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ITERATIVE PARTIAL EQUALIZATION OF ORBITAL ELECTRONEGATIVITY—A RAPID ACCESS TO ATOMIC CHARGES

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Abstract—A method is presented for the rapid calculation of atomic charges in σ-bonded and nonconjugated π-systems. Atoms are characterized by their orbital electronegativities. In the calculation only the connectivities of the atoms are considered. Thus only the topology of a molecule is of importance. Through an iterative procedure partial equalization of orbital electronegativity is obtained. Excellent correlations of the atomic charges with core electron binding energies and with acidity constants are observed. This establishes their value in predicting experimental data.

The electron distribution is one of the most important factors influencing the physical and chemical properties of molecules. Detailed information on the electron distribution can be obtained through various experimental and theoretical methods. But it has always been desired to associate part of the distribution with the individual atomic centers. Thus the picture of a molecule consisting of atoms carrying partial charges has emerged. And it has been attempted to explain the properties depending on the electron distribution from the values of these atomic charges.

Although chemists have an intuitive feeling for the qualitative nature of charge distributions the assignment of quantitative values is met with great difficulties. A simple method for determining atomic charges would be of great importance and would find many applications.

The definition of an atomic charge necessarily carries with it some arbitrariness by assigning the electron distribution to individual atoms. Any definition of atomic charges is relevant only when it can be used to correlate or predict physical or chemical properties of molecules.

Electron distributions are accessible through quantum mechanical calculations. From the wave functions thus obtained atomic charges can be determined. The most widely used method is the Mulliken population analysis.[1] But the results are heavily dependent on the level of the quantum mechanical approach being taken and the basis set chosen.

As a typical example for methane, the simplest organic molecule, charges on the H atom range (in units of 10^{-3} electron) from -10 (MINDO/3)[2], 13 (CNDO/2)[3], 18 (STO-3G)[4], 133 (STO)[5], 133 (EHT)[6], 0.152 (4-31G)[7], to 0.165 (6-31G*).[7]

Thus, the values differ not only by a factor of 15 but even in the sign of the charge. The problem with the population analysis lies mainly in the equal partitioning of the overlap charge between unequal atoms. Several other attempts have been proposed[8] to remedy this deficiency but none has found general acceptance.

The development of quantum mechanical methods and the concurrent advent of high speed computers apparently made other approaches to atomic charges obsolete. As we were interested in a fast method to access atomic charges for predicting reactivity in the synthetic design program EROS[9] we considered other approaches, too.

Electronegativity

Electronegativity was originally introduced[10] as an atomic property and deduced from bond energies. Mulliken's definition[11] (eqn 1) which relates the electronegativity χ_v of an atom to its ionization potential I_v and to the electron affinity E_v, put the electronegativity concept on a sounder theoretical basis.

$$\chi_v = \tfrac{1}{2}(I_v + E_v) \tag{1}$$

Mulliken also pointed out that in this definition the ionization potentials I_v and the electron affinities E_v of valence states have to be used. Thus electronegativity had become a characteristic of a specific valence state of an atom.

This idea was further elaborated by Hinze *et al.*[12–15] They introduced the concept of orbital electronegativity, the electronegativity of a specific orbital in a given valence state. Values for the orbital electronegativities were obtained from ground state ionization potentials and electron affinities and from valence state promotion energies deduced from spectroscopic data.[12,13,15,16]

Orbital electronegativities do not only depend on hybridization but also on the occupation number n of an orbital. An empty orbital ($n = 0$) has a higher electron attracting power than an orbital occupied by one electron ($n = 1$) and this, in turn, more than a doubly occupied orbital ($n = 2$). The concept of orbital electronegativity develops its full potential when applied to atoms in molecules. The difference of the orbital charge density of an atom in its unperturbed state ($n = 1$) and in a molecular environment is commonly interpreted as a partial charge q_{iv} residing in the orbital v of an atom A_i. This implies nonintegral values for the occupation number

n_{iv} ($n_{iv} = 1 - q_{iv}$). For the dependence of electronegativities on charge q_{iv} power series have been proposed.[12,17–19] Generally a linear equation was accepted as satisfactory.

Sanderson[20,21] first proposed that on bond formation atoms change their average electron density until total equalization of electronegativity is reached, i.e. all atoms have the same electronegativity. Based on the concept of electronegativity equalization group electronegativities,[22,23] dipole moments,[16] bond dissociation energies,[24] and atomic charges[21,25] were calculated. But total equalization of electronegativity leads to chemically unacceptable results. First, in a molecule or group, each atom of the same sort obtains the same charge. For example, in acetic acid all four hydrogen atoms receive the same charge, although undoubtedly, the carboxylic hydrogen has a lower electron density.

