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A NEW MODEL FOR CALCULATING ATOMIC CHARGES IN MOLECULES

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Although the qualitative concept of partial charges of atoms in molecules is widely accepted and used among chemists, the assignment of quantitative values is met with difficulties. Experimental methods give only indirect access to atomic charges and different interpretations might result in varying numerical values. Various theoretical definitions have been offered but the magnitude of the values is dependent on the approach being taken. The most widely used method is the Mulliken population analysis[1]. But this definition has deficiencies and the results are heavily dependent on the wave function chosen. A number of other quantum mechanical methods have therefore been suggested[2] but none has met common acceptance.

We were seeking for a fast method to calculate charges to use them in assigning reactivities in our synthetic design program EROS[3]. As quantum mechanical treatments require a fair amount of computer time and are limited to small to medium sized molecules these procedures were unsuitable for our purposes. Empirical approaches based on electronegativity and orbital electronegativity[4] have been made, too. Atomic charges were obtained by making use of the principle of electronegativity equalization[5-7]. But total equalization of electronegativity[5,6] leads to chemically unacceptable predictions, e.g., atoms of the same sort attain the same charge in all isomeric molecules or molecular fragments. For example, in acetic acid, hydrogen atoms on carbon and oxygen will receive the same charge.

We have developed an electrostatic model which leads to only partial equalization of orbital electronegativity (PEOE). The resulting charges correlate excellently with physical and chemical properties.

The model makes use of the Mulliken definition of electronegativity $\chi = 0.5\ (IP + EA)$. We approximate the function which joins the three electronegativity values of an atom in its anionic, neutral, and cationic state by a parabola of the form (q = charge):

$$\chi = a q^2 + b q + c \qquad (1)$$

Using the appropriate ionization potentials and electron affinities[4] the constants a, b, and c can be evaluated.

Different atoms respond differently towards more electronegative partners; the amount of charge released is inversely proportional to the ionization potential of the orbital considered. To compute the maximum electronegativity difference D_i required to induce a charge of +1 on an atom i, comparison with a reference atom is made. The value D_r of this reference atom obtained from a compound of known polarity has to be multiplied with the ratio IP_i/IP_r. Accepting a magnitude of 75% polarity in the NaF bond[5] with an electronegativity difference of 9.4 eV we obtain:

$$D_i = \frac{9.4}{0.75} \frac{IP_i}{IP_r} \qquad (2)$$

The magnitude of the reference polarity does not seriously affect the performance of our model. Changes in this value will cause only minor shifts in the absolute values of the atomic charges.

The amount of charge shifted between two atoms i and j is given by equation (3):

$$q = (x_j - x_i)/D_i \qquad \text{with} \quad x_j > x_i \qquad (3)$$

As charge separation is started on bond formation, the electronegativities are changed according to eq. (1). The modified electronegativities x_j' and x_i' give rise to a new, although smaller charge separation. To account for this we developed an iterative procedure to compute the final charges.

If the physical background were completely described by eq. (3) charge would be shifted until total equalization of electronegativity is attained. But after initial charge separation an electrostatic field q^2/r_{AB} exists which acts against further charge shifts. To account for this effect and for the influence of atoms which are not directly bonded to the atom considered we introduced a damping factor:

$$\beta = \left(\frac{1}{f}\right)^{\alpha-1}$$

Here, α gives the current iteration step and f = 2. This particular form was chosen to reflect the attenuation of inductive effects.

The final equation for the total charge Q_i on an atom i in a polyatomic molecule is then given by equation (4):

$$Q_i = \sum_{\alpha}\left\{\left[\sum_{j} \frac{1}{D_i}(x_j - x_i) + \sum_{k} \frac{1}{D_k}(x_k - x_i)\right] \left(\frac{1}{f}\right)^{\alpha-1}\right\} \qquad (4)$$

Here, j and k represent neighbors of i that are more or less electronegative than i, respectively.

The convergence of eq. (4) is usually reached at iteration step 6 when the amount of charge shifted is of the magnitude of 0.0002 electrons. Computation times are very short, e.g., on an AMDAHL 470 V6 for a molecule containing 15 to 20 atoms 0.2 - 0.3 sec. are required.

To test the validity of the atomic charges obtained by this method we compared them with results from quantum mechanical calculations and from experimental data. Table 1 shows the comparison with values from a Mulliken population analysis on ab initio wave functions[8].

