Conclusion

Binding energies of small molecules can be predicted by the EPCE-F2σ method within the ± 0.5-eV error range if accurate Hartree–Fock energies are available.

It was expected that the calculated correlation energies would depend on the choice of the molecular wave functions. Calculations have demonstrated that any molecular wave function yields a correlation energy which is within 5-6% of the experimental value. Generally, results are better than this range and we may conclude that the EPCE-F2σ method can predict the correlation energies of small molecules with an accuracy of usually less than 0.5 eV, although the discrepancies in C_2 and F_2, which many authors encountered, remain.

We have also investigated the correlation energies of some hydrocarbons, aromatics, and heterocyclic compounds. The results indicate that: (i) the absolute value of the correlation energy increases approximately 8.0 eV by addition of a CH_2 group; (ii) the absolute increase in correlation energy is approximately 2.0 eV after a π bond is broken and two CH bonds are formed; (iii) the correlation energy of a CH bond is approximately -0.66 eV; (iv) the interbond correlation is also very important.

The ratio of the correlation binding energy to the experimental value is approximately constant for noncyclic hydrocarbons and for aromatic compounds. Especially for very large molecules, the average value of the ratios can be used for predicting binding energies within an error range of 2-3 eV, which is considerably better than those possible say by approximate MO methods.

The HF energies of some large molecules are predicted by using the experimental binding energies, calculated correlation binding energies, and atomic HF energies. The errors in these calculations may be of the order of 0.1 au (*i.e.*, 2.7 eV). However, they would be a useful guide in finding better wave functions and energies by *ab initio* calculations.

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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.

Most of the chemical properties of molecular systems are 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.[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 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 *tabulations*, of electron density 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 used for evaluating atomic charges, and most of these have

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served advantageously in the correlation of atomic charge related properties. Of course the naive use of atomic charges is fraught with difficulties such as those due to neglect of the steric character of nonbonding electrons and the polarizability of atoms. It is now recognized that 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 spectroscpic 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.[16–25] 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 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. 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.

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 energies for gaseous compounds. It is well known that chemical shifts in these energies can be correlated with atomic charges by the so-called potential model equation[27]

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

In this equation, E_B is the binding energy for a particular core level in a particular atom (the "ionizing" atom), Q_i is the charge of the ionizing atom, V is the coulomb potential energy 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 atomic charges from an electronegativity equalization procedure thus "calibrated" with experimental binding energies are more suitable for theoretical calculations involving interatomic electrostatic interactions than atomic charges calculated by other, less empirical, 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

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).

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(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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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 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 Jaffe, are presented in Table I. The quantity q_{nm} refers to the negative charge transferred from atom n to atom m. The sum $\Sigma_{\mathrm{i} \neq \mathrm{m}} q_{\mathrm{ni}}$ 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. The parameters a, b, and 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 eq 1 with the appropriate least-squares adjusted values 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 eq 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 ($N_{\mathrm{nm}} > 1$), 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 $S_{\mathrm{nm}}/N_{\mathrm{nm}}$, we use the expression $S_{\mathrm{nm}}/(N_{\mathrm{nm}})^a$ (where $0 < a < 1$) as the weighting factor for the s electronegativity.[30] The parameter a accounts for the facts that σ bonds have greater orbital overlap than π bonds and that they probably contribute more heavily to q_{nm}.

The last term of eq 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

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

Hence

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

and

$$\frac{\mathrm{d}^2E}{\mathrm{d}Q^2} = \frac{\mathrm{d}x}{\mathrm{d}Q} = I - \mathrm{EA}$$

When the bond order between atoms n and m is greater than 1, 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 $q_{\mathrm{nm}}/N_{\mathrm{nm}}$. We use the *effective* charge per orbital, $q_{\mathrm{nm}}/(N_{\mathrm{nm}})^a$, to account for the fact that the σ bond contributes more heavily to q_{nm} than the π bonds. Thus the $1/(N_{\mathrm{nm}})^a$ factor serves a similar purpose in the two places where it appears in eq 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 $1/(N_{\mathrm{nm}})^a$ 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

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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 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, respectively, 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 hybridizations: 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.

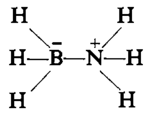
[31] The term h is (I − EA) times the factor 0.1 (empirically determined). We could eliminate this factor by changing the charge weighting coefficients to 0.1b, 0.1, and 0.1c; however, we have not done this for the sake of simplicity.

