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The Estimation of Atomic Charges by an Electronegativity Equalization Procedure Calibrated with Core Binding Energies

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Abstract: A simple procedure, based on the equalization of orbital electronegativities, has been devised for calculating atomic charges in molecules. The calculation involves four empirical parameters (only two of which are needed for most molecules) which have been evaluated by application of the potential model equation for calculating core binding energies to 126 experimental 1s binding energies for 66 gaseous compounds. The method yields standard deviations in the binding energies of carbon, nitrogen, oxygen, and fluorine of ±0.69, ±0.53, ±0.74, and ±0.36 eV, respectively. The calculated and experimental binding energies are used to test the expected correlation between the ligancy of an ionizing atom and the electronic relaxation energy and to test the "transition state" method of providing for relaxation energy.

Introduction

Most of the chemical properties of molecular systems, including spectra, reactivities, and macroscopic properties, are ultimately explicable in terms of the distribution of electron density within the molecules. Consequently methods for describing molecular electron distribution are of considerable interest to chemists. This interest is obvious from the many articles on this topic which have appeared in recent years.[1-11] For simple molecules, it is possible to calculate accurate electron densities by SCF-MO techniques and to display the data in the form of the now familiar electron density contour maps.[1,2] In favorable cases, X-ray and neutron diffraction data can yield similar plots.[12] However such plots, or even equivalent tabulations of electron density as a function of position, are not easily used except for making qualitative comparisons. The favorite and most practical method for quantitatively describing electron distribution in a molecule is the assignment of partial charges to the atoms. A wide variety of theoretical and empirical methods have been proposed for evaluating atomic charges. The theoretical methods differ either in the method used for calculating the over-all electron distribution or in the recipe used for apportioning electron density among atoms. The empirical methods differ either in the type of experimental measurement used or in the underlying theory or correlative method. In spite of the diversity of results obtained from these methods, most of them have served advantageously in the correlation of atomic charge-related properties. However, the naive use of atomic

charges is fraught with difficulties. Most of the difficulties which have been encountered are attributable to neglect of the steric character of nonbonding electrons and the polarizability of atoms. For example, the correlation of dipole moments with simple atomic charges alone is generally a hopeless task.[9,10,13]

There is need for a simple method for calculating atomic charges which not only has theoretical justification but also can be related to an experimental measurement that depends fairly directly on atomic charges. We believe that such a method is now possible in the form of the technique of electronegativity equalization calibrated with X-ray photoelectron spectroscopic core binding energies.

Electronegativity Equalization

The concept of atomic electronegativity equalization, introduced by Sanderson[14] and Iczkowski and Margrave,[15] has been developed into the concept of the equalization of the electronegativities of bonding orbitals.[16-24] Hinze, Whitehead and Jaffé[17] define orbital electronegativity as a quantity proportional to the derivative of the energy of an atom with respect to the charge in a particular atomic orbital. It is assumed that the orbital charge (i.e., 1 minus the occupation number) may have either an integral or nonintegral value, and that the energy may be expressed as a quadratic function of the orbital charge. Of course, the orbital electronegativities and their charge dependence are functions of orbital hybridization. By use of orbital electronegativities corresponding to reasonable estimates of the orbital hybridizations, charges for atoms in molecules have been calculated by assuming that electrons flow between orbitals until the energy is minimized. According to the assumptions of the method, the energy is minimized when the orbital electronegativities of each bond are equal.

Several difficulties arise in making atomic charge calculations by this method. First is the problem of providing for the fact that the energy-charge relationship for an orbital of a bonded atom is not the same as that for a free atom. In other words, how does the effective occupation number change as a consequence of orbital overlap?[25] Second is the problem of evaluating the change in electronegativity of a given

orbital due to changes in the charges of the other orbitals of the atom and due to changes in the formal charge[26] of the atom. Third is the problem of providing for the effect of bond order. One would expect that, other things being equal, a multiple bond would transfer charge more readily than a single bond.

Parameterization.-We have chosen to solve the problems enumerated above in a completely empirical way by introducing to the calculations four adjustable parameters which are evaluated using experimental core electron binding energy data for gaseous compounds. It is well known that chemical shifts in core electron binding energies for gaseous molecules can be correlated with atomic charges by the so-called potential model equation:[27]

$$E_B = kQ_i + V + \ell \qquad (1)$$

In this equation, E_B is the binding energy for a particular core level (relative to that of a reference compound), Q_i is the charge of the ionizing atom, V is the coulomb potential energy of an electron at the hypothetical vacated site of the ionizing atom in the midst of the other charged 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_i and V values. The energy V is calculated from the relation $V = \Sigma(Q/r)$, in which Q is the charge on an atom, r is its distance from the ionizing atom, and the sum is carried out over all the atoms except the ionizing atom. We believe that an electronegativity

equalization procedure which has been "calibrated" with experimental core electron binding energies will yield atomic charges having much more quantitative significance than those calculated by other methods.

We represent the electronegativity of the orbital of an atom, n, used in forming a bond to another atom, m, by x_{nm}. In the case of a multiple bond, x_{nm} refers to the effective, or weighted average, electronegativity of the orbitals involved. This effective orbital electronegativity may be calculated by the following expression.

$$x_{nm} = x(p)_n + \frac{S_{nm}}{(N_{nm})^a}\,[x(s)_n - x(p)_n] + h_n\left[\frac{bq_{nm}}{(N_{nm})^a} + \sum_{i\neq m} q_{ni} + cF_n\right] \qquad (2)$$

Here x(p) and x(s) correspond to the p and s orbital electronegativities, respectively, for atom n. In Table I we list these electronegativities for the elements in the compounds we used for calibration. The values are those calculated and adjusted to the Pauling scale by Hinze and Jaffé.[16] (Presumably Hinze and Jaffé's values for other elements can be used to extend the scope of this method.) The quantity S_{nm} is the fractional s character of the σ orbital used in the bond, calculated as the reciprocal of the sum of the number of σ bonding orbitals and filled nonbonding orbitals of atom n.[28] (For example, the S_{NN} values in N_2H_4 and N_2 are calculated to be 0.25 and 0.5, respectively.) The quantity N_{nm} is the bond order, which may have a nonintegral value when more than one resonance structure can be written for the compound. The parameter h_n is proportional to the

Table I

Atomic Parameters Used in Electronegativity Equalization Calculations

Atom	x(s)	x(p)	h
H	2.21		1.285
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[a]	4.40[a]	1.90[a]
Cl	6.26	2.95	1.11

[a]Estimated from the data of B.-M. Fung, J. Phys. Chem., 69, 596 (1965).

difference between the orbital ionization potential and the orbital electron affinity (I - EA) for atom n, assuming a hybridization typical of the bonds of that element.[29] The values of h for several elements, calculated from the data of Hinze and Jaffé, are presented in Table I. The quantity q_{nm} refers to the negative charge transferred from atom n to atom m. The sum $\sum_{i \neq m} q_{ni}$ corresponds to the sum of the negative charges transferred from atom n to all the atoms bonded to atom n except the atom m. The quantity F_n is the formal charge[26] on atom n. As in the case of N_{nm}, F can have a nonintegral value when more than one resonance structure can be written for the compound. The parameters a, b, c, and the common proportionality factor included in the h values are the parameters which were adjusted to fit the binding energy data. The parameters were chosen to minimize the overall standard deviation of the E_B values calculated for compounds of carbon, nitrogen, oxygen, and fluorine using equation 1 with the appropriate least-squares adjusted valued of k and ℓ. The best values found for a, b, and c were 0.7, 7.3, and 3.1, respectively.

The sum of the first two terms on the right hand side of equation 2 is the effective electronegativity of the orbital (or orbitals) of a neutral atom n used in the bond to atom m. For single bonds, this quantity is the simple weighted average of the s and p electronegativities for atom n. In the case of multiple bonds ($N_{nm} > 1$), we assume that the bond order in excess of unity is due to π bonding involving pure p atomic orbitals. Although the corresponding average s character of the bonding orbitals is then S_{nm}/N_{nm}, we use the expression $S_{nm}/(N_{nm})^a$ (where $0 < a < 1$) as the

weighting factor for the s electronegativity.[30] The parameter a accounts for the facts that σ bonds are stronger than π bonds and that they probably contribute more heavily to q_{nm}.