And further, isomeric groups receive the same group electronegativity, e.g. 1-fluorobutyl, 2-fluorobutyl, 3-fluorobutyl and 4-fluorobutyl get the same electronegativity although the group with fluorine closest to the point of attachment has the highest electron attracting power.

Pritchard[26] pointed out that changes in overlap should result in only partial equalization of electronegativity. Limited attempts to prevent total equalization of orbital electronegativity have been made. They suffer from limited applicability,[27,28,29] large number of parameters,[28,29] or the requirement for "chemically reasonable" starting values.[30,31]

In spite of these deficiencies we held the concept of electronegativity as promising enough to warrant the development of a model for calculating atomic charges on this basis. Our model[32,33] is heuristic in nature but for its main features sound physical arguments can be given.

The model

The set of atoms and the way they are connected determine a large part of molecular properties. It is therefore interesting to investigate how well atomic charges in a molecule could be reproduced by taking into account only properties of the constituent atoms of a molecule and the network of bonds.

Atomic properties

The dependence of electronegativity on charge. The electronegativity of an orbital does not only depend on the charge in this orbital but will also be influenced by the charges in the other orbital. For this dependence of orbital electronegativity on the total charge Q, irrespective of whether part of it resides in the orbital considered or in the other orbitals, we selected a polynomial of degree two.

$$\chi_{iv} = a_{iv} + b_{iv}Q_i + c_{iv}Q_i^2. \qquad (2)$$

This choice was made as (1) a second order polynomial provides more flexibility than a linear equation, (2) this approach is more in line with the findings of Iczkowski and Margrave[11] that the dependence of the energy of successive ionization states on charge is nearly completely reproduced when terms up to the third power are used, (3) it was shown[30] that the dependence of the ionization potential and the electron affinity of an orbital upon the sum of charges residing in the other orbitals q_s, can reasonably well be approximated by a three term power series, e.g. eqn (3)

$$I_v = \alpha + \beta q_s + \gamma q_s^2 \qquad (3)$$

Having settled on eqn (2) as the appropriate form for the dependence of electronegativity on charge, one needs three fixpoints to determine the coefficients a, b and c. The coefficient a is equal to the orbital electronegativity of the uncharged state taken from Ref. 13

$$\chi_{iv}(q = 0) = a_{iv} = \tfrac{1}{2}(I^0_{iv} + E^0_{iv}). \qquad (4)$$

It is usually assumed that bonds to halogen atoms involve some s-character on the part of the halogens. For Cl, Br and I averages of the values given by other investigators[12,27] and deduced from NQR experiments[34] were chosen, for fluorine an s-character of 13%, slightly higher than found in literature, was selected as it showed improved correlations with experimental data. Values for the orbital electronegativities for these percentages of s-character were obtained through linear interpolation between the electronegativities of an s- and a p-orbital.

As a second value the orbital electronegativity of positive ions were chosen. These values have been given for some important atomic ions[14] by applying Mulliken's definition of electronegativity to the cationic state

$$\chi^+_{iv}(q = +1) = \tfrac{1}{2}(I^+_{iv} + E^+_{iv}). \qquad (5)$$

For the positive ions of halogens no valence state orbital ionization potentials and electron affinities are given in ref 14. As values for the ionization potentials the second ionization potentials given in ref. 35 were selected, the electron affinities of the cationic states were set equal to the ionization potentials in the neutral states. With these values the electronegativity χ_i^+ of a pure p-orbital is obtained. Comparison with χ_i^+ values of other atoms suggests that χ_i^+ of an s-orbital is higher than that of a p-orbital by a factor of 1.80. Linear interpolation between these two values gives the value of the electronegativity of an orbital with the desired amount of s-character.

Hydrogen poses a special problem as there is no second ionization possible. Hinze and Jaffe[14] obtained for χ^+ a value of 20.02 eV and this value was used in eqns (8) and (9). On the other hand a linear dependence of electronegativity on charge[13] for hydrogen over the entire region seems unreasonable. The proton being such an outstanding species this value should be reached with particular steepness. This asks for a parabola with a smaller slope around q = 0. Such a slope was calculated as an average of the slopes with linear dependence and the one obtained by setting $\chi^+ = \frac{1}{2}IP^0$.

And finally, for the negative ions we again used Mulliken's electronegativity formula, setting the ionization potential of the negative ion equal to the electron affinity of the uncharged state and assuming the electron affinity of the negative ion to be zero.

$$\chi^-_{iv}(q = -1) = \tfrac{1}{2}(I^-_{iv} + E^-_{iv}) = \tfrac{1}{2}(E^0_{iv} + 0) = \tfrac{1}{2}E^0_{iv}. \qquad (6)$$

With three points fixed the coefficients a_{iv}, b_{iv}, and c_{iv} of eqn (2) can be determined for the various orbitals by the following equations:

$$a_{iv} = \tfrac{1}{2}(I^0_{iv} + E^0_{iv})$$

$$b_{iv} = \tfrac{1}{4}(I^+_{iv} + E^+_{iv} - E^0_{iv})$$

$$c_{iv} = \tfrac{1}{4}(I^+_{iv} - 2I^0_{iv} + E^+_{iv} - E^0_{iv})$$

The values are given in Table 1.