[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 $\mathrm{B{\equiv}N{:}}$ and $\mathrm{Li{-}\underset{\cdot\cdot}{\ddot{F}}{:}}$.

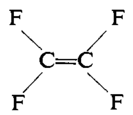
[33] Hyperconjugated resonance structures are clearly eliminated by this restriction. However, extension of the method to "hypervalent" molecules such as PF_5 will probably require the use of "no-bond" resonance structures corresponding to structures with "half-bonds."

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.

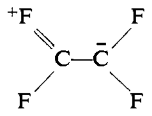
$^-C\equiv O^+$



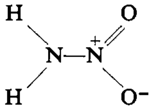
When more than one structure can be written for a molecule (*i.e.*, in the case of resonating molecules), the weighted average bond orders and formal charges are used. For example, we take the C–C bond order in benzene as 1.5. However, certain types of resonance structures are forbidden from consideration 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

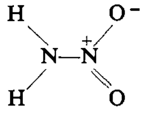


and rule out structures of the following type.

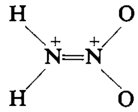


(b) Structures with adjacent atoms having the same nonzero formal charge are forbidden. Thus we consider only the following structures for NH_2NO_2

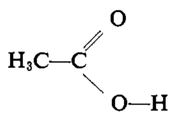




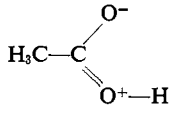
and ignore the following structure.



Acceptable structures with formal charges are weighted $^1/_9$ relative to structures without formal charges. Such weighting of the structures for acetic acid



and



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 $^-N{=}N^+{=}O$ structure, with two double bonds, twice as much as the $N{\equiv}N^+{-}O^-$ 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 eq 2 by simply interchanging n and m. Electronegativity equalization then leads to

$$\frac{b(h_m + h_n)}{(N_{nm})^a}q_{mn} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} = x(p)_n - x(p)_m + \frac{S_{nm}}{(N_{nm})^a}[x(s)_n - x(p)_n] - \frac{S_{mn}}{(N_{nm})^a}[x(s)_m - x(p)_m] + c(h_nF_n - h_mF_m) \quad (3)$$

An equation of this type is obtained for each bond in the compound. Thus, in general, the calculation of 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 eq 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

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(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*.

(36) J. W. Linnett, "The Electronic Structure of Molecules," Wiley, New York, N. Y., 1964.

