

Theoretical Chemistry Laboratory, McGill University, Montréal 2, Québec.

Group Orbital Electronegativities

By

M. A. WHITEHEAD, N. C. BAIRD and M. KAPLANSKY

The Self-consistent Group Orbital and Bond Electronegativity (SGOBE) method [4] for calculating the orbital charge distributions in polyatomic molecules is reviewed, and a simplification described. The charge distributions for several polyatomic molecules are calculated. The chemical significance of the results is discussed.

Es wird ein Überblick über die SGOBE-Methode zur Berechnung von Ladungsverteilungen in Molekülen gegeben und eine Vereinfachung dazu beschrieben. Die Ladungsverteilung einiger mehratomiger Moleküle wird berechnet und die chemische Bedeutung diskutiert.

La méthode auto-cohérente des orbitaux de groupe et électronegativités des liaisons (SGOBE) pour calculer la distribution de charge orbitale des atomes dans les molécules polyatomiques est résumée, et une simplification de la méthode SGOBE est décrite. Les distributions de charge de plusieurs molécules polyatomiques sont calculées, et la signification des résultats est discutée.

Introduction

Attempts have been made to extend the Atomic Electronegativity Concept (AEC) to organic and inorganic radicals. Estimates have been made [8] of the Effective Atomic Electronegativity of radicals, $\chi_{\text{eff}}^{\text{At}}$, by means of empirical relationships between $\chi_{\text{eff}}^{\text{At}}$ and (I) infrared stretching frequencies, (II) thermochemical data, (III) chemical reactivity, (IV) nuclear magnetic resonance chemical shifts, and (V) nuclear quadrupole resonance frequencies.

In this paper a simplification of the SGOBE method [4] is described. The electron charge distributions of atomic orbitals in molecules, and the orbital effective electronegativity χ_{eff} of radicals present in polyatomic molecules, are calculated using the Electronegativity Equalization Principle [9].

Throughout this paper all electronegativities are *Orbital Electronegativities*; no such concept as Atomic Electronegativities is used.

Background

1. The orbital electronegativity of orbital j on atom A is given by χ_j^{A} . It is related to the charge of orbital j , n_j^{A} by [4]

$$\chi_j^{\text{A}}(n_j^{\text{A}}) = b_j^{\text{A}} + 2c_j^{\text{A}}n_j^{\text{A}} \quad (1)$$

where b_j^{A} and c_j^{A} are parameters dependent on the atom A, its valence state, and the electron configuration of all the other orbitals on atom A.

2. The effective occupation number, integral or non-integral, of an atomic orbital is designated "charge".

3. The parameters b_j^{A} and c_j^{A} can be calculated [1] from the ionization potential and electron affinity of orbital j , I_{vj}^{A} and E_{vj}^{A} , using

$$b_j^A = \frac{1}{2} (3 I_{vj}^A - E_{vj}^A) \quad (2)$$

and

$$c_j^A = \frac{1}{2} (E_{vj}^A - I_{vj}^A) . \quad (3)$$

4. The modified principle of orbital Electronegativity Equalization [4] states that since two electrons forming a chemical bond are in equilibrium, the potential at each electron from the atomic cores A and B must be equal. Eq. (1) defines this potential. If χ^X represents the equilibrium electronegativity of the orbital of atom X, the principle requires that

$$\chi_{\text{equ}}^A = \chi_{\text{equ}}^B . \quad (4)$$

The total charge of the molecular orbital is 2. If the orbitals forming the bond are j of A and k of B, and the asterisk denotes equilibrium values,

$$n_j^{A*} + n_k^{B*} = 2$$

whence the ionic character of the bond i_{jk}^{AB} is given by

$$i_{jk}^{AB} = |n_j^{A*} - 1| = \left| \frac{\Delta \chi_{jk}^{AB}}{2(c_j^A + c_k^B)} \right| . \quad (5)$$

$\Delta \chi_{jk}^{AB}$ is the orbital electronegativity difference $|\chi_j^A - \chi_k^B|$ for the condition $n_j^A = n_k^B = 1$, that is the free atomic condition before bond formation. The principle is equivalent to minimizing the energy of the molecular orbital, expressed as a sum of the atomic orbital energies.