The coefficients c_{iv} of the quadratic term in eqn (2) are small indicating that a linear approach for the dependence of orbital electronegativity on charge is a rather good approximation.

The orbital electronegativity of an atom A_i in the +1 state, χ^+_{iv}, is given by setting $Q_i = +1$ in eqn (2)

$$\chi^+_{iv} = a_{iv} + b_{iv} + c_{iv} \qquad (8)$$

In order to maintain a state of +1 at atom A_i in a molecule an atom A_j bonded to A_i must have an electronegativity which is at least as high as χ^+_{iv}. As χ^+_{iv} relates an electronegativity value to the removal of one electron it can be used to scale any electronegativity difference between two bonded atoms to a charge transfer in electron units (see eqn 8).

The network of bonds

The procedure. Any method calculating atomic charges in σ-bonded systems must be able to represent the inductive effect. Two fundamental questions have to be answered: (1) How does the charge on a multivalent atom change on successive substitution, and (2) how does the inductive effect decrease with increasing number of bonds between the atoms under consideration?

It has been shown that the principle of total equalization of electronegativity leads to chemically unacceptable results. The assumption that the electronegativities of atoms connected by a bond totally equalize is unsound also on physical grounds. The driving force for the transfer of charge between two bonded atoms A and B ($\chi_B > \chi_A$) is the gain in electrostatic energy.

But on charge transfer an electrostatic field is generated which makes further charge transfer more difficult. It must effect a damping of the charge transfer before total equalization of electronegativity is reached. To allow for this damping influence of the electrostatic field an iterative "ansatz" according to eqn (8) was made.[36]

$$q^{<\alpha>} = \frac{\chi_B^{<\alpha>} - \chi_A^{<\alpha>}}{\chi_A^+}\left(\frac{1}{2}\right)^{\alpha} \qquad (8)$$

Table 1. Parameters for the dependence of orbital electronegativity on charge (eqn 2): (a) te = tetrahedral (sp^3), tr = trigonal (sp^2), di = digonal (sp); (b) the hybridization was adjusted to a bond angle of 106° (methanol); (c) s-character of 13%; (d) s-character of 17%; (e) s-character of 17%; (f) s-character of 23%.

Atom	Valence State ^{a}	a	b	c
H		7.17	6.24	-0.56
C	tetetete	7.98	9.18	1.88
	trtrtrπ	8.79	9.32	1.51
	didiππ	10.39	9.45	0.73
N	te^{2}tetete	11.54	10.82	1.36
	tr^{2}trtrπ	12.87	11.15	0.85
	di^{2}diππ	15.68	11.7	-0.27
O	te^{2}te^{2}tete ^{b}	14.18	12.92	1.39
	tr^{2}trtrπ	17.07	13.79	0.47
F	s^{2}p^{2}p^{2}p ^{c}	14.66	13.85	2.31
Cl	s^{2}p^{2}p^{2}p ^{d}	11.00	9.69	1.35
Br	s^{2}p^{2}p^{2}p ^{e}	10.08	8.47	1.16
J	s^{2}p^{2}p^{2}p ^{f}	9.90	7.96	0.96
S	te^{2}te^{2}tete	10.14	9.13	1.38

In this equation α gives the number of the iteration step. In the first iteration step ($\alpha = 1$) only part (1/2) of the electronegativity of atom B is allowed to exert its influence on atom A and transfer charge. This is done to consider the electrostatic field generated through charge transfer in the following iteration steps. With the charge $q^{<1>}$ calculated through eqn (8) new electronegativities $\chi_B^{<2>}$ and $\chi_A^{<2>}$ are calculated by eqn (2) and with them eqn (8) reentered, now having a damping factor of 1/4. The total charge of an atom is obtained as the sum of the individual charge transfers. Equation (8) ensures a rapid convergence of the procedure.

In polyatomic molecules all neighbors directly bonded to an atom A_i must be taken into account simultaneously within an iteration step. For neighbors A_j of atom A_i which are more electronegative than A_i the value χ_i^+ is taken, whereas for neighbors A_k which are less electronegative than A_i the value χ_k^+ must be considered as electrons are taken away from the electropositive atom. This leads to eqn (9) for the charge generated on atom A_i in each iteration step

$$q_i^{<\alpha>} = \left[\sum_j \frac{1}{\chi_{i\nu}^+} (\chi_{j\mu}^{<\alpha>} - \chi_{i\nu}^{<\alpha>}) + \sum_k \frac{1}{\chi_{k\lambda}^+} (\chi_{k\lambda}^{<\alpha>} - \chi_{i\nu}^{<\alpha>}) \right] \left(\frac{1}{2} \right)^{\alpha} \qquad (9)$$

After each step the total charge $Q_i^{<\alpha>}$ is calculated from eqn (10) and with it eqn (2) is entered to gain new electronegativities.

$$Q_i^{<\alpha>} = \sum_{\alpha} q_i^{<\alpha>}. \qquad (10)$$

Thereby with each iteration step the influence of successive spheres of neighbors is exerted onto an atom. Obviously, eqn (9) considers only the directly bonded neighbors of an atom. In these equations the geometry of the molecule is not taken into account. The approach is purely topological in nature.