Table II. Experimental and Calculated 1s Binding Energies

Compound	Q_1	E_B, eV Exptl	E_B, eV Calcd
$\mathrm{CH_4}$	−0.060	0.0	−0.60
$\mathrm{C_2H_6}^{a}$	−0.047	−0.2	−0.50
$\mathrm{CH_3F}^{b}$	0.076	2.8	2.17
$\mathrm{CH_2F_2}^{c}$	0.214	5.55	5.02
$\mathrm{CHF_3}^{b}$	0.355	8.3	7.76
$\mathrm{CF_4}^{b}$	0.498	11.0	10.49
$\mathrm{CH_3Cl}^{b}$	0.020	1.6	1.24
$\mathrm{CH_2Cl_2}^{b}$	0.099	3.1	3.00
$\mathrm{CHCl_3}^{b}$	0.178	4.3	4.71
$\mathrm{CCl_4}^{b}$	0.256	5.5	6.32
$\mathrm{C_2F_6}^{d}$	0.392	8.91	9.72
c-$\mathrm{C_4F_8}^{d}$	0.274	6.3	8.24
$\mathrm{CH_3OH}^{e,f}$	0.048	1.75	1.33
$\mathrm{\mathit{C}H_3CH_2OH}^{e}$	−0.041	0.2	−0.01
$\mathrm{CH_3\mathit{C}H_2OH}^{e}$	0.060	1.6	1.42
$\mathrm{H_2CO}^{e}$	0.111	3.3	2.70
$\mathrm{\mathit{C}H_3CHO}^{e}$	−0.023	0.6	0.74
$\mathrm{CH_3\mathit{C}HO}^{e}$	0.122	3.2	2.66
$\mathrm{(\mathit{C}H_3)_2CO}^{e}$	−0.022	0.5	0.70
$\mathrm{(CH_3)_2\mathit{C}O}^{e}$	0.132	3.1	2.62
$\mathrm{HCO_2H}^{e}$	0.230	5.0	4.54
$\mathrm{\mathit{C}H_3CO_2H}^{e}$	−0.014	0.7	1.25
$\mathrm{CH_3\mathit{C}O_2H}^{e}$	0.233	4.7	4.40
$\mathrm{C_2H_5O(CO)CH_2\mathit{C}H_3}^{e}$	−0.045	0.1	−0.06
$\mathrm{C_2H_5O(CO)\mathit{C}H_2CH_3}^{e}$	−0.003	1.7	1.07
$\mathrm{C_2H_5O(\mathit{C}O)CH_2CH_3}^{e}$	0.241	3.8	4.10
$\mathrm{C_2H_2}^{f}$	−0.062	0.4	−0.96
HCN^{f}	0.081	2.6	2.04
$\mathrm{OC\mathit{C}CO}^{g}$	0.032	0.8	2.87
$\mathrm{O\mathit{C}CCO}^{g}$	0.146	4.2	3.62
$\mathrm{CO}^{e,f}$	0.172	5.3	3.62
$\mathrm{CO_2}^{e}$	0.294	6.8	5.95
$\mathrm{\mathit{C}H_2CHF}^{d}$	−0.046	0.18	0.18
$\mathrm{CH_2\mathit{C}HF}^{d}$	0.078	2.54	1.91
$\mathrm{\mathit{C}H_2CF_2}^{d}$	−0.030	0.37	1.26
$\mathrm{CH_2\mathit{C}F_2}^{d}$	0.219	5.14	4.62
$\mathrm{\mathit{C}HFCF_2}^{d}$	0.109	2.93	4.02
$\mathrm{CHF\mathit{C}F_2}^{d}$	0.235	5.28	5.65
$\mathrm{CH\mathit{C}HCHCHO}^{h}$	−0.022	−0.4	0.21
$\mathrm{\mathit{C}HCHCHCHO}^{h}$	0.053	0.8	1.02
$\mathrm{CH\mathit{C}HCHCHNH}^{h}$	−0.028	−0.9	−0.28
$\mathrm{\mathit{C}HCHCHCHNH}^{h}$	0.006	0.1	0.00
c-$\mathrm{C_3H_6}^{i}$	−0.033	−0.3	−0.30
$\mathrm{(NC)_2C_2\mathit{C}H_2(CN)_2}^{i}$	−0.017	1.4	2.09
$\mathrm{(NC)_2\mathit{C}_2CH_2(CN)_2}^{i}$	0.100	4.1	4.65
$\mathrm{(N\mathit{C})_2C_2CH_2(CN)_2}^{i}$	0.096	3.1	2.87
$\mathrm{C_2H_4O}^{f,i}$	0.067	1.8	1.86
$\mathrm{(NC)_2\mathit{C}_2O(CN)_2}^{i}$	0.201	6.0	6.80
$\mathrm{(N\mathit{C})_2C_2O(CN)_2}^{i}$	0.102	3.4	3.47
$\mathrm{C_6H_6}^{e}$	−0.032	−0.5	−0.50
$\mathrm{C_6H_5F}$ (CF carbon)^{c}	0.106	2.43	2.15
$\mathrm{C_6H_5F}$ (CH carbons)^{c}	−0.027	0.39	0.06
o-$\mathrm{C_6H_4F_2}$ (CF carbons)^{c}	0.118	2.87	3.01
o-$\mathrm{C_6H_4F_2}$ (CH carbons)^{c}	−0.025	0.72	0.47
m-$\mathrm{C_6H_4F_2}$ (CF carbons)^{c}	0.107	2.92	2.54
m-$\mathrm{C_6H_4F_2}$ (CH carbons)^{c}	−0.020	0.70	0.69
p-$\mathrm{C_6H_4F_2}$ (CF carbons)^{c}	0.106	2.74	2.45
p-$\mathrm{C_6H_4F_2}$ (CH carbons)^{c}	−0.019	0.76	0.75
1,3,5-$\mathrm{C_6H_3F_3}$ (CF carbons)^{c}	0.107	3.02	2.91
1,3,5-$\mathrm{C_6H_3F_3}$ (CH carbons)^{c}	−0.008	0.56	1.52
$\mathrm{C_6F_6}^{c}$	0.132	3.57	4.96

