists lies mainly in the fact that the measured core electron binding energies show shifts with changes in chemical environment. Several methods are available for predicting or correlating these chemical shifts in binding energy. Ab initio SCF calculations, either with or without the imposition of Koopmans' theorem, can give good results, but such calculations are expensive and are readily applied only to relatively simple molecules.[1-4] The thermodynamic method, based on the concept of equivalent cores, gives good results whenever the required thermodynamic data are available or calculable.[5-9] The method of correlation with atomic charge gives variable results, depending on the sophistication of the treatment.[4,10-12] Poor results are usually obtained when Pauling charges are employed, especially when the electrostatic potential at the site of the ionizing atom is ignored. Fair results are usually obtained when CNDO charges are employed with inclusion of the electrostatic potential term. In view of the importance of the concept of atomic charges to chemists, the atomic charge correlation method is potentially very valuable. We felt that it would be possible to devise a simple empirical method for estimating atomic charges that would correlate with binding energy data more closely than charges calculated by any other existing method. In this paper we describe the development and application of such a method.[13,14]

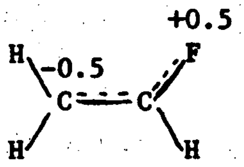
The Method

Our method for estimating the atomic charges of a molecule involves the estimation of the charges (q) transferred between the pairs of adjacently bonded atoms in the molecule, assuming an initial charge distribution corresponding to the hypothetical 100% covalent structure. The atomic charges of the 100% covalent structure are defined as the formal atomic charges[15] of the classical valence bond structure, or, when more than one structure can be written, as the average of all the acceptable resonance structures which can be written for the species. The structure is required, when possible, to be in accord with the Octet Rule. Thus we write the following 100% covalent structures for the molecules N_2O, HCOOH, and C_2H_3F:

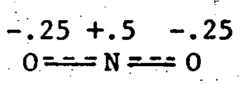


$\overset{-}{N}=\overset{+}{N}=O$

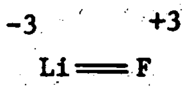




In the case of electron-deficient molecules, Linnett-type structures[16] or structures consistent with simple molecular orbital theory should be used. Thus the following structures are written for the molecules NO_2 and LiF:



$\overset{-.25}{O}\overset{+.5}{N}\overset{-.25}{O}$

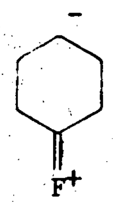


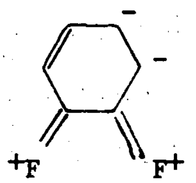
$\overset{-3}{Li}\equiv\overset{+3}{F}$

For elements heavier than neon, pπ bonding is excluded unless such bonding is necessary to satisfy the Octet Rule.[17] Thus for ONCl we write

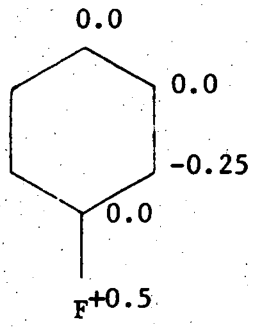
$O=N-Cl$

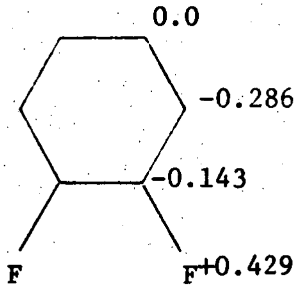
In the case of highly delocalized bonding systems, we ignore individual resonance structures in which atoms of opposite formal charge are separated by more than one atom or in which atoms having formal charges of the same sign are adjacent. Thus we rule out the following resonance structures for fluorobenzene and o-difluorobenzene:[18]





The 100% covalent charge distributions for these molecules are as follows:



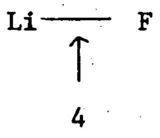


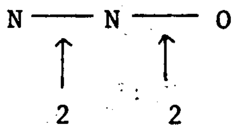
The negative charge q transferred from an atom A to an attached atom B is calculated from the relation