The model as given above is applicable to σ-bonded systems and to nonconjugated π-systems. For the treatment of conjugated π-systems an extension of the model has been developed.[37] In nonconjugated π-systems the σ-charges inflict a polarization onto the π-electrons. These additional π-charges were calculated, too, but are in most cases only small. In the correlations with charges of non-conjugated π-systems total charges are considered.

The program

The above procedure PEOE (*P*artial *E*qualization of *O*rbital *E*lectronegativity) has been written as a PL/1 program. It works on the same data structure used in the reaction simulation and synthetic design program EROS.[9] Here it was of advantage to employ in this program system a topological representation of molecules giving direct access to all individual atoms and bonds. Further, multiple bonds are characterized as such and charges are explicitly handled making hybridization states easily recognizable. The parameters $a_{i\nu}$, $b_{i\nu}$, and $c_{i\nu}$ for eqn (2) are contained in tables and are accessed after identification of valence states and bonding orbitals.

Each iteration starts at an arbitrary atom and cycles through all atoms. The procedure given by eqns (2), (9) and (10) is such that in each iteration step electroneutrality is automatically preserved.

Performance of the procedure

The form of the damping factor $(1/2)^{\alpha}$ guarantees that rapid convergence is achieved. In fact, the amount of charge shifted usually falls below 0.001 electron in the fourth or fifth iteration step. In all cases it suffices to terminate the procedure with the sixth iteration step.

As an example methyl fluoride is given in Table 2.

Table 2. Computation of charge distribution for methyl-fluoride; charges in units of 10^{-3} electrons electronegativities in eV.

Cycle	q_C	q_F	q_H	χ_C	χ_F	χ_H
0				7.98	14.66	7.17
1	114	-175	20	9.06	12.30	7.29
2	91	-218	42	8.83	11.75	7.43
3	84	-237	51	8.76	11.50	7.49
4	81	-246	55	8.73	11.39	7.51
5	79	-251	58	8.72	11.33	7.52
6	79	-253	58	8.72	11.31	7.53

It should be noted from Table 2 that in each iteration step the electroneutrality rule is obeyed, i.e. the sum of all partial charges gives the overall charge of the system under consideration.

Of outstanding importance is the speed of the procedure. For a molecule of ten to fifteen atoms the program needs about 0.01 to 0.02 sec of computation time on an AMDAHL 470 V6. Thus, the calculation of atomic charges is several powers of ten faster than with quantum mechanical methods. Particularly important is that computation times increase only about linearly with the number of atoms, whereas with quantum mechanical computations the increase is with the third or fourth power of the number of atoms. Even a molecule like cholic acid (69 atoms), economically inaccessible to quantum mechanical procedures, requires only 0.31 sec of computation time with the iterative partial equalization of orbital electronegativity method.

Evaluation of charges

Core electron binding energies. Core electron binding energies obtained through ESCA measurements can be used in "possibly the least ambiguous simple way to estimate charges".[38] Quite early, a simple classical atomic potential model was used to correlate shifts in binding energies with charge.[39] Various other correlations involving charge values have been given.[40–46] A near linear charge dependence of core electron binding energies was observed in many cases, although sometimes problems arose[39,45,46] with the selection of a method for the calculation of atomic charges.

Conversely core electron binding energies have been used to calibrate methods for estimating atomic charges.[47–49] This has led to the opinion that through ESCA measurements and their interpretation "the chemists are closer than ever to the elusive goal of defining atomic charges in molecules"[38]

Potential models have been frequently[39,42,44,50,51] applied for the correlation of core electron binding energy shifts. According to such a model the ESCA shifts are related to the charge on an atom and the molecular potential on this atom due to the charges on all other atoms. If there is a linear relationship between the charge on an atom and the molecular potential it should be possible to correlate ESCA shifts directly with the charge on the atom considered.

We have tested this latter more direct approach. Figure 1 shows a correlation of C-1s core electron binding energy shifts for halogen-containing methane derivatives.