The last term of equation 2 is the change in the effective electronegativity due to charges which develop on atom n. An increase in positive charge causes an increase in electronegativity. We divide the charge on atom n into three parts: the charge caused by the polarization of the bond between atoms n and m, the charge caused by the polarization of all the other bonds to atom n, and the formal charge on atom n. Each of these charges is weighted differently, using the coefficients b, unity, and c, respectively. Although these weighting coefficients are independent of the identity of atom n (i.e., although we assume the effects of the three types of charge to be in the same proportion for all elements), the absolute effect of the charges on the electronegativity varies from element to element in proportion to the value of h for the atom. This use of the factor h is justifiable because h is proportional[31] to I - EA and hence it is proportional to the derivative of the electronegativity with respect to charge. From the quadratic relation between energy and charge, we write

$$E = \left(\frac{I - EA}{2}\right)Q^2 + \left(\frac{I + EA}{2}\right)Q$$

Hence,

$$\frac{dE}{dQ} = x = (I - EA)Q + \left(\frac{I + EA}{2}\right)$$

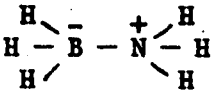
and

$$\frac{d^2E}{dQ^2} = \frac{dx}{dQ} = I - EA$$

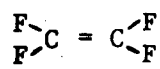
When the bond order between atoms n and m is greater than one, the charge q_{nm} may be looked upon as the sum of the charges transferred through the orbitals involved in the bond. The average charge per orbital is q_{nm}/N_{nm}. We use the effective charge per orbital, $q_{nm}/(N_{nm})^a$, to account for the fact that the σ bond contributes more heavily to q_{nm} than the π bonds. Thus the $1/(N_{nm})^a$ factor serves a similar purpose in the two places where it appears in equation 2. The charge q_{ni} is believed to affect the electronegativities of the constituent orbitals of the nm bond independently and more or less equally. The same is believed true of F_n. Hence neither of these charges is reduced by the $1/(N_{nm})^a$ factor.

Molecular Structure Assumptions.-The bond orders, N, and formal charges, F, used in this method correspond to simple valence bond structures. The structures are limited, when possible, to those in which all atoms heavier than helium possess complete octets of valence electrons[32] and in which each atom is bonded to at least one other atom.[33] For most molecules, all the formal charges are zero and it is an easy matter to evaluate the bond orders. Thus HCN has a single bond and a triple bond, C_2H_4 has four single bonds and a double bond, CF_4 has four single bonds, etc. For some molecules the only octet-satisfying structure which can be written is one involving formally charged atoms. Thus for carbon monoxide and ammonia-borane we must write the following structures.

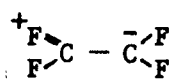
$$^{-}C \equiv O^{+}$$



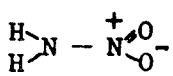
When more than one structure can be written for a molecule (i.e., in the case of resonating molecules), the weighted average bond orders and formal charges are used. For example, we take the C-C bond order in benzene as 1.5. However certain types of resonance structures are forbidden from consideration unless no other structures can be written. (a) Structures with formal charges on atoms of different elements which contradict electronegativities are forbidden. Thus we consider only the following conventional structure for C_2F_4,

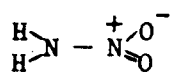


and rule out structures of the following type.

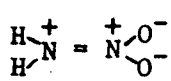


(b) Structures with adjacent atoms having the same non-zero formal charge are forbidden. Thus we consider only the following structures for NH_2NO_2,





and ignore the following structure.



Acceptable structures with formal charges are weighted 1/9 relative to structures without formal charges. Such weighting of the structures for acetic acid,

corresponds to average bond orders of 1.90 and 1.10 for the carbonyl C-O and hydroxyl C-O bonds respectively, and formal charges -0.1 and +0.1 for the carbonyl oxygen and hydroxyl oxygen, respectively.[34] Acceptable structures with widely distributed π bonding are weighted more than those with localized π bonding. Thus we weight the $^{-}N{=}\overset{+}{N}{=}O$ structure, with two double bonds, twice as much as the $N{\equiv}\overset{+}{N}{-}O^{-}$ structure, with a single bond and a triple bond.[35] Such weighting leads to average bond orders of 2.33 and 1.67 for the N-N and N-O bonds, respectively, and average formal charges of -0.667 and +1 for the nitrogen atoms and -0.333 for the oxygen atom.

Odd molecules for which classical Lewis structures cannot be written can be treated by Linnett's technique.[36] Thus for nitric oxide, the bond order is 2.5 and the formal charges on the nitrogen and oxygen atoms are -0.5 and +0.5, respectively.

Calculations.-The equalization of the electronegativities of the atomic orbitals of bonded atoms corresponds to equating x_{nm} and x_{mn}. The expression for x_{mn} can be obtained from equation 2 by simply interchanging n and m. Electronegativity equalization then leads to

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

$$= x(p)_n - x(p)_m + \frac{S_{nm}}{(N_{nm})^a} [x(s)_n - x(p)_n] - \frac{S_{mn}}{(N_{nm})^a} [x(s)_m - x(p)_m]$$

$$+ c(h_n F_n - h_m F_m) \qquad (3)$$

An equation of this type is obtained for each bond in the compound. Thus, in general, the calculation of the various q values for a compound containing a number of bonds equal to j requires the simultaneous solution of j linear equations with j unknowns. The charge of any atom can then be obtained using the relation

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

Because of the symmetry of most molecules, such calculation ordinarily is not as formidable as one might suspect. We shall give sample calculations for two molecules, CF_4 and N_2O, to illustrate the method.

In the case of carbon tetrafluoride, all four bonds are equivalent, and there is only one q value, q_{CF}, to be determined. By appropriate substitution into equation 3 (using the values 0.7, 7.3, and 3.1 for a, b, and c), we obtain the following equation.

$$\frac{7.3(1.12 + 1.70)}{1^{0.7}} q_{CF} + 1.12(3)q_{CF} - (1.70)(0)$$

$$= 3.90 - 1.75 + \frac{0.25}{1^{0.7}}(10.31 - 3.90) - \frac{0.25}{1^{0.7}}(4.84 - 1.75)$$

$$+ 3.1[1.70(0) - 1.12(0)]$$

From this we readily calculate $q_{CF} = 0.124$. Hence $Q_C = +0.496$ and $Q_F = -0.124$.

In nitrous oxide, there are two different bonds. Using the symbols N_T and N_C for the terminal and central nitrogen atoms, respectively, we obtain the following two equations.

$$9.7721\ q_{N_CN_T} + 1.21\ q_{N_CO} = -6.2529$$

$$1.21\ q_{N_CN_T} + 13.9692\ q_{N_CO} = -4.6266$$

These equations yield $q_{N_CN_T} = -0.605$ and $q_{N_CO} = -0.279$, which, when account is taken of the weighted average formal charges, give $Q_{N_T} = -0.062$, $Q_{N_C} = +0.116$, and $Q_O = -0.054$.

The calculation of atomic charges in a ring compound by the procedure outlined above involves more equations than are required to obtain a unique set of q values. The values of q for the bonds of a ring, considered consistently in a clockwise or counterclockwise sense, may be uniformly increased or decreased by a constant without changing the atomic Q values.

We have chosen to eliminate "ring currents" by equating the sum of the ring q values to zero. This procedure permits us to eliminate one ring q value and one equation from the set of equations to be solved simultaneously.[37]

Core Binding Energy Correlation

A total of 126 core binding energies for 66 different gaseous compounds were used for calibrating the method - i.e., for evaluating the adjustable parameters. These binding energies included 61 carbon 1s binding energies from 41 compounds, 20 nitrogen 1s binding energies from 19 compounds, 21 oxygen 1s binding energies from 18 compounds, and 24 fluorine 1s binding energies from 23 compounds. The electrostatic potential term in equation 1 was calculated using bond distance and bond angle data from the literature.[38] (In a few cases, it was necessary to estimate such data.) In Table II we have listed, for each core ionization, the calculated charge of the ionizing atom, the experimental and calculated binding energies, and the reference to the experimental value. In Figures 1, 2, 3 and 4 we have plotted E_B(expt) against E_B(calc) for carbon, nitrogen, oxygen and fluorine, respectively. The overall standard deviation, minimized by adjustment of the parameters, is ±0.61 eV. The individual standard deviations for carbon, nitrogen, oxygen and fluorine are ±0.69, ±0.53, ±0.74, and ±0.36 eV, respectively. The least-squares adjusted values of k and ℓ used in equation 1 for each element are given in Table III.