5. The use of eq. (5) is complicated when orbital j is on a polyvalent atom, the other orbitals of which may or may not be bonded. A tetravalent carbon atom in the tetrahedral valence state (te^4), has four bonding orbitals 1, 2, 3 and 4. The parameters b_1 and c_1 are calculated from eqs. (2) and (3) using values of I_{v1} and E_{v1} for the case

$$n_2 = n_3 = n_4 = 1 . \quad (6)$$

Usually each of the bonds formed by orbitals 2, 3 and 4 will be polar, and eq. (6) will not hold. Thus before eq. (1) can be applied to calculations, the parameters b_1 and c_1 must be corrected for n_2 , n_3 and n_4 differing from unity. This will be considered below.

Theory

The energy changes which occur when electrons are added to an orbital are effected by the character and charge of every other valency orbital of the atom, and if the energy of an orbital is expressed by [4]

$$E(n_j) = a_j + b_j n_j + c_j n_j^2 \quad (7)$$

then the parameters a_j , b_j and c_j are dependent on the nuclear charge Z , on the charge and hybridization characters of all the other orbitals of the atom, and on the hybridization character of j . The dependence of the parameters, and of I_{vj} and E_{vj} , upon the charge of each of the valence state orbitals is given in Tab. 1 for carbon in the tetrahedral state. (All energy data is from reference 3.) The values of I_{vj} and E_{vj} show that they depend mainly on the total charge, n_T , of the three

Table 1. *The parameters for tetrahedral carbon*

n_K	n_l	n_m	n_T	a_j^*	b_j^*	c_j^*	$I_{vj} [3]^*$	$E_{vj} [3]^*$
0	0	0	0	0	69.36	-10.89	58.47	36.70
1	0	0	1	58.47	51.12	-9.48	41.64	22.69
1	1	0	2	100.12	34.36	-7.66	26.70	11.38
2	0	0	2	95.17	35.34	-7.72	27.62	12.18
1	1	1	3	126.82	21.25	-6.64	14.61	1.34
2	1	0	3	122.79	22.32	-6.90	15.41	1.60
1	1	2	4	138.20	9.03	-4.47	4.57	-4.36
0	2	2	4	134.97	9.09	-4.26	4.83	-3.68
1	2	2	5	139.81	0.30	-1.69	-1.39	-4.78
2	2	2	6	132.34	-2.34	-0.39	-2.73	-3.51

* a_j , b_j and c_j are the parameters for eq. (7) for one of the sp^3 tetrahedral orbitals of carbon, te_j , I_{vj} and E_{vj} represent the Ionization Potential and Electron Affinity of te_j , n_k , n_l and n_m are the charges of the three remaining orbitals te_k , te_l and te_m while $n_T = n_k + n_l + n_m$.

other equivalent te orbitals and depend only slightly on the particular configuration, (for the normal states of an atom where I_{vj} and $E_{vj} > 0$).

The variation of E_{vj} and I_{vj} with n_T for the te^4 valence state of carbon, is shown in Figs. 1a and 2. From these curves E_{vj} and I_{vj} can be calculated for a carbon atom in a molecule; the particular carbon configuration used is that which most closely represents the distribution in a real molecule. For carbon in the tetrahedral valence state in organic and most inorganic molecules, the values of n_2 , etc. are expected to be nearer to unity than zero or two. Values of E_{vj} and I_{vj} for a given n_T are therefore chosen such that the charges n_2 , n_3 , and n_4 are as close to unity as possible. Curves similar to those in Figs. 1 and 2 have been constructed for all elements down to Chlorine.

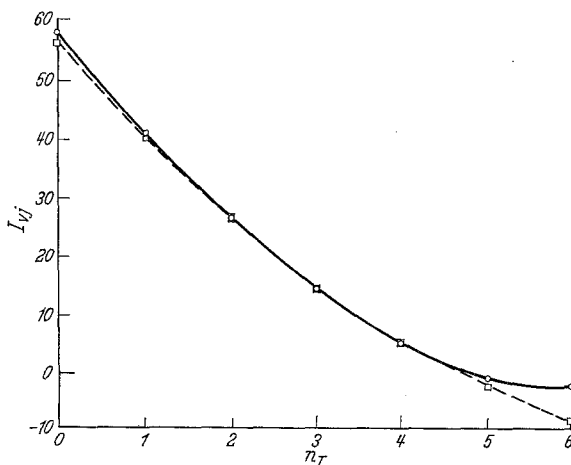


Fig. 1. I_{vj} represents the ionization potential of te_j , and $n_T = n_k + n_l + n_m$. The solid curve represents that given by the calculations of HINZE et al.; the dotted curve represents the results from eq. (7). The parameters of (7) α , β and γ were evaluated from the HINZE data for $n_T = 2, 3$ and 4

Careful consideration of several types of equations showed that the curves were best approximated by a three term power series in n_T :

$$I_{vj} = \alpha_j + \beta_j n_T + \gamma_j n_T^2 \quad (8)$$

$$E_{vj} = \delta_j + \epsilon_j n_T + \zeta_j n_T^2 \quad (9)$$

where α_j etc. are constants depending on (I) the hybridization of the orbitals j , k , l and m , and (II) the nuclear charge Z .