The excellent correlation (r = 0.993, standard deviation = 0.18 eV) demonstrates, that the simple model in which the C-1s core electron binding energy depends on the charge on carbon is valid for this series of compounds. Further, the values for the charges from the iterative partial equalization of orbital electronegativity method of these compounds are of high quality for reproducing ESCA shifts. The measurements analyzed here suggest the additivity of inductive effects. This is supported by evidence from

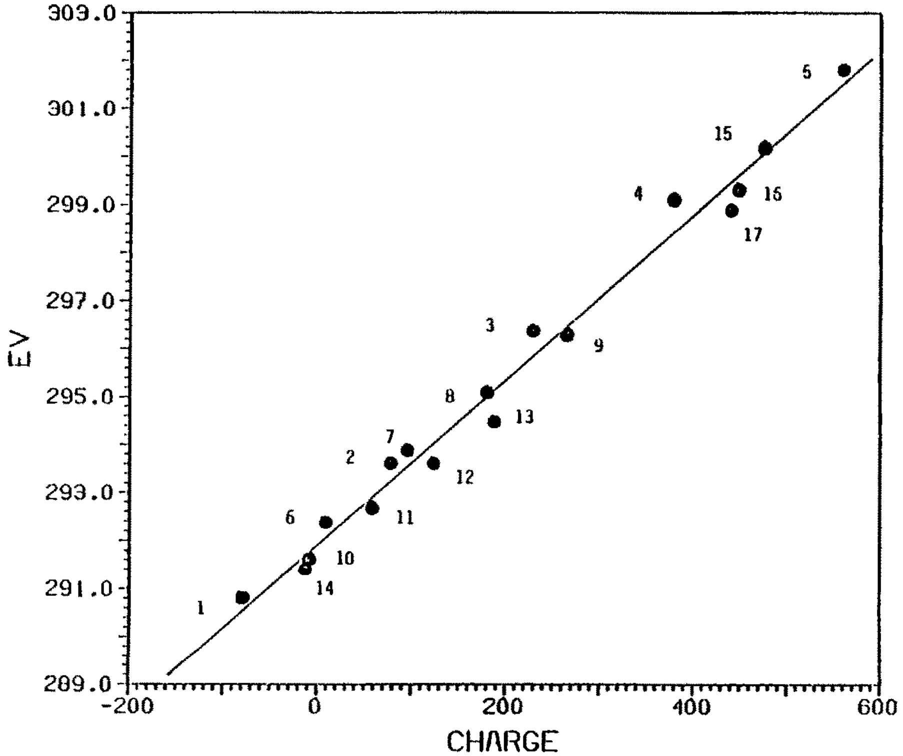

Fig. 1. C–1s binding energies of halogenated methanes vs. charge on carbon atom (in me) from our method; exp. values: Refs. 32, 54 (the reference point for the CF_3X compounds is not given explicitly: the values have been recalculated by us relative to CF_4) and D. W. Davis, D. A. Shirley and T. D. Thomas, *J. Chem. Phys.* **56**, 671 (1972): 1, CH_4; 2, CH_3F; 3, CH_2F_2; 4, CHF_3; 5, CF_4; 6, CH_3Cl; 7, CH_2Cl_2; 8, $CHCl_3$; 9, CCl_4; 10, CH_3Br; 11, CH_2Br_2; 12, $CHBr_3$; 13, CBr_4; 14, CH_3J; 15, CF_3Cl; 16, CF_3Bri; 17, CF_3J.

quantum mechanical calculations,[40,41] ESCA shifts,[40–42,52] and alkyl inductive effects.[53]

For some of the above compounds a correlation with the sum of Pauling electronegativity differences has already been quite successful.[44,52] But this approach is directly applicable only to compounds with one central atom and monovalent ligands. It cannot be applied to the general case of σ-bonded systems.

To extend the study to a wider variety of compounds, selected as unbiased as possible, all those compounds were taken for which STO-3G charges were available[4] and for which C-1s core electron binding energies have been determined. Altogether these were 17 compounds and 22 values (Table 3).

The PEOE charges give an excellent correlation with the carbon core electron binding energies (Fig. 2) with r = 0.987 and a standard deviation of 0.27 eV.

The largest deviation is caused by acetylene where relaxation effects in the π-electrons probably play an important role. If this point is disregarded in the correlation the standard deviation drops to 0.18 eV. Although ESCA shifts can be determined on careful calibration to within 0.1 eV a much higher uncertainty is to be expected when absolute values determined in different laboratories—as is done here—are