Relaxation Energy.-It is well known that the ejection of a core electron from a molecule is accomplished by a relaxation process in which valence electrons flow toward the ionizing atom.[39-43] The measured binding energy includes the effect of this relaxation. When values of Q_i and Q corresponding to the initial state of the ionizing molecule are employed

Table II

Experimental and Calculated 1s Binding Energies

Compound	Q_i	E_B, eV	
		Exptl.	Calcd.
CH_4	-.060	0.0	-0.60
C_2H_6[a]	-.047	-0.2	-0.50
CH_3F[b]	.076	2.8	2.17
CH_2F_2[c]	.214	5.55	5.02
CHF_3[b]	.355	8.3	7.76
CF_4[b]	.498	11.0	10.49
CH_3Cl[b]	.020	1.6	1.24
CH_2Cl_2[b]	.099	3.1	3.00
$CHCl_3$[b]	.178	4.3	4.71
CCl_4[b]	.256	5.5	6.32
C_2F_6[d]	.392	8.91	9.72
cyclo-C_4F_8[d]	.274	6.3	8.24
CH_3OH[e,f]	.048	1.75	1.33
$\underline{C}H_3CH_2OH$[e]	-.041	0.2	-0.01
$CH_3\underline{C}H_2OH$[e]	.060	1.6	1.42
H_2CO[e]	.111	3.3	2.70
$\underline{C}H_3CHO$[e]	-.023	0.6	0.74
$CH_3\underline{C}HO$[e]	.122	3.2	2.66
$(\underline{C}H_3)_2CO$[e]	-.022	0.5	0.70
$(CH_3)_2\underline{C}O$[e]	.132	3.1	2.62
HCO_2H[e]	.230	5.0	4.54
$\underline{C}H_3CO_2H$[e]	-.014	0.7	1.25
$CH_3\underline{C}O_2H$[e]	.233	4.7	4.40
$C_2H_5O(CO)CH_2\underline{C}H_3$[e]	-.045	0.1	-0.06
$C_2H_5O(\underline{C}O)CH_2CH_3$[e]	-.003	1.7	1.07

Table II, contd.

Compound	Q_i	E_B, eV	
		Exptl.	Calcd.
$C_2H_5O(\underline{C}O)CH_2CH_3$[e]	.241	3.8	4.10
C_2H_2[f]	-.062	0.4	-0.96
HCN[f]	.081	2.6	2.04
$OC\underline{C}CO$[g]	.032	0.8	2.87
$O\underline{C}CCO$[g]	.146	4.2	3.62
CO[e,f]	.172	5.3	3.62
CO_2[e]	.294	6.8	5.95
$\underline{C}H_2CHF$[d]	-.046	0.18	0.18
$CH_2\underline{C}HF$[d]	.078	2.54	1.91
$\underline{C}H_2CF_2$[d]	-.030	0.37	1.26
$CH_2\underline{C}F_2$[d]	.219	5.14	4.62
$\underline{C}HFCF_2$[d]	.109	2.93	4.02
$CHF\underline{C}F_2$[d]	.235	5.28	5.65
$\overline{C\underline{H}CHCHCHO}$[h]	-.022	-0.4	0.21
$\overline{\underline{C}HCHCHCHO}$[h]	.053	0.8	1.02
$\overline{C\underline{H}CHCHCHNH}$[h]	-.030	-0.9	-0.28
$\overline{\underline{C}HCHCHCHNH}$[h]	.006	0.1	0.00
cyclo-C_3H_6[i]	-.033	-0.3	-0.30
$(NC)_2C_2\underline{C}H_2(CN)_2$[i]	-.017	1.4	2.09
$(NC)_2\underline{C}_2CH_2(CN)_2$[i]	.100	4.1	4.65
$(N\underline{C})_2C_2CH_2(CN)_2$[i]	.096	3.1	2.87
C_2H_4O[f,i]	.067	1.8	1.86
$(NC)_2\underline{C}_2O(CN)_2$[i]	.201	6.0	6.80
$(N\underline{C})_2C_2O(CN)_2$[i]	.102	3.4	3.47
C_6H_6[e]	-.032	-0.5	-0.50
C_6H_5F (CF carbon)[c]	.106	2.43	2.15
C_6H_5F (CH carbons)[c]	-.027	0.39	0.06

Table II, contd.

Compound	Q_i	E_B, eV	
		Exptl.	Calcd.
o-$C_6H_4F_2$ (CF carbons)[c]	.118	2.87	3.01
o-$C_6H_4F_2$ (CH carbons)[c]	-.025	0.72	0.47
m-$C_6H_4F_2$ (CF carbons)[c]	.107	2.92	2.54
m-$C_6H_4F_2$ (CH carbons)[c]	-.020	0.70	0.69
p-$C_6H_4F_2$ (CF carbons)[c]	.106	2.74	2.45
p-$C_6H_4F_2$ (CH carbons)[c]	-.019	0.76	0.75
1,3,5-$C_6H_3F_3$ (CF carbons)[c]	.107	3.02	2.91
1,3,5-$C_6H_3F_3$ (CH carbons)[c]	-.008	0.56	1.52
C_6F_6[c]	.132	3.57	4.96
N_2	.000	0.0	-0.46
HCN[j]	-.152	-3.1	-3.74
$(NC)_2C_2(CN)_2$[i]	-.149	-2.8	-3.04
$(NC)_2C_2CH_2(CN)_2$[i]	-.150	-3.2	-3.26
ONF_3[j]	.459	7.1	7.59
NF_3[j]	.233	4.3	4.37
N_2F_4[j]	.164	2.4	3.49
$\underline{N}NO$[j]	-.062	-1.3	-1.24
$N\underline{N}O$[j]	.116	2.6	1.72
NO[j]	.019	0.8	-0.10
NO_2[j]	.180	3.0	3.00
CH_3NO_2[d]	.162	2.23	1.84
$C_6H_5NO_2$[e]	.178	1.7	2.11
ONCl[j]	.074	1.5	0.82
N_2H_4[j]	-.150	-3.8	-3.46
$C_6H_5NH_2$[e]	-.187	-4.4	-3.95

Table II, contd.

Compound	Q_i	E_B, eV	
		Exptl.	Calcd.
NH_3[j]	-.211	-4.3	-4.05
CH_3NH_2[j]	-.203	-4.8	-4.34
$(CH_3)_2NH$[j]	-.194	-5.0	-4.64
$(CH_3)_3N$[j]	-.186	-5.2	-4.95
O_2	.000	0.0	-0.27
C_3O_2[g]	-.162	-3.5	-3.16
CO[e,f]	-.172	-0.95	-3.31
CO_2[e,f]	-.147	-2.35	-2.01
CH_3CHO[e]	-.194	-5.5	-4.31
$(CH_3)_2CO$[e]	-.193	-4.1	-4.36
$H(C\underline{O})OH$[f]	-.235	-4.79	-4.77
$H(CO)\underline{O}H$[f]	-.208	-3.17	-2.91
$CH_3(C\underline{O})OH$[e]	-.234	-4.9	-4.82
$CH_3(CO)\underline{O}H$[e]	-.208	-3.1	-2.92
$C_2H_5O(C\underline{O})C_2H_5$[e]	-.234	-5.5	-4.91
$C_2H_5\underline{O}(CO)C_2H_5$[e]	-.205	-4.3	-3.94
H_2O[e,f]	-.240	-3.6	-3.97
CH_3OH[e,f]	-.236	-4.4	-4.68
C_2H_5OH[e]	-.235	-4.5	-4.68
C_2H_4O[f]	-.229	-4.9	-5.22
$(NC)_2C_2(CN)_2$[i]	-.214	-3.2	-2.84
N_2O[e,f]	-.054	-2.1	-0.90
NO[e]	-.019	0.2	-0.61
NO_2[e]	-.090	-1.8	-1.42
CH_3NO_2[d]	-.218	-4.35	-4.80

Table II, contd.