Compound	Q_1	E_B, eV Exptl	E_B, eV Calcd
$\mathrm{N_2}$	0.000	0.0	−0.46
HCN^{j}	−0.152	−3.1	−3.74
$\mathrm{(NC)_2C_2(CN)_2}^{i}$	−0.149	−2.8	−3.04
$\mathrm{(NC)_2C_2CH_2(CN)_2}^{i}$	−0.150	−3.2	−3.26
$\mathrm{ONF_3}^{j}$	0.459	7.1	7.59
$\mathrm{NF_3}^{j}$	0.233	4.3	4.37
$\mathrm{N_2F_4}^{j}$	0.164	2.4	3.49
$\mathrm{\mathit{N}NO}^{j}$	−0.062	−1.3	−1.24
$\mathrm{N\mathit{N}O}^{j}$	0.116	2.6	1.72
NO^{j}	0.019	0.8	−0.10
$\mathrm{NO_2}^{j}$	0.180	3.0	3.00
$\mathrm{CH_3NO_2}^{d}$	0.162	2.23	1.84
$\mathrm{C_6H_5NO_2}^{e}$	0.178	1.7	2.11
ONCl^{j}	0.074	1.5	0.82
$\mathrm{N_2H_4}^{j}$	−0.150	−3.8	−3.46
$\mathrm{C_6H_5NH_2}^{e}$	−0.187	−4.4	−3.95
$\mathrm{NH_3}^{j}$	−0.211	−4.3	−4.05
$\mathrm{CH_3NH_2}^{j}$	−0.203	−4.8	−4.34
$\mathrm{(CH_3)_2NH}^{j}$	−0.194	−5.0	−4.64
$\mathrm{(CH_3)_3N}^{j}$	−0.186	−5.2	−4.95
$\mathrm{O_2}$	0.000	0.0	−0.27
$\mathrm{C_3O_2}^{g}$	−0.162	−3.5	−3.16
$\mathrm{CO}^{e,f}$	−0.172	−0.95	−3.31
$\mathrm{CO_2}^{e,f}$	−0.147	−2.35	−2.01
$\mathrm{CH_3CHO}^{e}$	−0.194	−5.5	−4.31
$\mathrm{(CH_3)_2CO}^{e}$	−0.193	−4.1	−4.36
$\mathrm{H(C\mathit{O})OH}^{f}$	−0.235	−4.79	−4.77
$\mathrm{H(CO)\mathit{O}H}^{f}$	−0.208	−3.17	−2.91
$\mathrm{CH_3(C\mathit{O})OH}^{e}$	−0.234	−4.9	−4.82
$\mathrm{CH_3(CO)\mathit{O}H}^{e}$	−0.208	−3.1	−2.92
$\mathrm{C_2H_5O(C\mathit{O})C_2H_5}^{e}$	−0.234	−5.5	−4.91
$\mathrm{C_2H_5\mathit{O}(CO)C_2H_5}^{e}$	−0.205	−4.3	−3.94
$\mathrm{H_2O}^{e,f}$	−0.240	−3.6	−3.97
$\mathrm{CH_3OH}^{e,f}$	−0.236	−4.4	−4.68
$\mathrm{C_2H_5OH}^{e}$	−0.235	−4.5	−4.68
$\mathrm{C_2H_4O}^{f}$	−0.229	−4.9	−5.22
$\mathrm{(NC)_2C_2O(CN)_2}^{i}$	−0.214	−3.2	−2.84
$\mathrm{N_2O}^{e,f}$	−0.054	−2.1	−0.90
NO^{e}	−0.019	0.2	−0.61
$\mathrm{NO_2}^{e}$	−0.090	−1.8	−1.42
$\mathrm{CH_3NO_2}^{d}$	−0.218	−4.35	−4.80
$\mathrm{CF_4}$	−0.124	0.0	−0.27
$\mathrm{CHF_3}^{c}$	−0.133	−0.9	−1.13
$\mathrm{CH_2F_2}^{c}$	−0.141	−1.87	−1.95
$\mathrm{CH_3F}^{c}$	−0.149	−2.6	−2.75
$\mathrm{CF_2Cl_2}^{d}$	−0.132	−0.88	−0.97
$\mathrm{C_2F_6}^{d}$	−0.130	−0.25	−0.28
$\mathrm{CH_3CF_3}^{d}$	−0.132	−1.39	−1.21
$\mathrm{CH_3CHF_2}^{d}$	−0.140	−2.22	−1.96
$\mathrm{C_2H_5F}^{d}$	−0.148	−3.15	−2.76
$\mathrm{CH\mathit{F}CF_2}^{d}$	−0.134	−1.47	−1.77
$\mathrm{CHFC\mathit{F}_2}^{d}$	−0.126	−0.77	−1.39
$\mathrm{CH_2CF_2}^{d}$	−0.127	−1.21	−1.62
$\mathrm{CH_2CHF}^{d}$	−0.135	−2.27	−2.44
$\mathrm{C_6F_6}^{c}$	−0.132	−1.26	−0.18
1,3,5-$\mathrm{C_6H_3F_3}^{c}$	−0.134	−2.13	−1.97
o-$\mathrm{C_6H_4F_2}^{c}$	−0.133	−2.27	−2.17
m-$\mathrm{C_6H_4F_2}^{c}$	−0.134	−2.34	−2.14
p-$\mathrm{C_6C_4F_2}^{c}$	−0.134	−2.34	−2.16
$\mathrm{C_6H_5F}^{c}$	−0.134	−2.64	−2.32
c-$\mathrm{C_4F_8}^{d}$	−0.137	−0.46	−0.70
HF^{k}	−0.151	−1.4	−1.77
$\mathrm{BF_3}^{d}$	−0.154	−0.9	−1.12
$\mathrm{NF_3}^{d}$	−0.078	−0.75	−0.21
$\mathrm{F_2}^{l}$	0.000	1.3	1.08