Table 3. Comparison of atomic charges on carbon and C-1s core electron binding energy shifts. All charges in millielectrons; core level shifts (ε_{C-1s}) relative to methane. (a) Ref. 4; (b) our values; (c) W. B. Perry and W. L. Jolly, *Inorg. Chem.* **13**, 1211 (1974); (d) Ref. (42); (e) T. D. Thomas, *J. Chem. Phys.* **52**, 1373 (1970); (f) Ref. 43; (g) D. W. Davis, D. A. Shirley and T. D. Thomas, In *Electron Spectroscopy* (Edited by D. A. Shirley), North-Holland, Amsterdam (1972); (h) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.* **52**, 3295 (1970); (i) Ref. 47

		ab initio[a]	PEOE[b]	ε_{C-1s}[c]	ref
1	CH_4	- 73	- 78	0	
2	CH_3CH_3	- 26	- 68	-0.2	c
3	$CH_2{=}CH_2$	-156	-106	-0.1	d
4	$HC{\equiv}CH$	-182	-122	0.4	e
5	CH_3F	169	79	2.8	d
6	CH_2F_2	383	230	5.6	d
7	CHF_3	532	380	8.28	d
8	CF_4	674	561	11.0	d
9	$^{*}CH_3CH_2F$	- 58	- 37	0.2	d
10	$CH_3{}^{*}CH_2F$	209	87	2.4	d
11	$^{*}CH_3CF_3$	- 99	39	1.1	d
12	$CH_3{}^{*}CF_3$	546	387	7.6	d
13	CH_3OH	136	33	1.6	f
14	CH_3OCH_3	161	36	1.4	c
15	H_2CO	-167	115	3.3	g
16	$^{*}CH_3CHO$	- 61	- 9	0.6	f
17	$CH_3{}^{*}CHO$	211	123	3.2	f
18	$^{*}CH_3COCH_3$	- 64	- 6	0.5	f
19	$CH_3{}^{*}COCH_3$	260	131	3.1	f
20	HCN	- 70	51	2.6	h
21	$^{*}CH_3CN$	62	23	2.1	i
22	$CH_3{}^{*}CN$	21	60	2.1	i

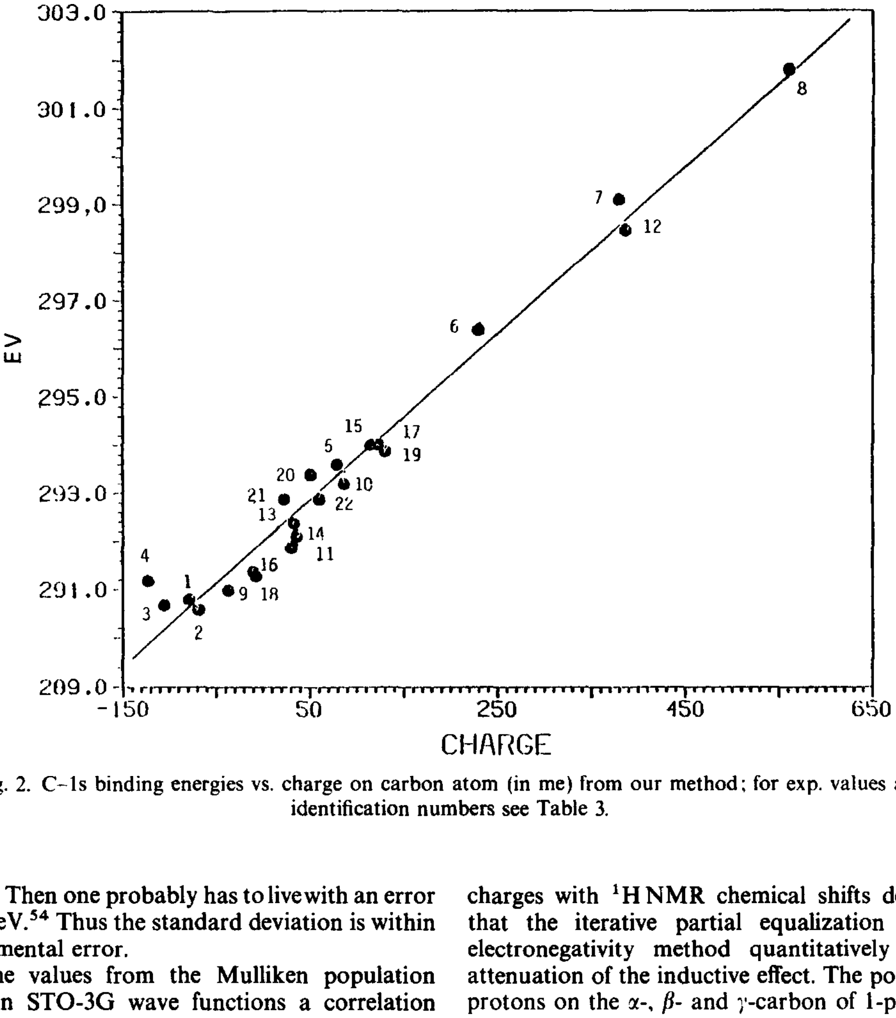

Fig. 2. C-1s binding energies vs. charge on carbon atom (in me) from our method; for exp. values and identification numbers see Table 3.

compared. Then one probably has to live with an error of 0.2–0.3 eV.[54] Thus the standard deviation is within the experimental error.