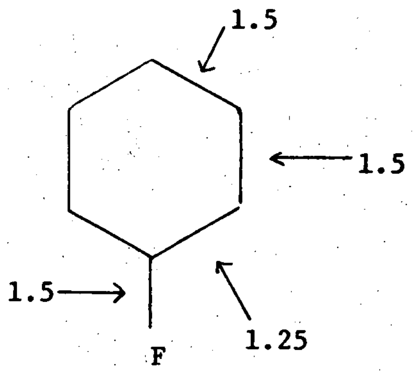
$$q = q_{max} \cdot f[p(x_B - x_A)] \qquad (1)$$

where q_{max} is the maximum charge transferrable, x_B and x_A are "electronegativity parameters" for atoms B and A appropriate for the particular bond under consideration, p is a "bond polarizability factor," and $f[p(x_B - x_A)]$ is an empirically determined function of $p(x_B - x_A)$ which has values between 0 and 1. Atoms A and B are always chosen so that $x_B \geq x_A$.

One evaluates q_{max} by assuming that the electron-donating atom can transfer its share (one-half) of the electrons in the A-B bond and, when the electron-accepting atom lacks an octet, enough of its nonbonding electrons to complete the octet of the electron-accepting atom. For species in accord with the Octet Rule, q_{max} is equivalent to the bond order. Values of q_{max} for the bonds in several molecules are indicated in the following structures.[18]







The bond polarizability factor, p, is a function of q_{max}, as shown in Table I. Interpolation may be used to obtain p values corresponding to q_{max} values not tabulated. Values of the function $f[p(x_B - x_A)]$ (that is, of q/q_{max}) are tabulated as a function of $p(x_B - x_A)$ in Table II. Interpolation is also possible in this table.

The value of x for an atom involved in a particular bond (i.e., x_A or x_B) is calculated from the relation

$$x = x_o + 0.127\ Q' + h \qquad (2)$$

where x_o is an empirical constant characteristics of the element, Q' is

Table I. Values of the Polarizability Factor

q_{max}	p
0	1.144
.5	1.072
1.0	1.000
1.5	0.928
2.0	0.856
2.5	0.784
3.0	0.718
3.5	0.638
4.0	0.568

Table II. Values of q/q_{max}

$p(x_B - x_A)$	q/q_{max}	$p(x_B - x_A)$	q/q_{max}	$p(x_B - x_A)$	q/q_{max}
.02	.026	.60	.499	1.75	.909
.04	.050	.62	.510	1.80	.918
.06	.072	.64	.520	1.85	.926
.08	.094	.66	.530	1.90	.934
.10	.115	.68	.539	1.95	.941
.12	.134	.70	.548	2.00	.947
.14	.154	.72	.557	2.10	.957
.16	.173	.74	.566	2.20	.966
.18	.192	.76	.574	2.30	.973
.20	.211	.78	.583	2.40	.979
.22	.229	.80	.591	2.50	.984
.24	.247	.85	.611	2.60	.989
.26	.265	.90	.630	2.70	.993
.28	.282	.95	.650		
.30	.299	1.00	.669		
.32	.315	1.05	.688		
.34	.331	1.10	.707		
.36	.347	1.15	.726		
.38	.363	1.20	.745		
.40	.377	1.25	.764		
.42	.391	1.30	.782		
.44	.404	1.35	.800		
.46	.417	1.40	.815		
.48	.430	1.45	.830		
.50	.443	1.50	.845		
.52	.455	1.55	.860		
.54	.466	1.60	.874		
.56	.477	1.65	.886		
.58	.488	1.70	.898		

the atomic charge calculated from the 100% covalent formal charge and the q values for all the bonds to the atom <u>except</u> the bond under consideration, and h is a term which accounts for the increase in the effective electronegativity of an atom when its bonding orbital is hybridized either sp or sp^2. To evaluate h, the following relation, in which n = 1 or 2 (for sp or sp^2 hybridization, respectively) and in which q_{max} refers to the bond in question, is used:

$$h = 0.15/(nq_{max}) \qquad (3)$$

The value of h is taken as zero for any atom more electronegative than carbon and for any bonding orbital with more p character than an sp^2 hybrid orbital. Values of x_o for the elements considered in this study are given in Table III.