The dotted curves in Figs. 1 and 2 show how well eqs. (8) and (9) reproduce the variation of E_{vj} and I_{vj} with n_T , especially in the area of interest. The parameters for several atoms in their valence states are listed in Tab. 2. Thus I_{vj} , E_{vj} , b_j and c_j can be calculated when n_k , n_l and n_m differ from unity, and hence the electronegativity of j . This value of χ_j is the effective orbital electronegativity of the radical, χ_j^R .

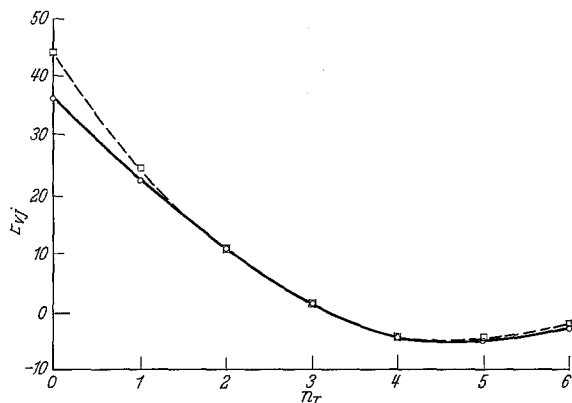


Fig. 2. E_{vj} represents the electron affinity of te_j , and $n_T = n_k + n_l + n_m$. The solid curve represents that given by the calculations of HINZE et al.; the dotted curve represents the results from eq. (8). The parameters of (8) δ , ϵ and ζ were evaluated from the HINZE data for $n_T = 2, 3$ and 4

This method is analogous to the SGOBE method [4], which required $E(n_j)$ versus n_j curves to be plotted, extrapolation of these curves to the point of interest, estimation of $E(n_j + 1)$, $E(n_j)$ and $E(n_j - 1)$ from the curves, and calculation of E_{vj} , I_{vj} , b_j and c_j from the energy terms. A tetravalent carbon atom requires the plotting of twenty separate curves to cover all possible cases [4]. The method developed above simplifies the calculations of the SGOBE method for finding b_j

and c_j . The validity of the assumptions and approximations can be seen from the values of χ_{eff}^R calculated for the radicals CH_3 , CH_2Cl , $CHCl_2$ and CCl_3 in the hydrides RH. Using a pure p bonding orbital on the chlorine atom, they differ from the SGOBE results by 0%, 0%, 0.7% and 1.3% respectively.

The total charge n_T can be the sum of the n from one or more orbitals; one can consider the dependence of I_{vj} and E_{vj} upon only some of the n_T , keeping the rest constant; thus $n_T = \sum_{i=1}^{1, 2 \text{ or } 3} n_i$. Different values of the parameters

Table 2. The parameters of the I_{vj} and E_{vj} equations

Element	Valence State	α^*	β^*	γ^*	δ^*	ϵ^*	ζ^*
C	te	57.067	-17.240	1.029	39.020	-18.245	1.895
Si	te	32.822	-6.779	-0.075	26.566	-8.873	0.315
N	te	100.067	-28.174	1.972	64.500	-21.895	1.702
	$sppp$	48.229	-21.101	1.977	29.017	-19.921	2.902
O	te	120.724	-23.124	0.801	92.759	-23.248	1.184
	$sppp$	78.883	-26.033	1.833	48.034	-19.444	1.367
S	te	109.407	-26.980	1.640	45.930	-7.440	-0.159
	$sppp$	49.893	-15.385	0.962	28.008	-8.351	-0.064
B	te	34.841	-15.663	1.715	14.157	-6.236	-0.039
C	$trtrtr\pi$	56.622	-19.110	1.319	44.465	-20.880	2.169

* The α , β and γ are parameters of the I_{vj} eq. (8) and the δ , ϵ and ζ belong to the eq. (9) for E_{vj} . In the case of the te valence states the parameters were calculated for te_j where $n_T = n_k + n_l + n_m$; in the $sppp$ valence state the parameters are for p_j where $n_T = n_k^p + n_l^p$, and n_m^s assumed a lone pair s orbital; in $trtrtr\pi$ the parameters are for π_j and $n_T = n_k^{tr} + n_l^{tr} + n_m^{tr}$

α_j, β_j etc. will be obtained depending on the number of orbitals contributing to n_T .