With the values from the Mulliken population analysis on STO-3G wave functions a correlation coefficient of 0.938 and a standard deviation of 0.64 eV was obtained (Fig. 3). This poor correlation shows that values from a Mulliken population analysis on STO-3G wave functions scantily reflect core electron binding energies in a simple atomic potential model.

The transmission of inductive effects can be discussed with the points for a α- and β-C atom of ethylfluoride. In Fig. 2 they lie close to the correlation line both showing a small deviation into the same direction to lower ESCA shifts. Thus the electron withdrawing effect of a fluorine atom on the α-carbon and the transmission of the inductive effect to the β-carbon are excellently reproduced by the iterative partial equalization of orbital electronegativity model. A more stringent test molecule is 1,1,1-trifluoromethane where the combined effect of three fluorine atoms exists and deficiencies in reproducing the transmission effect should show up more clearly. But again the points for the α- and β-carbon are close to the correlation line of Fig. 2 both slightly deviating into the same direction. Also, the values for the two carbon atoms of ethanol[55] fit nicely into the correlation of Fig. 2.

Thus both PEOE charges and the ESCA shifts support the commonly accepted picture of a successive attenuation of the inductive effect. The magnitude of this effect is quantitatively reproduced in our calculations. There is no evidence for the charge alternation effect as found in Mulliken population analyses.[3,4,56] In addition, correlations[57] of hydrogen charges with ^{1}H NMR chemical shifts demonstrate that the iterative partial equalization of orbital electronegativity method quantitatively gives the attenuation of the inductive effect. The points for the protons on the α-, β- and γ-carbon of 1-propanol or 1-chloropropane all fall on the correlation line obtained from a study of ^{1}H NMR chemical shifts of a whole series of compounds.[57,58] Thus the transmission of the inductive effect to atoms even four bonds away from the electron attracting atom is excellently reproduced.

Acidity constants

A major incentive for the development of a model to calculate atomic charges was the intention to use them for the prediction of chemical reactivities. The charges should be employed for the selection of chemical reactions in the computer simulation of reactions and in synthetic planning.[9]

Noting the similarity between losing a proton and accepting a negative charge the utility of PEOE atomic charges in predicting the acidity of molecules was studied. The acidity of a molecule depends on many factors. Predominant among these are charge and polarizability effects in the neutral molecule and the corresponding ion. Further, the size of the species involved is of influence, as a negative charge can be better distributed in a larger ion. Apart from these structural effects solvent effects play a decisive role. In order to be able to correlate acidity constants with atomic charges, the influence of the other effects has to be kept constant. To this end various neutral molecules only consisting of one or two atoms of the

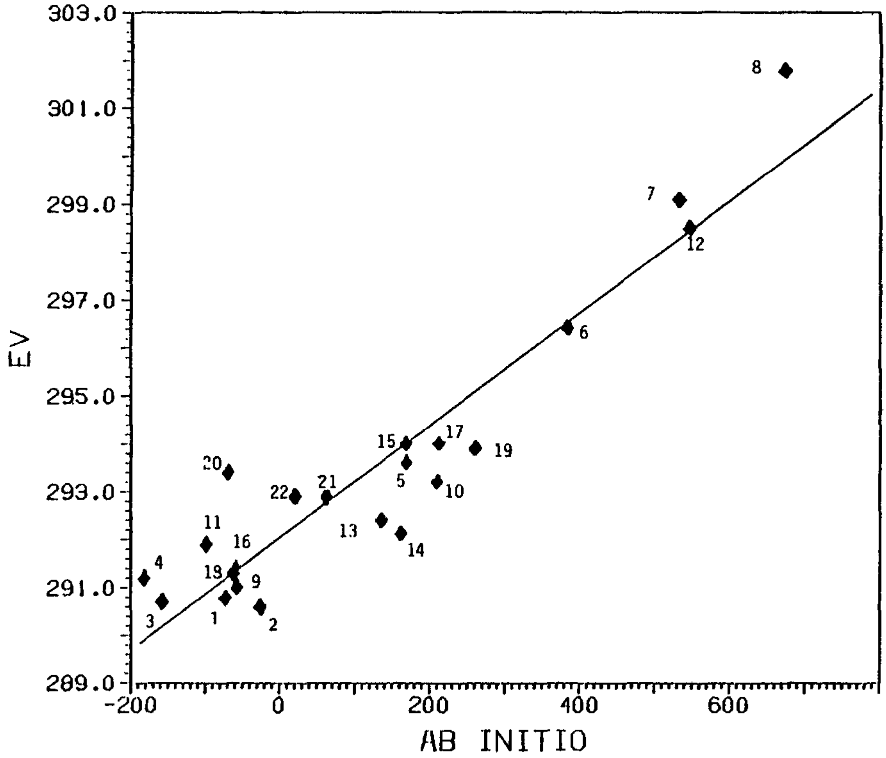

Fig. 3. C–1s binding energies vs charge on carbon atom (in me) by Mulliken population analysis (ref. 4); for exp. values and identification numbers see Table 3.