Calibration With Theoretical Charges

The parameters p and x_o in Tables I and III and the function q/q_{max} in Table II were empirically evaluated such that the atomic charges calculated for 30 ground-state heteronuclear diatomic species were in good agreement with the charges calculated for these species from high quality wave functions by Bader, Beddall and Cade.[19] In effect, our method was calibrated using the theoretical charge data. Our method reproduces their calculated charges with an average deviation of ±0.036. The charges obtained by the two methods can be compared for a few diatomic species by reference to Table IV.

It should be pointed out that, in this calibration with the diatomic data, it was unnecessary to consider the terms involving Q' and h in

Table III. Values of the Electronegativity Parameters, x_o, for Some Elements

H	2.313	N	3.000
Li	1.038	O	3.433
Be	1.598	F	4.044
B	1.980	Ne	4.400
C	2.414	Cl	3.000

Table IV. A Comparison of Estimated Atomic Charges for Ground-State Diatomic Species

Species	Charge on the More Electropositive Atom	
	Calcd. by Bader *et al.*[19]	Calcd. by our method
LiF	0.84	0.844
BO^+	1.79	1.804
LiF^+	.93	.930
BN^+	1.57	1.590
LiO^+	.92	.892
BeF^-	-.08	-.096
CO	.92	.908
CN^-	.36	.350
BF^+	1.57	1.598
CO^+	1.60	1.590

equation 2. The Q' term could be ignored, even though the atoms had finite formal charges, because the quantity $Q'_B - Q'_A$ for a diatomic species of the second row of the periodic table is always equal to the difference in the atomic numbers of B and A.[20] Consequently the coefficient of Q' in equation 2 can be set equal to any quantity (including zero) if the x_o value for each element is decreased by that quantity times the atomic number of the element. If we let p represent the coefficient of Q' in equation 2, and Z_A and Z_B the atomic numbers of A and B, then we can write

$$\begin{aligned} x_B - x_A &= (x_B - pZ_B + pQ'_B) - (x_A - pZ_A + pQ'_A) \\ &= x_B - x_A - p[(Z_B - Z_A) - (Q'_B - Q'_A)] \\ &= x_B - x_A. \end{aligned}$$

The parameter h in equation 2 can be ignored when considering diatomic species because, by our convention, neither atom in such a species is either sp or sp^2 hybridized.

Our first approximation to the function $f[p(x_B - x_A)]$ was obtained by plotting the q/q_{max} values of Bader et al. against Δx values calculated using Pauling electronegativities.[21] The points formed a family of curves corresponding to different values of q_{max}. These curves could be made to coincide by multiplying the Δx values for each curve by appropriately chosen values of p. Small adjustments were made in both the x values and in the smooth curves drawn through the points until the deviations from the smooth curves were minimized. Thus the optimum values of x_o for the elements from lithium to fluorine and the function $f[p(x_B - x_A)]$ were obtained. It will be noted that the x_o values for the elements from lithium to fluorine are very close, if not equal, to the Pauling electronegativities. Therefore for neon and chlorine, for which Bader et al. provided no calculated data, we simply used the Pauling electronegativities. Because of the unique character of hydrogen, we did not make the corresponding approximation in that case.