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[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, "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 707. [d] D. W. Davis and D. A. Shirley, unpublished data. [e] Reference 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. Lett.*, **11**, 224 (1971). [h] U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, *Phys. Scr.*, **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.

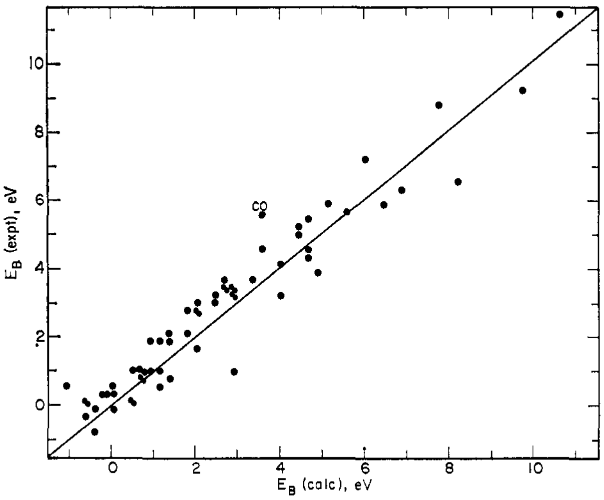

Figure 1. Plot of E_B(exptl) *vs.* E_B(calcd) for carbon 1s electrons (point for carbon monoxide marked). The E_B(exptl) values are from X-ray photoelectron spectroscopic measurements, and the E_B(calcd) values are calculated from eq 1, using the appropriate parameters from Table III and Q values calculated by the electronegativity equalization procedure.

central nitrogen atoms, respectively, we obtain the following two equations.

$$9.7721 q_{\mathrm{N_cN_T}} + 1.21 q_{\mathrm{N_cO}} = -6.2529$$

$$1.21 q_{\mathrm{N_cN_T}} + 13.9692 q_{\mathrm{N_cO}} = -4.6266$$

These equations yield $q_{\mathrm{N_cN_T}} = -0.605$ and $q_{\mathrm{N_cO}} = -0.279$, which, when account is taken of the weighted average formal charges, give $Q_{\mathrm{N_T}} = -0.062$, $Q_{\mathrm{N_c}} = +0.116$, and $Q_{\mathrm{O}} = -0.054$.

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

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 eq 1 was calculated using bond distance and bond angle data from the literature.[37] (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 1–4 we have plotted E_B(exptl) against E_B(calcd) 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 eq 1 for each element are given in Table III.