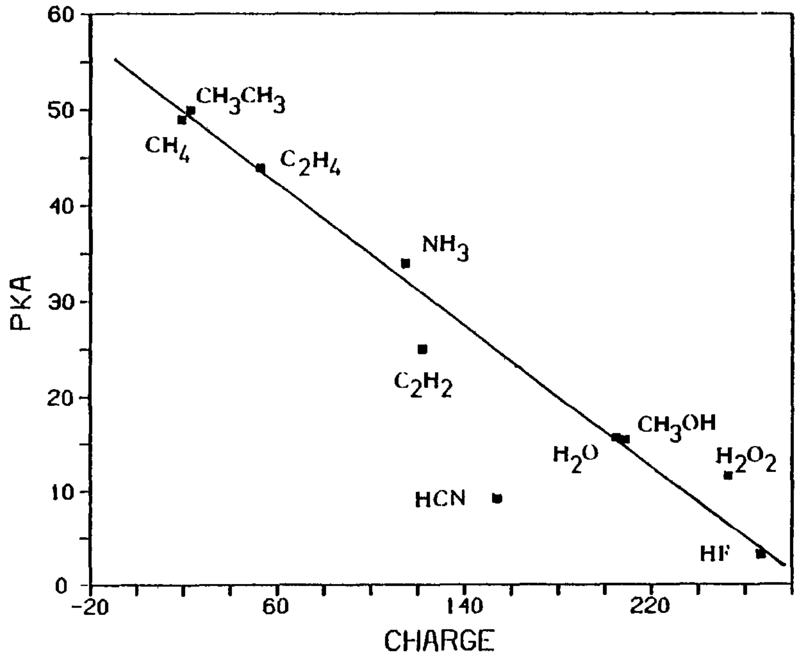

Fig. 4. pK_a values (in water) vs charge on hydrogen atom (in me) by our method; exp. values: NH_3, J. March *Advanced Organic Chemistry*. McGraw-Hill, New York (1968), all other values: A. Streitwieser, Jr. and C. H. Heathcock, *Introduction to Organic Chemistry*. Macmillan, New York (1976). The correlation line has been drawn disregarding the points for C_2H_2, HCN and H_2O_2.

first period and hydrogen were selected. The size of the molecules and their polarizabilities should be of comparable magnitude. Figure 4 shows a correlation of the acidity constants in water with the charges on hydrogen of the respective neutral molecule.

A good linear correlation is indeed observed. Note that the acidities cover a range of nearly 50 pK units, from the rather acidic hydrogen fluoride to the extremely weak alkanes. Sizeable deviations occur only for acetylene, hydrogen cyanide and hydrogen peroxide. As only the neutral molecules have been taken into account the implicit assumption was made that the electronic effects in the anions are all constant or correlate with the charges in the neutral molecules. This assumption must fail with anions where appreciable electronic relaxation occurs. This is the case with the cyanide and the acetylide anion. The π-electrons are more prone to reorganization. This leads to an extra stabilization of these anions and thereby an enhanced acidity. Apparently, in the vinyl anion this effect is only minor.

In the hydrogen peroxide anion the development of a negative charge on oxygen is made more difficult by the free electrons on the adjacent oxygen atom. Therefore the anion is destabilized and the acidity of hydrogen peroxide is lower than is to be expected from considerations of charge effects on the neutral molecule alone. Neglecting the three points for acetylene, hydrogen cyanide, and hydrogen peroxide for the above reasons, a correlation coefficient of 0.999 is obtained. With values from Mulliken population analysis on an STO-3G basis set[4] the coefficient of the correlation with the acidity constants of the same compounds drops to 0.950.

CONCLUSION

The present approach provides an extremely fast access to atomic charges in organic molecules with σ-bonded and nonconjugated π-systems. Correlations with physical and chemical data establish the significance of the charge values. In a recent study of a structure-activity relationship for sweet and bitter character PEOE charges have been used successfully.[59]

With the iterative partial equalization of orbital electronegativity method the great diversity of charge distributions encountered in the organic molecules has been traced back to few fundamental data. Thus for the cornucopia of organic molecules consisting of C, H, O, and N atoms only 27 starting values, the coefficient for eqn (2) (see Table 1), are needed to compute the charge distributions. The fundamental data were not calculated from the experimental data with which they were correlated. Rather, values deduced from ionization potentials and electron affinities have been chosen.

The success of the iterative partial equalization of orbital electronegativity approach demonstrates that as a good approximation it suffices to consider the identity of the individual atoms and their connectivities to reproduce the charge distributions in molecules. Thus the topology of a molecule determines the nature of the electron distribution.

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