Calibration With Core Binding Energies

The electronegativity parameter for hydrogen, the coefficient of Q' in equation 2, and the hybridization correction term h in the same equation were chosen so as to minimize the standard deviation between 129 experimental and calculated core binding energies for compounds of boron, carbon, nitrogen, oxygen, and fluorine. The calculations were made using an equation based on the potential model:[4]

$$E_B = kQ + V + \ell \tag{4}$$

In this equation, E_B is the core binding energy in eV (relative to that of an arbitrarily chosen reference compound), Q is the charge of the ionizing atom, V is the coulomb potential energy of an electron at the hypothetical vacated site of that atom in the midst of the other atoms of the molecule, and k and ℓ are empirical constants, determined by least-squares fitting of the binding energy data for a given element to the calculated Q and V values. The energy V was calculated from the relation $V = \sum(q/r)$, in which q is the charge on an atom, r is its distance from the site of the ionizing atom, and the sum is carried out over all the atoms. The charges were calculated, not for the ground state molecules, but for the hypothetical molecules having valence electron distributions half-way between those of the ground state and those of the final state[2,14,22,23]. The calculations were made by using the average of the initial and final x_o values for the ionizing atom. The average x_o value was calculated by application of the principle of equivalent cores.[5-7] Thus, we used the relation

$$x_o(\text{"ave"}) = \frac{x_o(z) + x_o(z + 1)}{2} + 0.0635$$

where $x_o(z)$ is the x_o value for the ionizing element, $x_o(z + 1)$ is the x_o value for the next element in the periodic table, and the 0.0635 term corresponds to the additional formal charge of +0.5.

The inverse dependence of h on n and q_{max} (as shown in equation 3) was chosen because of its simplicity and its qualitative agreement with intuition. The electronegativity of an orbital increases with its s character, and both increase on going from sp^2 to sp hybridization (i.e., as n changes from 2 to 1). Similarly, both the electronegativity and s character increase upon going from a double bond orbital to an sp^2 single bond orbital, or from a triple bond orbital to an sp single bond orbital (i.e., as q_{max}, the bond order, decreases). The factor 0.15 was obtained empirically. It should be emphasized that h is included in equation 2 only for atoms using sp or sp^2 hybridized orbitals.

In our initial attempts to correlate binding energies with our calculated charges using equation 4, very poor correlations were obtained because the magnitudes of the potential terms, V, were too great. However, we found by trial that good correlations were obtained if all our calculated atomic charges are multiplied by the factor 0.2, and therefore we have applied this factor in all the applications of our calculated charges to equation 4. Although this factoring procedure is completely *ad hoc*, it is justifiable in view of the arbitrary method of atomic charge apportionment used by Bader *et al*. for the molecules with which we calibrated our method. Indeed, the charges calculated by Bader *et al*. do seem too large when compared with corresponding values obtained from Mulliken population analyses and Pauling's method. In Table V we list values of our factored calculated atomic charges for a few simple molecules and for the corresponding hypothetical neutral half-ionized core molecules.

Table V. Some Factored[a] Calculated Charges

Molecule and atom[b]		Initial State	Neutral half-ionized core state
CH_4	C	-0.067	-0.261
	H	+0.017	+0.065
$N(CH_3)_3$	N	-0.274	-0.348
	C	+0.007	+0.025
	H	+0.028	+0.030
CHF_3	F	-0.167	-0.180
	F	--	-0.167
	C	+0.423	+0.434
	H	+0.078	+0.079

[a] All Q values multiplied by the factor 0.2.

[b] The ionizing atom is listed first.

The Correlation of Core Binding Energies

The experimental and calculated binding energies are listed in Table VI. The calculations were made using equation 4 and the k and ℓ values listed in Table VII. The overall standard deviation is ±0.61 eV; the standard deviations for the compounds of boron, carbon, nitrogen, oxygen, and fluorine are ±0.59, ±0.64, ±0.83, ±0.75, and ±0.25 eV, respectively. A plot of experimental binding energies vs. calculated binding energies (the reference states chosen so as to bring all the points together on the graph) is shown in Figure 1. The results indicate that the relatively simple method which we have devised for estimating atomic charges is useful for correlating and predicting core electron binding energies for compounds of the first row of the periodic table.