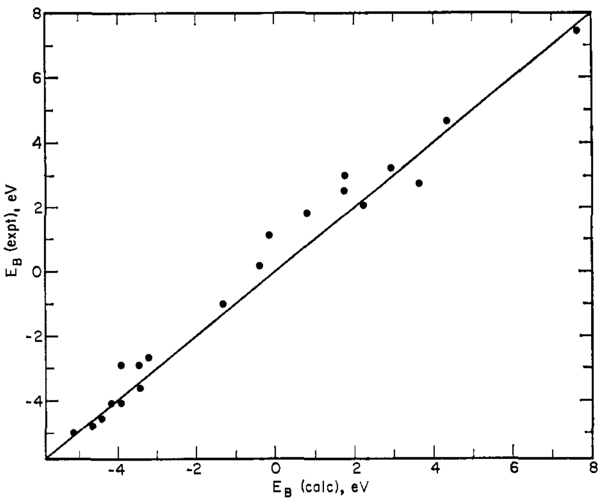

Figure 2. Plot of E_B(exptl) *vs.* E_B(calcd) for nitrogen 1s electrons. See comments in the caption of Figure 1.

Table III. Values of k and l Used in Eq 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

If we assign all of the standard deviation in E_B to uncertainty in the kQ_i term in eq 1, then our overall standard deviation of ±0.61 eV and the average k value of 31.8 correspond to an atomic charge uncertainty of ±0.019.

Relaxation Energy. It is well known that the ejection of a core electron from a molecule is accompanied by a relaxation process in which valence electrons flow toward the ionizing atom.[38–42] 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 in eq 1, no provision is made for the electronic relaxation associated with the photoemission process. The fact that eq 1 is fairly successful in correlating binding energies in spite of the neglect of this factor is evidence that the electronic relaxation energies of many molecules are similar. 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 itom, *i.e.*, with the ligancy of of the ionizing atom.[43] 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.

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(37) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11** (1958); *ibid.*, No. **18** (1965).

(38) P. S. Bagus, *Phys. Rev. A*, **139**, 619 (1965).

(39) P. S. Bagus and H. F. Schaefer, *J. Chem. Phys.*, **56**, 224 (1972).

(40) L. C. Snyder, *J. Chem. Phys.*, **55**, 95 (1971).

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

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

(43) D. W. Davis and D. A. Shirley, *Chem. Phys. Lett.*, **15**, 185 (1972).

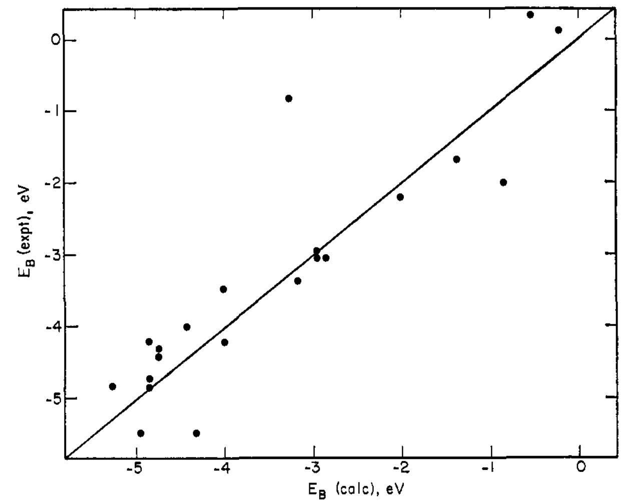

Figure 3. Plot of E_B(exptl) *vs.* E_B(calcd) for oxygen 1s electrons. See comments in the caption of Figure 1.

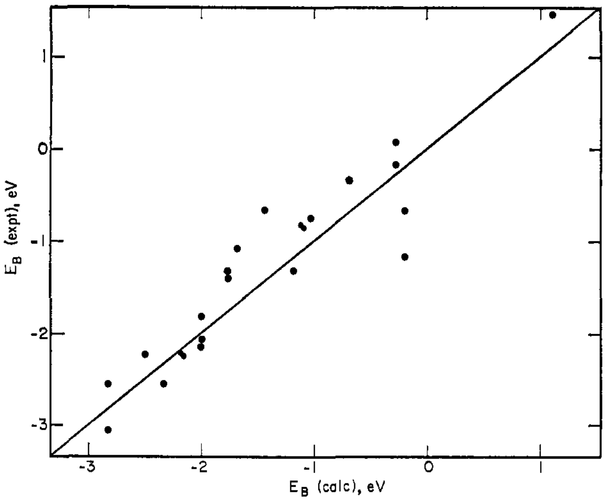

Figure 4. Plot of E_B(exptl) *vs.* E_B(calcd) for fluorine 1s electrons. See comments in the caption of Figure 1.