Compound	Q_i	E_B, eV	
		Exptl.	Calcd.
CF_4	-.124	0.0	-0.27
CHF_3[c]	-.133	-0.9	-1.13
CH_2F_2[c]	-.141	-1.87	-1.95
CH_3F[c]	-.149	-2.6	-2.75
CF_2Cl_2[d]	-.132	-0.88	-0.97
C_2F_6[d]	-.130	-0.25	-0.28
CH_3CF_3[d]	-.132	-1.39	-1.21
CH_3CHF_2[d]	-.140	-2.22	-1.96
C_2H_5F[d]	-.148	-3.15	-2.76
$CH\underline{F}CF_2$[d]	-.134	-1.47	-1.77
$CHFC\underline{F}_2$[d]	-.126	-0.77	-1.39
CH_2CF_2[d]	-.127	-1.21	-1.62
CH_2CHF[d]	-.135	-2.27	-2.44
C_6F_6[c]	-.132	-1.26	-0.18
1,3,5-$C_6H_3F_3$[c]	-.134	-2.13	-1.97
o-$C_6H_4F_2$[c]	-.133	-2.27	-2.17
m-$C_6H_4F_2$[c]	-.134	-2.34	-2.14
p-$C_6C_4F_2$[c]	-.134	-2.34	-2.16
C_6H_5F[c]	-.134	-2.64	-2.32
cyclo-C_4F_8[d]	-.137	-0.46	-0.70
HF[k]	-.151	-1.4	-1.77
BF_3[d]	-.154	-0.9	-1.12
NF_3[d]	-.078	-0.75	-0.21
F_2[ℓ]	.000	1.3	1.08

Table II, contd.

[a]T. D. Thomas, J. Chem. Phys., 52, 1373 (1970). [b]T. D. Thomas, J. Amer. Chem. Soc., 92, 4184 (1970). [c]D. W. Davis, D. A. Shirley and T. D. Thomas, paper in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland, Amsterdam, 1972, p. 707. [d]D. W. Davis and D. A. Shirley, unpublished data. [e]Ref 27. [f]D. W. Davis, J. M. Hollander, D. A. Shirley and T. D. Thomas, J. Chem. Phys., 52, 3295 (1970). [g]U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, Chem. Phys. Letters, 11, 224 (1971). [h]U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, Physica Scripta, 3, 237 (1971). [i]G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson, and C. Nordling, J. Amer. Chem. Soc., 94, 8009 (1972). [j]P. Finn, R. K. Pearson, J. M. Hollander and W. L. Jolly, Inorg. Chem., 10, 378 (1971). [k]P. Finn and W. L. Jolly, unpublished data. [ℓ]T. D. Thomas, unpublished data.

Table III

Values of k and ℓ used in equation 1.

Ionizing Atom	k	ℓ
C	31.06	0.47
N	31.21	-0.46
O	30.43	-0.27
F	34.54	1.08

in equation 1, no provision is made for the electronic relaxation associated with the photoemission process. The fact that equation 1 is fairly successful in correlating binding energies in spite of the neglect of this factor is evidence that the electronic relaxation energy is approximately the same for many molecules. However one would not expect all relaxation energies to be the same. Because the relaxation essentially corresponds to a flow of electron density from neighboring atoms to the ionizing atom, one would expect that the magnitude of the relaxation energy would increase with the number of atoms directly bonded to the ionizing atom, i.e., with the ligancy of the ionizing atom.[44] The extensive data in Table II provide the opportunity to look for a correlation between the ligancies of the ionizing atoms and both the magnitude and direction of the deviations between the experimental and calculated binding energies. Both the carbon and nitrogen compounds include examples of ionizing atoms with ligancies 1, 2, 3 and 4, whereas the oxygen compounds include examples of only ligancies 1 and 2. The fluorine compounds only show ligancy 1 and therefore cannot be examined for a correlation. In Table IV we give the average deviations as a function of ligancy for the compounds of carbon, nitrogen and oxygen. The relaxation is an exothermic process; a greater relaxation energy corresponds to a lower binding energy. Consequently we expect that atoms of high ligancy (having a relatively high relaxation energy) should have relatively positive deviations, E_B (calc) - E_B (expt). Indeed, this trend is exactly that observed in Table IV; the sums of the deviations

(hence also the average deviations) increase with increasing ligancy for compounds of carbon, nitrogen, and oxygen. (Unfortunately, the results for the oxygen compounds are statistically insignificant.) Thus the data of Table IV, at least those for carbon and nitrogen, are consistent with the proposed relaxation mechanism.

Further support for the idea that the relaxation energy increases with increasing ligancy is found in recent data of Khodeyev et al.[45] These investigators found that gaseous Bi has a core binding energy 1 eV higher than that of gaseous Bi_2.

The potential model of equation 1 is based on a hypothetical "sudden" process in which the valence electrons remain fixed. If we wish to use this model and also to account for relaxation, we cannot use the valence electron distribution of the initial molecule (the calculated binding energy would be too high) or of the final ion (the calculated binding energy would be too low). We have previously pointed out that a valence electron distribution between these two extremes, near the average distribution, would be expected to give the right binding energy.[46] This procedure is equivalent to a quantum mechanical calculation outlined by Liberman[47] and Hedin and Johansson[48] and is somewhat analogous to Slater's method for calculating excitation energies, in which one assumes occupation numbers half-way between those of the initial and final states.[49] In the present case the concept of equivalent cores can be used to calculate the atomic charges of the ionized molecule by simply replacing the ionizing atoms

Table IV

The Sum of the Deviations E_B(calc) - E_B(expt), in eV, for Compounds with Ionizing Atoms of Different Ligancies

Ligancy	Ionizing Atom		
	Carbon	Nitrogen	Oxygen
1	-1.70[a]	-0.37	-0.02
2	-0.23	-0.52	+0.02
3	+0.02	+0.33	
4	+0.11	+0.49[b]	

[a]Corresponds to one compound, CO. [b]Corresponds to one compound, ONF_3.

with an atom of the next element in the periodic table, plus a +1 charge. The average values of these charges and those of the original neutral molecule correspond to the valence electron distribution midway between the initial and final states. Davis and Shirley[44] applied this method with CNDO calculations to 35 carbon 1s, 9 nitrogen 1s, and 10 oxygen 1s shifts. For the carbon and nitrogen compounds, the standard deviation dropped from 1.06 to 0.84 and from 2.35 to 1.30 eV, respectively on going from the initial state method to the "half-ionized" method, whereas for the oxygen compounds, the standard deviation correspondingly increased from 0.84 to 1.15 eV.

We have applied a similar method to all the chemical shift data for compounds of carbon, nitrogen, oxygen, and fluorine in Table II, using the method for calculating charges which we have described. Calculations were made for hypothetical transition state molecules in which various weights were assigned to the initial and final state charges. The standard deviations are plotted in Figure 5 as a function of the fractional final state character of the transition state. The plot for the fluorine binding energies shows no improvement in the standard deviation upon the introduction of final state character into the transition state. This result is reasonable because in this group of compounds all the fluorine atoms are monoligated and consequently would be expected to have comparable relaxation energies. The increase in the standard deviation upon the addition of even a small amount of final state character is probably a consequence of the

fact that the parameters of the charge estimation method were optimized for the initial state molecules. The plots for the carbon and nitrogen binding energies, in which there presumably is a wide distribution of relaxation energies, show a distinct reduction in standard deviation upon the introduction of a little final state character into the transition state. We believe that the minima occur below 50% final state character because of the optimization of the charge estimation method for initial state molecules. Undoubtedly it would be possible to parameterize the method so as to have the minima near the 50% point. We have no explanation for the fact that the plot for the oxygen binding energies shows no minimum except for the fact that, inasmuch as the oxygen atoms show only two ligancies, one would not expect a very wide spread of relaxation energies.

The overall results tend to confirm the validity of the method used to correct for relaxation energies. However, when our method of atomic charge estimation is used, there is generally little advantage in making this correlation. One obvious exception is the carbon 1s binding energy of carbon monoxide, the only monoligated carbon compound. Here the deviation changed from -1.68 eV for the initial state calculation to -0.22 eV upon the introduction of 20% final state character into the transition states. If we use initial state charges and omit carbon monoxide, the standard deviation for the carbon compounds drops to ±0.66 eV and the values of k and ℓ change to 30.97 and 0.42, respectively.