Computer Calculation

The calculation of the atomic charges of a diatomic molecule by the method we have described is a simple matter requiring less than five minutes. For a molecule such as NF_3, about 10 minutes calculation time is required, and for a relatively complicated molecule such as CH_3NH_2, more than 30 minutes time is generally required. A FORTRAN IV computer program for making these atomic charge calculations has been written; a print-out of this program will be sent to those interested upon request.

Acknowledgement.— This work was supported by the U. S. Atomic Energy Commission. We are grateful to John Illige for help with some of the initial calculations.

Table VI. Experimental and Calculated 1s Binding Energies

Compound	E_B, eV Exptl.	Calcd.	Ref.
BF_3	0.0	-0.43	--
BCl_3	-2.65	-3.28	24,25
$B(OCH_3)_3$	-4.7	-4.44	24,25
$B(OC_2H_5)_3$	-5.2	-4.59	25
$B(CH_3)_3$	-6.4	-6.68	24
$B(C_2H_5)_3$	-7.3	-6.70	25
$B(C_2H_5)_2Cl$	-5.8	-5.47	25
BH_3CO	-7.6	-6.72	24
$BH_3N(CH_3)_3$	-9.1	-9.52	24
$BH_3N(C_2H_5)_3$	-9.6	-9.55	25
$BH_2N(C_2H_5)_2$	-8.5	-7.39	25
B_2H_6	-6.3	-6.92	24,25
$B_2H_5N(CH_3)_2$	-7.5	-7.35	25
B_5H_9	-8.6	-9.02	25
	-6.7	-7.06	25
1,5-$C_2B_3H_5$	-6.8	-7.86	25
1,6-$C_2B_4H_6$	-7.4	-7.17	25
CH_4	0.0	-0.04	--
C_2H_6	-0.2	-0.29	26
CH_3Cl	1.6	1.51	27
CH_2Cl_2	3.1	2.91	27
$CHCl_3$	4.3	4.15	27

Table VI. Experimental and Calculated 1s Binding Energies, cont.

Compound	Exptl.	Calcd.	Ref.
CCl_4	5.5	5.12	27
CH_3F	2.8	2.32	27
CHF_3	8.3	7.47	27
CF_4	11.0	10.00	27
CO	5.3	4.22	4, 28
C_2H_4O	2.0	1.57	28
CH_3OH	1.75	1.46	4, 28
C_2H_5OH	0.2	0.25	4
	1.6	1.08	4
C_2H_2	0.4	-0.28	28
HCN	2.6	3.06	28
CO_2	6.8	6.52	4
C_3O_2	0.8	2.69	29
	4.2	4.16	29
CH_2O	3.3	3.25	4
CH_3CHO	0.6	1.23	4
	3.2	2.74	4
$(CH_3)_2CO$	0.5	1.07	4
	3.1	2.21	4
HCO_2H	5.0	4.64	4
CH_3CO_2H	0.7	1.98	4
	4.7	4.14	4
$C_2H_5CO_2C_2H_2$	0.1	0.56	4
	1.7	1.33	4

Table VI. Experimental and Calculated 1s Binding Energies, cont.

Compound	Exptl.	Calcd.	Ref.
$C_2H_5CO_2H_5$,cont.	3.8	3.67	4
C_4H_4O	-0.4	-o.46	30
	0.8	1.16	30
C_4H_5N	-0.9	-1.02	30
	0.1	0.06	30
CH_2CHF	0.18	0.06	31
	2.54	2.90	31
CH_2CF_2	0.37	1.34	31
	5.14	5.82	31
$CHFCF_2$	2.93	4.23	31
	5.28	6.15	31
C_6H_6	-0.5	-0.92	4
C_6H_5F	0.39	-0.32	12
	2.43	2.43	12
o-$C_6H_4F_2$	0.72	0.07	12
	2.87	3.25	12
m-$C_6H_4F_2$	0.70	0.37	12
	2.92	2.83	12
p-$C_6H_4F_2$	0.76	0.52	12
	2.74	2.33	12
1,3,5,-$C_6H_3F_3$	0.56	1.27	12
	3.02	3.17	12
C_6F_6	3.57	4.96	12

Table VI. Experimental and Calculated 1s Binding Energies, cont.