Eqs. (8) and (9) are subject to one limitation: all the orbitals summed into n_T must have the same hybridization. If j, k and l represent three p orbitals and m represents an s orbital, the value of I_{vj} (and E_{vj}) for $n_k = n_l = 1, n_m = 0$ differs from that for $n_k = 0, n_l = n_m = 1$. It is not possible to calculate them for $n_T = n_k + n_l + n_m$, since to express I_{vj} (or E_{vj}) for three values of n_T , and, for example, find the value of I_{vj} (or E_{vj}) for $n_T = 2$, yields two possible results:

$$I_{vj}^{(1)} \text{ for } n_k = n_l = 1, n_m = 0 \quad (\text{removal of } s \text{ electron}) \quad (\text{I})$$

$$I_{vj}^{(2)} \text{ for } n_k = n_m = 1, n_l = 0 \quad (\text{removal of } p \text{ electron}) \quad (\text{II})$$

which generate two different parabolae since the s and p orbital electrons shield the p electron in orbital j differently, from the nucleus. The parameters in Tab. 11 for the $sppp$ valence states of several atoms were calculated with $n_m = 2$.

Method

Expressing E_{vj} and I_{vj} in the form of eqs. (8) and (9) simplifies the use of the Principle of Electronegativity Equalization in calculating the atomic orbital charge distributions in molecules from the SGOBE approach. The procedure can be illustrated by an example such as CH_3NH_2 , in which all the carbon and nitrogen bonding orbitals are tetrahedral, and the hydrogen orbitals are atomic $1s$ orbitals. The atomic orbital charges are denoted by n_A, n_B etc. as in Fig. 3. An iterative computer program is used to calculate the equilibrium charge distribution for which the bond electronegativities χ_{equ} of the two orbitals forming the bond are equal:

1. The charge n_A is chosen to be a chemically reasonable value and n_B is calculated from

$$n_A + n_B = 2 \quad (\text{I})$$

2. The nitrogen orbital electronegativity equals the hydrogen orbital electronegativity in the NH bond

$$\chi_{\text{equ}}^A = \chi_{\text{equ}}^B \quad (\text{II})$$

The χ_{equ}^A for hydrogen is calculated from eq. (1) with the values of b_A and c_A from a previous paper [1].

3. Substituting eqs. (8) and (9) into eqs. (2) and (3) gives b_B and c_B as a function of $n_T^{(1)}$:

$$b_B = (1.5 \alpha_B - 0.5 \delta_B) + (1.5 \beta_B - 0.5 \varepsilon_B) n_T^{(1)} + (1.5 \gamma_B - 0.5 \zeta_B) (n_T^{(1)})^2 \quad (\text{III})$$

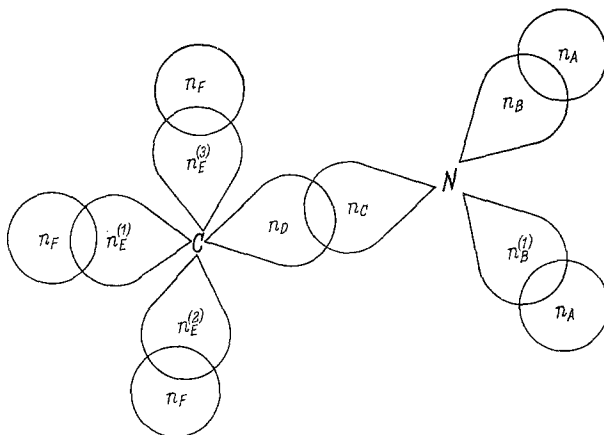


Fig. 3. Labelling of the orbitals in $\text{H}_3\text{C NH}_2$, to illustrate the iterative method for calculating charge densities of orbitals

$$c_B = 0.5 (\delta_B - \alpha_B) + 0.5 (n_T^{(1)})^2 (\varepsilon_B - \beta_B) + 0.5 (n_T^{(1)})^2 (\zeta_B - \gamma_B) \quad (\text{IV})$$

where $n_T^{(1)} = n_B^{(1)} + n_C$.

Since n_B and χ_{equ}^B are known, $n_T^{(1)}$, can be calculated from III.

4. In a symmetrical molecule, such as the above, $n_B^{(1)} = n_B$ hence

$$n_C = n_T^{(1)} - n_B \quad (\text{V})$$

The first bond of the molecule is now fully analysed on the basis of the initial choice of n_A . Consider next the CN bond.