Other Correlations

Many chemical and physical properties can be correlated with atomic charges. To demonstrate the versatility of charges calculated by this electronegativity equalization procedure, we have plotted, in Figure 6, proton nmr chemical shifts[50] for CH_3X compounds against the hydrogen atom charges and, in Figure 7, ^{13}C nmr chemical shifts[51] for the hydrocarbons $(CH_3)_{4-n}CH_n$ against the carbon atom charges. The correlations are at least as good as those obtained with charges obtained by other techniques.

The term $\sum_{i \neq m} q_{ni}$ in equation 2 corresponds to the classical inductive effect. The fact that the coefficient for this term, unity, is small compared to the coefficients b and c indicates that the method predicts a rather small inductive effect. The following diagram shows the calculated charges of the carbon atoms in n-octyl fluoride. The charge of a carbon

Q_c		Q_c + .03346
	F	
	|	
.08876	CH_2	.12222
	|	
-.02595	CH_2	.00751
	|	
-.03300	CH_2	.00046
	|	
-.03344	CH_2	.00002
	|	
-.03347	CH_2	-.00001
	|	
-.03351	CH_2	-.00005
	|	
-.03427	CH_2	-.00081
	|	
-.04655	CH_3	-.01309

atom in an infinitely long $-CH_2-$ chain is calculated to be -.03346. By calculating the ratios of successive values of Q_c + .03346, we find that

0 0 0 0 3 9 0 2 0 0 6

the inductive transmission coefficient for adjacent sp^3 carbon atoms is about 0.062. The discrepancy between this value and the commonly quoted[52] value of 0.33 is probably due to the fact that the latter value includes the "through space" field effect as well as the "through bond" inductive effect.

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(25) B. Voight and J. P. Dahl [Acta Chem. Scand., 26, 2923 (1972)] show how difficult it is from a theoretical point of view to correct electronegativity equalization for overlap.

(26) The formal charge is simply the charge which the atom would have if the bonding electrons in each bond were equally apportioned between the pair of bonded atoms. It should not be confused with the net, or "actual," atomic charge which takes into account the bond polarizations. Neither should it be confused with the oxidation state, another quite different formalism.

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(28) We have rounded off nonintegral numbers of lone pairs to the next lower integer. However, it would make little difference to use the nonintegral values. The method described for calculating S_{nm} is reasonable as long as there are no symmetry restrictions on the s and p characters of the σ bonding and nonbonding orbitals. Special consideration would have to be given to molecules such as $N(SiH_3)_3$ (in which the nitrogen lone pair occupies essentially a pure p orbital) and PF_5 (in which the phosphorus uses essentially a pure p orbital in bonding to the axial fluorines). The idea of equally apportioning the s character among the σ bonding and nonbonding orbitals is reasonable for atoms from the first row of the periodic table. (Practically all

of the compounds which we have used in our "calibration" of the method contain only elements lighter than neon.) Extension of the method to heavier atoms will probably require modification of this simple method of estimating S_{nm}.

(29) The I - EA values for the s orbitals of H, B, C, N, O, F, and Cl are 12.85, 9.21, 12.10, 12.87, 17.63, 13.87, and 9.57, resp., and the corresponding values for the p orbitals are (excluding H) 8.10, 10.93, 11.88, 15.13, 17.36, and 11.30. The h values correspond to the following hydridizations: H, pure s; B, sp^2; C and N, sp^3; O, F and Cl, almost pure p.

(30) The formula given for the weighting factor for the s electronegativity is valid only for bond orders of one or greater. (All the bonds in the compounds used to "calibrate" the method qualify in this respect.) To permit inclusion of bond orders less than one, N should be replaced by $1 + \pi$, where π is the π bond order.

(31) The term h is (I - EA) times the factor 0.1 (empirically determined). We could eliminate this factor by changing the charge weighting coefficients to 0.1b, 0.1, and 0.1c; however, we have not done this for the sake of simplicity.

(32) Because of the lack of the necessary core electron binding energy data, we have not yet considered molecules which are so electron deficient as to preclude octets for some atoms. Perhaps a reasonable rule would be to use structures with formal charges of zero as far

as possible. Thus for the isoelectronic species BN and LiF we would write the structures B≡N: and Li—$\ddot{\underset{..}{F}}$:.

(33) Hyperconjugated resonance structures are clearly eliminated by this restriction. However, extension of the method to "hypervalent" molecules such as PF_5 will probably require the use of "no-bond" resonance structures corresponding to structures with "half bonds."

(34) The relative weighting of formal charge and zero formal charge structures was applicable to the compounds used in our "calibration" of the method only in the cases of carboxylic acids and esters. Thus our weighting procedure is somewhat ad hoc and rarely applicable.

(35) Nitrous oxide was the only molecule in which the problem of the weighting of such structures arose. Hence our choice of weighting factors, although plausible, is completely ad hoc.

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Figure Captions

Figure 1. - Plot of E_B(expt) vs E_B(calc) for carbon 1s electrons (point for carbon monoxide marked).

Figure 2. - Plot of E_B(expt) vs E_B(calc) for nitrogen 1s electrons.

Figure 3. - Plot of E_B(expt) vs E_B(calc) for oxygen 1s electrons.

Figure 4. - Plot of E_B(expt) vs E_B(calc) for fluorine 1s electrons.

Figure 5. - Plot of standard deviation vs fraction of final state character in transition state.

Figure 6. - Plot of proton nmr chemical shifts for CH_3X compounds vs hydrogen atom charges. Nmr data from ref 50.

Figure 7. - Plot of ^{13}C nmr chemical shifts for $(CH_3)_{4-n}CH_n$ hydrocarbons vs carbon atom charges. Nmr data from ref 51. Solid circles correspond to CH_n carbons; open circles correspond to CH_3 carbons.