Compound	Exptl.	Calcd.	Ref.
ONF_3	7.1	6.96	32
NF_3	4.3	5.27	32
NO_2	3.0	2.45	32
N_2F_4	2.4	4.03	32
ONCl	1.5	0.40	32
NO	0.8	0.83	32
N_2	0.0	-0.93	--
N_2H_4	-3.8	-3.58	32
NH_3	-4.3	-3.40	32
CH_3NH_2	-4.8	-4.13	32
$(CH_3)_2NH$	-5.0	-4.87	32
$(CH_3)_3N$	-5.2	-5.62	32
N_2O	-1.3	-0.94	32
	2.6	1.67	32
HCN	-3.1	-3.83	32
CH_3NO_2	2.23	1.28	31
$C_6H_5NO_2$	1.7	1.24	4
$C_6H_5NH_2$	-4.4	-3.10	4
O_2	0.0	-0.09	--
CO	-0.95	-2.62	4, 28
NO	0.2	-1.29	4
NO_2	-1.8	-1.62	4
H_2O	-3.6	-3.72	4, 28
CH_3OH	-4.4	-4.78	4, 28

Table VI. Experimental and Calculated 1s Binding Energies, cont.

Compound	Exptl.	Calcd.	Ref.
C_2H_5OH	-4.5	-4.83	4
C_2H_4O	-4.9	-5.62	28
CO_2	-2.35	-1.99	4, 28
C_3O_2	-3.5	-3.32	29
CH_3CHO	-5.5	-4.92	4
$(CH_3)_2CO$	-4.1	-5.05	4
HCO_2H	-4.79	-4.59	28
	-3.17	-2.57	28
CH_3CO_2H	-4.9	-4.74	4
	-3.1	-2.71	4
$C_2H_5CO_2C_2H_5$	-5.5	-4.83	4
	-4.3	-3.78	4
N_2O	-2.1	-1.62	4, 28
CH_3NO_2	-4.35	-2.96	31
CF_4	0.0	-0.04	--
CHF_3	-0.9	-1.13	12
CH_2F_2	-1.87	-2.05	12
CH_3F	-2.6	-2.83	12
C_2H_5F	-3.15	-2.89	31
CH_3CHF_2	-2.22	-2.13	31
CH_3CF_3	-1.39	-1.32	31
C_2F_6	-0.25	-0.01	31
HF	-1.4	-1.47	33
CF_2Cl_2	-0.88	-0.91	31

Table VI. Experimental and Calculated 1s Binding Energies, cont.

Compound	Exptl.	Calcd.	Ref.
NF_3	-0.75	-0.60	31
BF_3	-0.9	-0.66	31
C_6H_5F	-2.64	-2.24	12
$0-C_6H_4F_2$	-2.27	-2.12	12
$m-C_6H_4F_2$	-2.34	-2.06	12
$p-C_6H_4F_2$	-2.34	-2.26	12
$1,3,5-C_6H_3F_3$	-2.13	-1.92	12
C_6F_6	-1.26	-1.47	12
CH_2CHF	-2.27	-2.32	31
CH_2CF_2	-1.21	-1.30	31
$CHFCF_2$	-1.47	-1.97	31
	-0.77	-1.37	31

Table VII. Values of k and ℓ[a]

Ionizing atom	k	ℓ
B	23.84	-6.63
C	24.10	2.89
N	25.45	0.64
O	35.13	2.79
F	30.92	1.40

[a] All Q values multiplied by the factor 0.2.

References

* Work done under the auspices of the U.S. Atomic Energy Commission.

(1) H. Basch and L. C. Snyder, Chem. Phys. Letters, 3, 333 (1969).