Both the carbon and nitrogen compounds include examples of ionizing atoms with ligancies 1–4, 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 sums of the 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(calcd) − E_B(exptl). 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.) Further support for the idea that the relaxation energy increases with increasing ligancy is found in recent data of Khodeyev, *et al.*[44] These investigators found that gaseous Bi has a core binding energy 1 eV higher than that of gaseous Bi_2.

Table IV. The Sum of the Deviations E_B(calcd) − E_B(exptl), 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.

The potential model of eq 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.[45] This procedure is equivalent to a quantum mechanical calculation outlined by Liberman[46] and Hedin and Johansson[47] 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.[48] 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 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[43] 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

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(44) Y. S. Khodeyev, H. Siegbahn, K. Hamrin, and K. Siegbahn, Uppsala University Institute of Physics Report UUIP-802, Dec 1972.

(45) W. L. Jolly, *Discuss. Faraday Soc.*, **54**, 13 (1972).

(46) D. Liberman, *Bull. Amer. Phys. Soc.*, **9**, 731 (1964).

(47) L. Hedin and A. Johansson, *J. Phys. Soc., London* (*At. Mol. Phys.*), **2**, 1336 (1969).

(48) J. C. Slater, *Advan. Quantum Chem.*, **6**, 30 (1972).

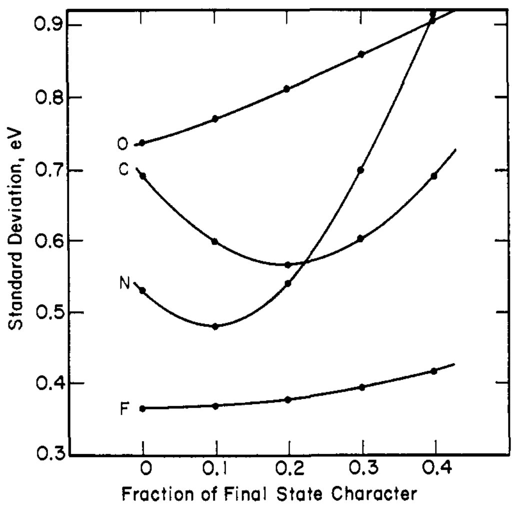

Figure 5. Plot of standard deviation *vs.* fraction of final state character in transition state.

Table V. Atomic Charges Calculated by Different Methods

Molecule and atom	Charge calculation method: This method	CNDO/2[a]	BBC[b]	Politzer[c]
*C*O	0.172	0.042	0.92	0.14
C*O*	−0.172	−0.042	−0.92	−0.14
*N*NO	−0.062	−0.145	0.39	−0.08
N*N*O	0.116	0.469	−0.07	0.33
NN*O*	−0.052	−0.324	−0.32	−0.25
*F*CN	−0.104	−0.114	−0.71	−0.02
F*C*N	0.172	0.293	1.72	0.23
FC*N*	−0.068	−0.179	−1.02	−0.21

[a] Reference 49. [b] Reference 1. [c] Reference 3.

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.

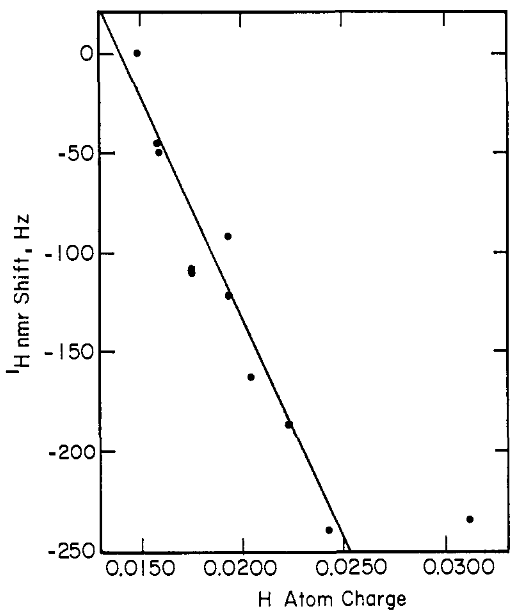

Figure 6. Plot of proton nmr chemical shifts for CH_3X compounds *vs.* hydrogen atom charges. Nmr data from ref 50.