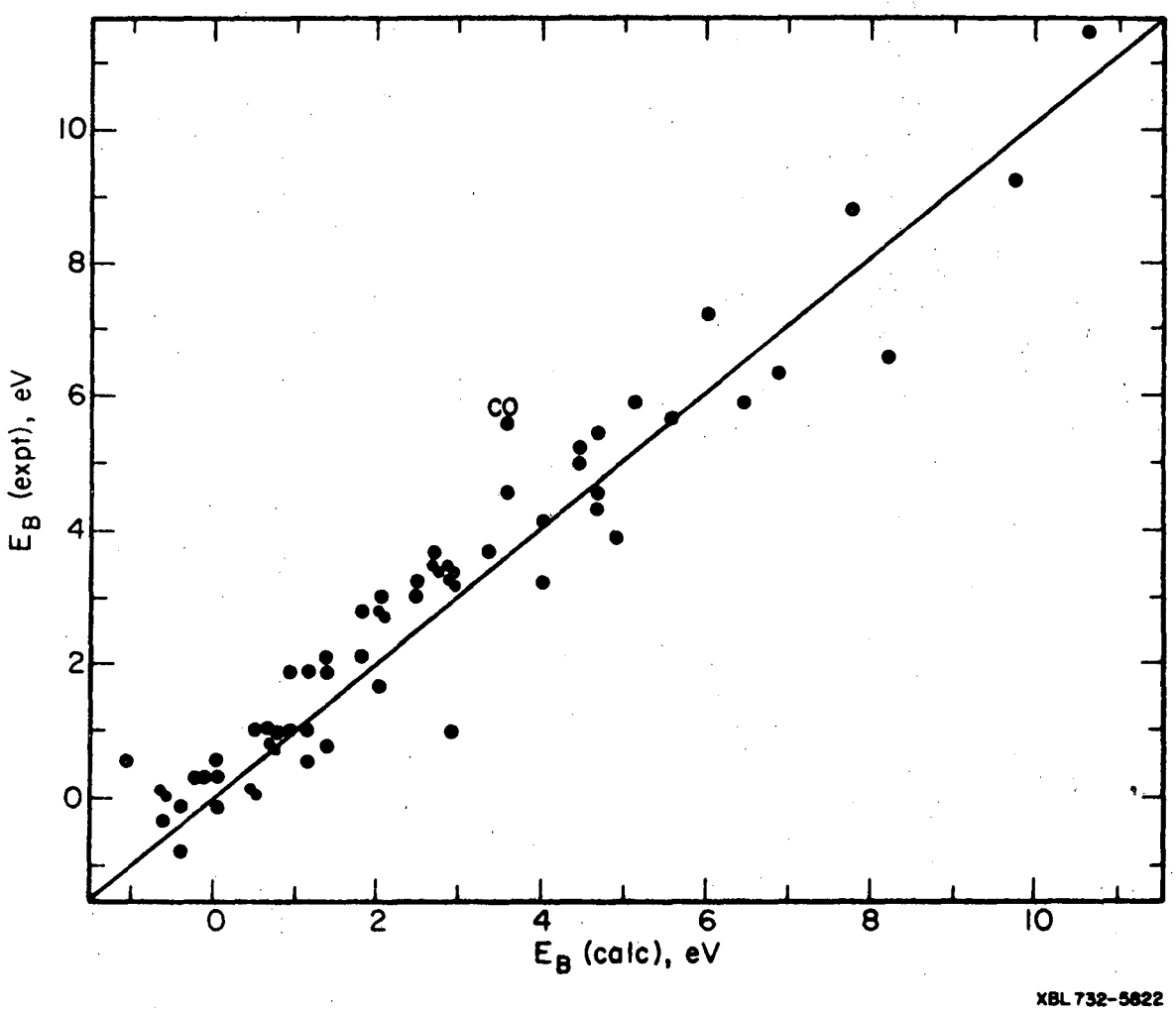


Fig. 1

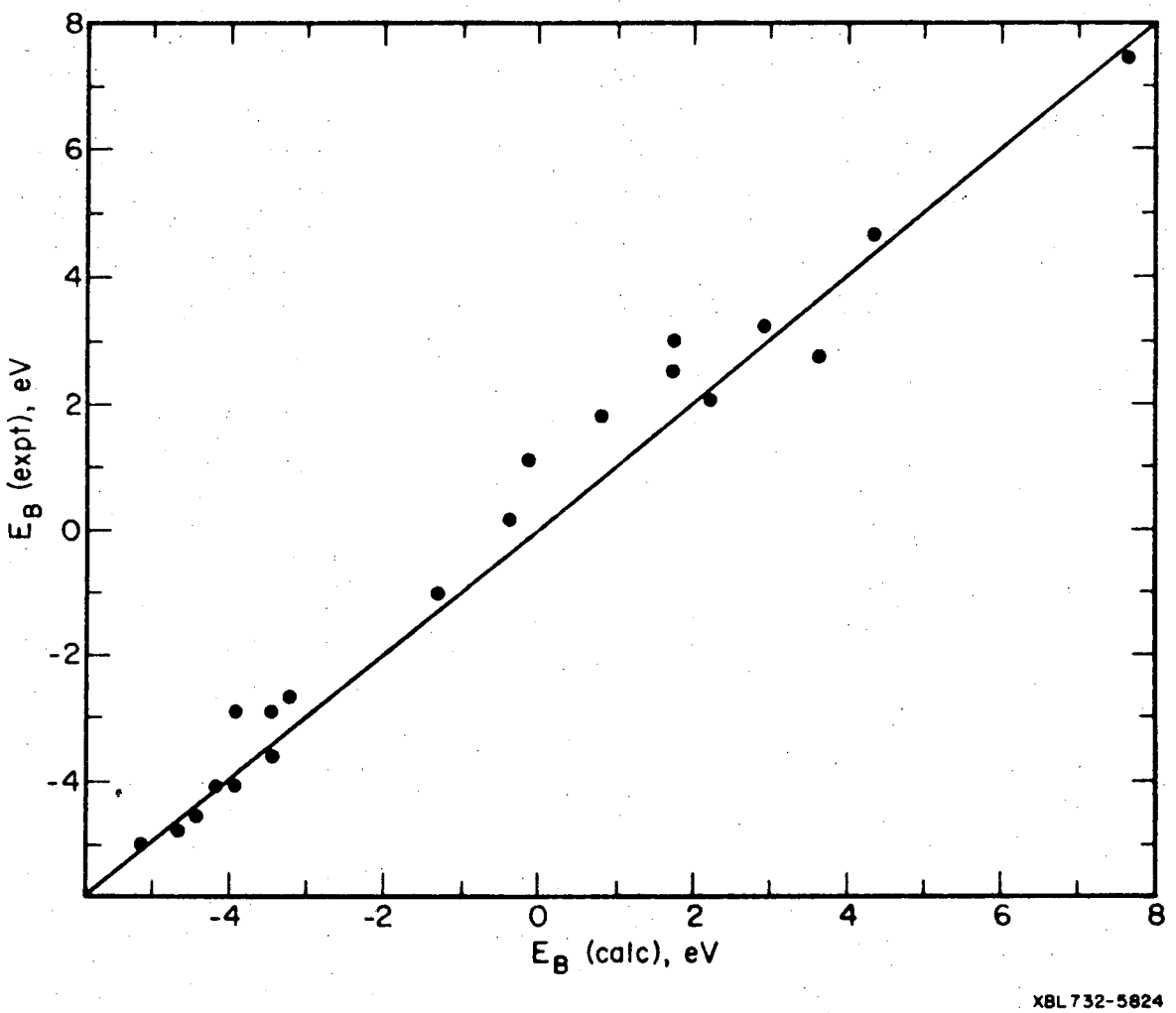


Fig. 2