(2) L. Hedin and A. Johansson, J. Phys. B: Atom. Molec. Phys., 2, 1336 (1969).

(3) M. E. Schwartz, Chem. Phys. Letters, 5, 50 (1970).

(4) K. Siegbahn et al., "ESCA Applied to Free Molecules," North-Holland Publ. Co., Amsterdam, 1969.

(5) W. L. Jolly and D. N. Hendrickson, J. Amer. Chem. Soc., 92, 1863 (1970).

(6) J. M. Hollander and W. L. Jolly, Accounts Chem. Res., 3, 193 (1970).

(7) W. L. Jolly, paper in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 629-645.

(8) D. T. Clark and D. B. Adams, Nature Phys. Sci., 234, 95 (1971).

(9) D. C. Frost, F. G. Herring, C. A. McDowell and I. S. Woolsey, Chem. Phys. Letters, 13, 391 (1972).

(10) M. E. Schwartz, J. D. Switalski, and R. E. Stronski, paper in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 605-627.

(11) J. Hedman, M. Klasson, B. J. Lindberg, and C. Nordling, paper in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 681-689.

(12) D. W. Davis, D. A. Shirley, and T. D. Thomas, paper in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 707-711.

(13) A description of this method at an earlier of its development is given in ref. 14.

(14) W. L. Jolly, *Faraday Disc. Chem. Soc.*, *54*, 00 (1972).

(15) The formal charge of an atom in a molecule is the charge which the atom would have if the bonding electrons were equally shared between the bonded atoms.

(16) J. W. Linnett, "The Electronic Structure of Molecules," John Wiley and Sons, New York, 1964.

(17) Except for simple chlorides in which the chlorine atoms are monovalent, we have avoided the consideration of compounds containing elements heavier than neon because of the difficulty of assessing the contributions of d orbitals to the bonding.

(18) In these structures the hydrogen atoms are not shown. These atoms have zero formal charges and the bonds to them have $q_{max} = 1$.

(19) R. F. W. Bader, P. M. Beddall, and P. E. Cade, *J. Amer. Chem. Soc.*, *93*, 3095 (1971).

(20) For example, in BO^+, the formal charges are -1 for B and +2 for O ($\Delta = 3$), corresponding to the difference in the atomic numbers of 3.

(21) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N. Y., 1960.

(22) D. Liberman, *Bull. Am. Phys. Soc.*, *9*, 731 (1964).

(23) D. W. Davis and D. A. Shirley, Unpublished calculations, March, 1972.

(24) P. Finn and W. L. Jolly, *Inorg. Chem.*, *94*, 1540 (1972).

(25) D. A. Allison, G. Johansson, C. J. Allan, U. Gelius, H. Siegbahn, J. Allison and K. Siegbahn, Uppsala University Institute of Physics Report UUIP-767, March 1972.

(26) T. D. Thomas, J. Chem. Phys., 52, 1373 (1970).

(27) T. D. Thomas, J. Amer. Chem. Soc., 92, 4184 (1970).

(28) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, J. Chem. Phys., 52, 3295 (1970).

(29) U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, Chem. Phys. Letters, 11, 224 (1971).

(30) U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, Physica Scripta, 3, 237 (1971).