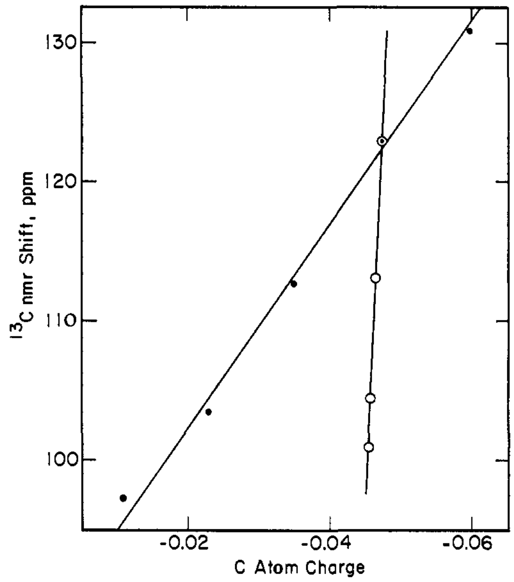

Figure 7. Plot of ^{13}C nmr chemical shifts for $(CH_3)_{4-n}CH_n$ hydrocarbons *vs.* carbon atom charges. Nmr data from ref 51. Solid circles correspond to CH_n carbons; open circles correspond to CH_3 carbons.

Comparison with Other Data

Some idea of the quantitative significance of the atomic charges calculated by our electronegativity equalization procedure can be obtained by comparing the charges with those calculated by other methods. In Table V we list the atomic charges for carbon monoxide, nitrous oxide, and cyanogen fluoride calculated by our method, the CNDO/2 method,[49] and the methods

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(49) P. J. Pople and D. S. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

of Bader, Beddall, and Cade[1] (BBC) and Politzer.[3] The data show that the calculated charges are strongly dependent on the recipe used for apportioning electron density among atoms. The BBC charges are very different from those of the other three methods, which are in qualitative agreement.

To demonstrate the versatility of the charges from 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 $\Sigma_{i \neq m} q_{ni}$ in eq 2 corresponds to the classical inductive effect. The fact that the coefficient for this term, unity, is small compared with the coefficients b and c indicates that the method predicts a rather small inductive effect. Chart I shows the calculated charges of the carbon atoms in n-octyl fluoride. The charge of a carbon atom in an infinitely long $-CH_2-$ chain is calculated to be -0.03346. By calculating the ratios of successive values of $Q_c + 0.03346$, we find that 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.

Chart I

Q_c	F	$Q_c + 0.03346$
0.08876	CH_2	0.12222
−0.02595	CH_2	0.00751
−0.03300	CH_2	0.00046
−0.03344	CH_2	0.00002
−0.03347	CH_2	−0.00001
−0.03351	CH_2	−0.00005
−0.03427	CH_2	−0.00081
−0.04655	CH_3	−0.01309

Acknowledgment. This research was supported by the U. S. Atomic Energy Commission.

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(51) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

(52) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 128–131.

Properties of Atoms in Molecules. V. An Easy Procedure for Estimating Atomic Charges from Calculated Core-Electron Energies[1]

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Abstract: Good linear relationships have been developed, for the atoms C, N, O, F, and Cl, between the charge on the atom when it forms part of a molecule and the calculated orbital energy of its 1s electrons. The charges used in obtaining these correlations were determined by a previously proposed integration procedure; with these relationships, however, it is now possible to estimate the atomic charges in many molecules simply by solving a set of simultaneous linear equations. Results are presented for a large number of molecules, and several cases are discussed in detail. The results for pyrazine and for lithium isocyanide are used to show how atomic charges computed by this method can help to understand and to predict chemical and physical properties of molecules.

Earlier papers in this series have presented and discussed a procedure for calculating the charge on an atom in a molecule directly from the molecular electronic density function.[3,4] This procedure has been applied to many diatomic and linear polyatomic molecules, and the results have been shown to be in good agreement with the properties of these molecules.[3–5]

Since these computations involve rather lengthy numerical integration, it would be desirable to have some alternate, simpler method for obtaining essentially the same results. It will now be shown that good estimates of these charges can be obtained for a large number of molecules by simply solving a set of linear simultaneous equations, provided that a good all-electron molecular orbital wave function is available for the molecule. The calculation of atomic charges then becomes a matter of a few minutes with a desk calculator.

Procedure

It has already been shown that the charges computed by numerical integration for fluorine in a series of diatomic fluorides and oxygen in a series of diatomic

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