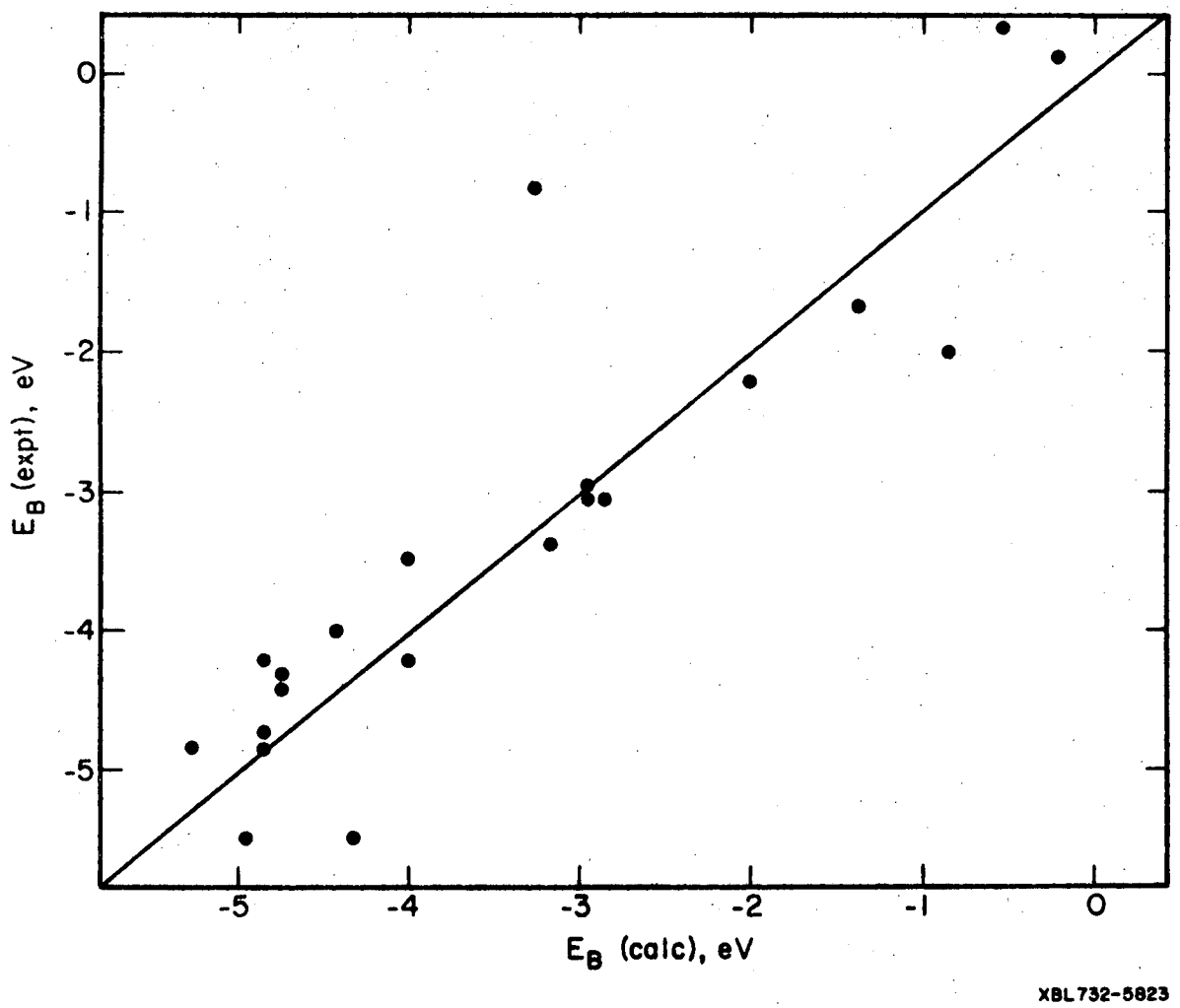


Fig. 3

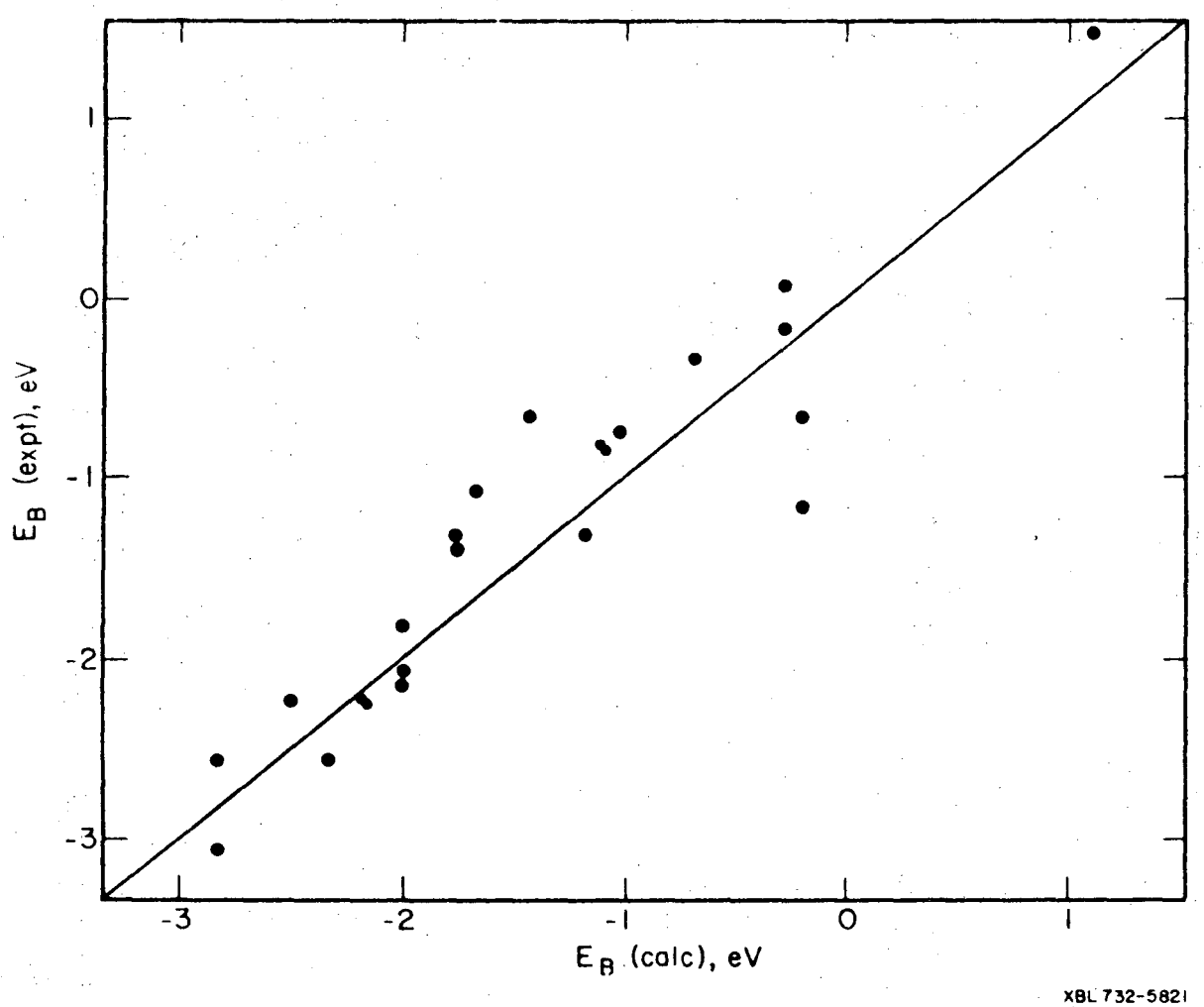
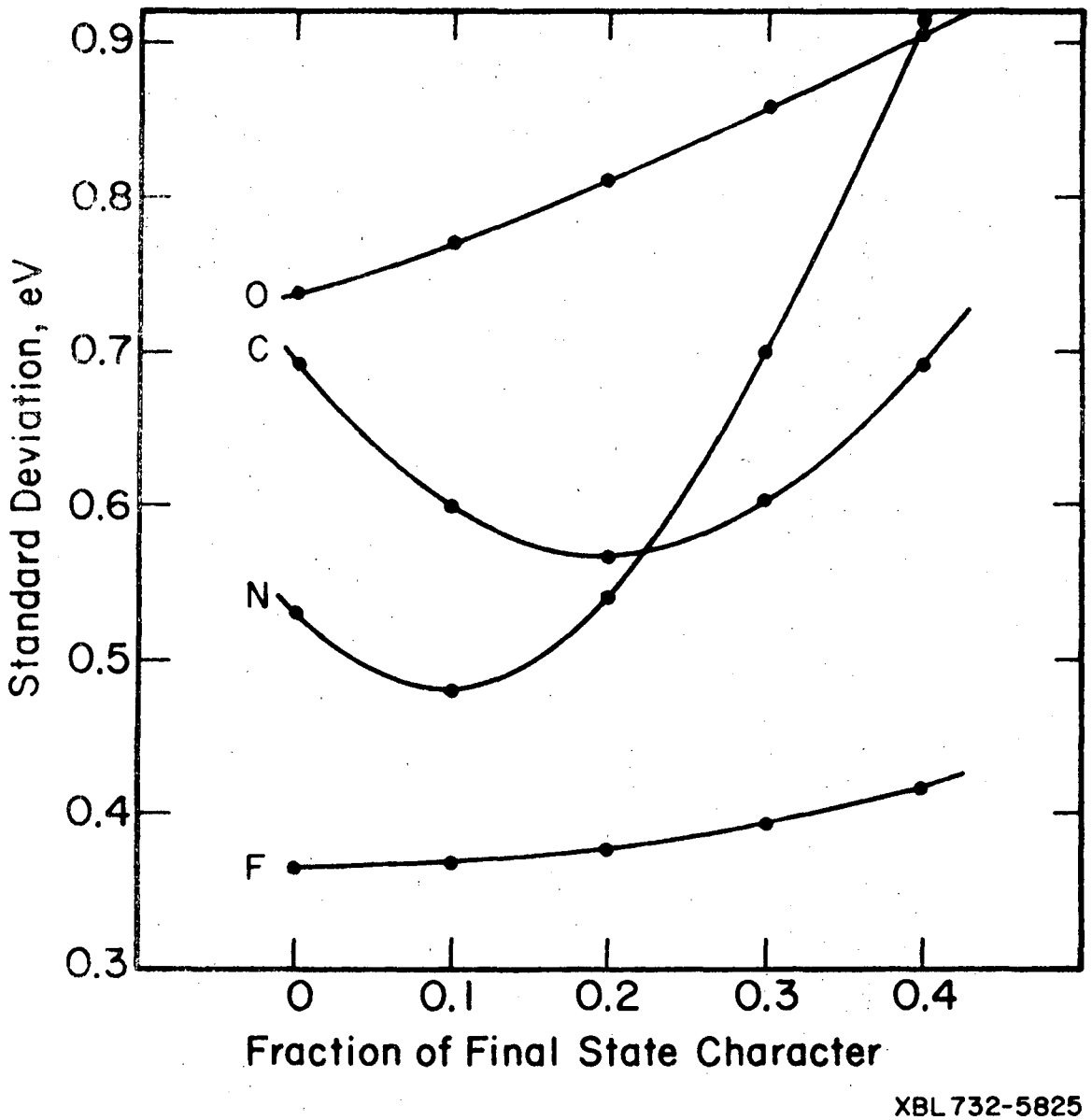