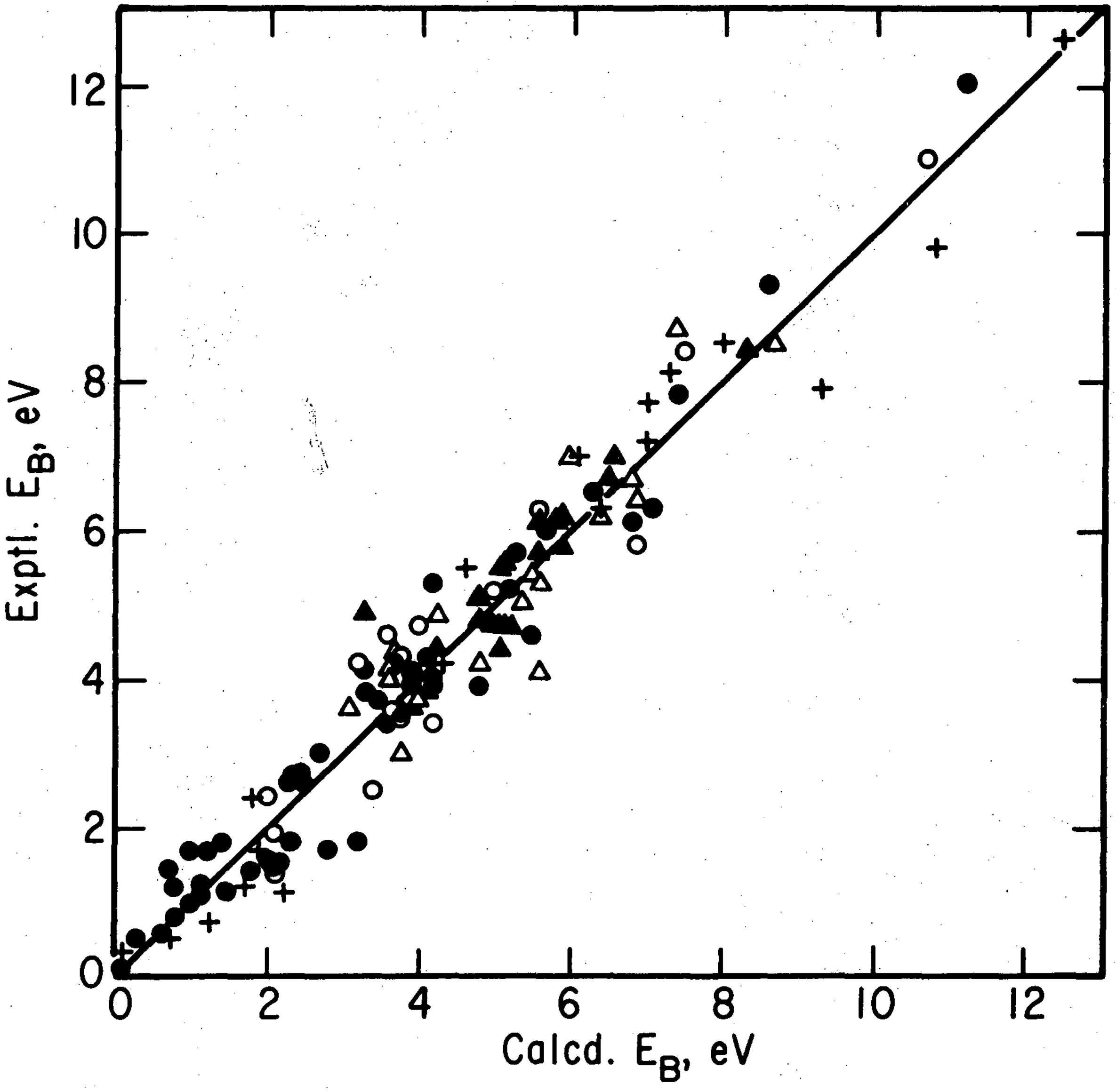
(31) D. W. Davis and D. A. Shirley, Unpublished data.

(32) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, Inorg. Chem., 10, 378 (1971).

(33) P. Finn and W. L. Jolly, Unpublished data.

FIGURE CAPTION

Figure 1.-- Plot of experimental 1s binding energies vs the corresponding calculated energies for compounds of boron, carbon, nitrogen, oxygen, and fluorine. The reference states have been chosen so as to cluster the points together on the graph. The open circles correspond to boron compounds, the closed circles to carbon compounds, the crosses to nitrogen compounds, the open triangles to oxygen compounds, and the closed triangles to fluorine compounds.



XBL 728-1487

Fig. 1

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