	CH_4	NH_3	H_2O	HF
ab initio[8]	18	162	203	228
our work	17	109	189	215

Table 1: Charges on hydrogen (in 10^{-3} e)

For CH_4, H_2O, and HF the correlation gives a straight line. NH_3 does not come close to this line. But by using an anisotropic basis set a value of 125 x 10^{-3} e was obtained[9] for NH_3, which is a value close to our correlation line. Thus, we are more confident in our estimate for NH_3 than in the rather high value from the population analysis of ref. 8.

For correlating our charges with experimental data we have selected C-1s ESCA shifts. ESCA shifts have been chosen because a number of theoretical and experimental investigations[10] have demonstrated that there is a simple relationship between ESCA shifts and atomic charges. As Figure 1 shows, we obtain an excellent correlation of the C-1s shifts with our PEOE charges, the correlation coefficient being R = 0.984. Also contained in Figure 1 are values of charges obtained from population analyses of ab initio calculations[8]. These show a larger scattering, especially for the carbonyl carbons, the correlation coefficient being 0.964 only.

The best least squares line of our correlation can serve to predict ESCA shifts of carbon compounds:

$$E\ (C\text{-}1s) = 0.224 \cdot q + 1.112 \qquad (\text{relative to } CH_4)$$

The successful correlation of our calculated charges both with theoretical and experimental values encourages us to further investigate the significances of these charges. Thus, we are studying correlations of PEOE charges with ^{13}C- and ^{1}H- NMR chemical shifts and are testing their usefulness in predicting chemical reactivity.

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1 CH_3F
2 CH_2F_2
3 CHF_3
4 CF_4
5 CH_4
6 CH_3OH
7 $CH_3\overset{*}{C}OCH_3$
8 $\overset{*}{C}H_3COCH_3$
9 $CH_3\overset{*}{C}HO$
10 $\overset{*}{C}H_3CHO$
11 $\overset{*}{C}H_3CN$
12 $CH_3\overset{*}{C}N$
13 CH_2O

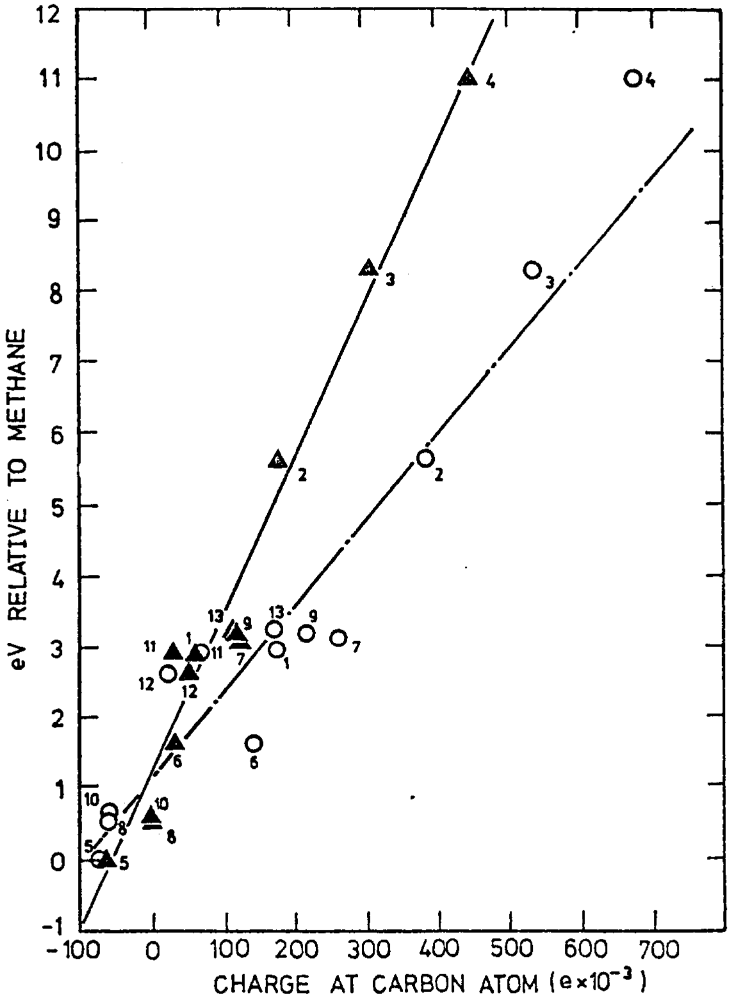

Figure 1: Correlation of ESCA C-1s shifts with PEOE charges (▲) and charges from population analyses on *ab initio* wave functions[8] (○)
Best lines calculated by least squares method

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