Fig. 4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0.8
0.7
0.6
0.5
0.4
0.3
Standard Deviation, eV
O
C
N
F
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0.2
0.3
0.4
Fraction of Final State Character
XBL 732-5825

Fig. 5

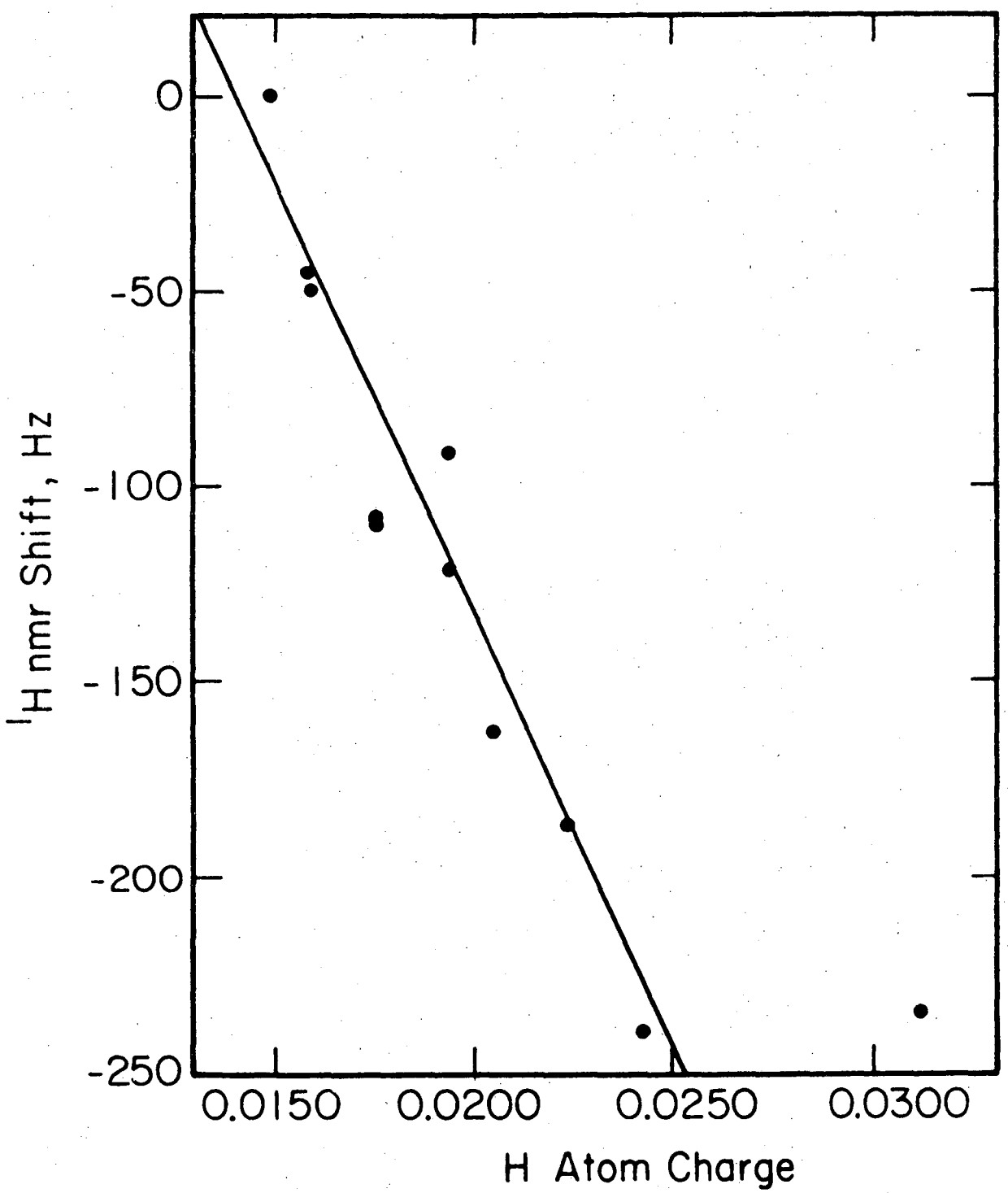

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Fig. 6

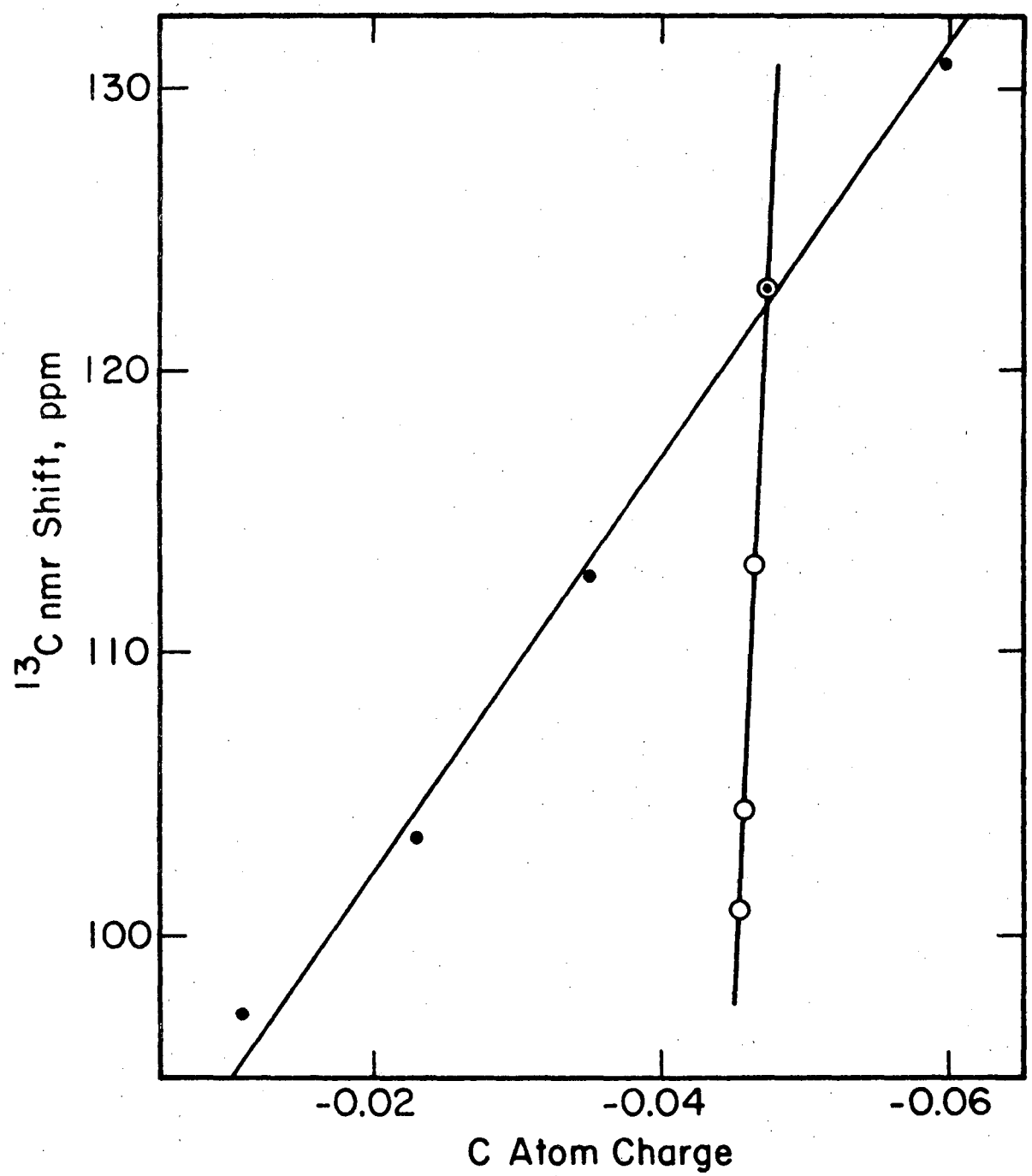

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Fig. 7

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