5. I_{v_c} and E_{v_c} are evaluated in terms of the known $n_T^{(2)}$, defined by

$$n_T^{(2)} = 2n_B \quad (\text{VI})$$

and used to give b_C , c_C and χ_{equ}^C .

6. The remaining steps are the same as sections (3) and (4) above, and yield $n_T^{(3)}$. Since

$$n_T^{(3)} = 3n_E$$

then n_E is found.

7. n_F is found from $n_E + n_F = 2$.

8. χ_{equ}^E is found by the procedure used to find χ_{equ}^C .

9. χ_{equ}^F is evaluated with b_F and c_F from the published $[I]$ values for hydrogen.

10. If $\chi_{\text{equ}}^E \neq \chi_{\text{equ}}^F$ the original choice of n_A is incorrect: a new value of n_A is chosen using the fact that if $\chi_{\text{equ}}^E > \chi_{\text{equ}}^F$, then the new value of n_A must be less than the starting choice of n_A , and vice versa.

11. When $|\chi_{\text{equ}}^E - \chi_{\text{equ}}^F| < 0.001$ the molecular charge distribution is self consistent, and the iterations cease. This programme was written in Fortran IV for the McGill IBM 7040 computer.

Results

The charge distributions of several organic molecules are given in Tab. 3—5.

In chlorine containing compounds, no *a priori* assumption of the hybridization present in the chlorine bonding orbital can be made. Combining the present method with nuclear quadrupole resonance theory and data [12] gives an estimate of the amount of *s-p* hybridization in the chlorine bonding orbital, since ρ , the ratio of the nuclear quadrupole coupling constant of a chlorine atom in a molecule to that of a free chlorine atom, is related to

(I) the ionic character $i = |n_{Cl} - 1|$ of the C-Cl bond.

(II) the extent of *s* and *d* hybridization of the chlorine bonding orbital — *s* and *d* respectively

and (III) the extent of π electron transfer from the chlorine p_π orbitals to the carbon p_π orbitals.

The relation is

$$\rho = (1 - s + d - i - \pi) + i(s + d) \quad (10)$$

In the aliphatic chlorides both π and d are assumed [12] to be very small giving

$$\rho = (1 - i)(1 - s) \quad (11)$$

Since ρ is known and i and s are related, this equation is soluble. The parameters of the electronegativity eq. (1) have been calculated for several hybridizations of the chlorine orbital $[I]$, and the electron charge distributions of the alkyl halides and ionic character i of the C-Cl bond, were solved for each hybridization. A plot of i versus s is a straight line (Fig. 4, Curve $[I]$).

Table 3. Charge distributions in some simple compounds for the orbitals specified in the diagrams


Compound	Hybridization	n_A	n_B	n_C	comments
HO ^A —H	O <i>te</i>	1.183			bond angle data
	O <i>sppp</i>	1.060			
	O <i>true</i>	1.159			
HS ^A —H	S <i>te</i>	1.088			bond angle data
	S <i>sppp</i>	1.007			
	S <i>true</i>	1.027			
H ₂ N ^A —H	N <i>te</i>	1.094			bond angle data
	N <i>sppp</i>	1.004			
	N <i>true</i>	1.085			
H ₃ Si ^A —H	Si <i>te</i>	1.003			bond angle data
H ₃ C ^A —H	C <i>te</i>	1.015			bond angle data
H ₃ C— ^B C ^A —H ₃	C <i>te</i>	1.018	1.00		bond angle data
H ₃ CC _C — ^B C ^A —H ₃ H ₂	C <i>te</i>	1.019	0.996	1.020	bond angle data
H ₃ —C _C — ^B N ^A —H ₂	N <i>te</i>	1.091	1.105	1.039	bond angle data
	N <i>sppp</i>	1.010	0.984	1.015	
	N <i>true</i>	1.083	1.093	1.037	
H ₃ —C _C — ^B O ^A —H	O <i>te</i>	1.168	1.219	1.063	bond angle data
	O <i>sppp</i>	1.060	1.060	1.030	
	O <i>true</i>	1.146	1.187	1.056	
H ₃ —C _C — ^B S ^A —H	S <i>te</i>	1.084	1.100	1.038	
	S <i>sppp</i>	1.014	0.987	1.015	
	S <i>true</i>	1.028	1.009	1.020	
(CH ₃) ₃ C— ^B C ^A —H ₃	C <i>te</i>	1.020	0.990		
HC≡C ^A —H	C <i>didipπ</i>	1.119			
 —H	C <i>trtrtrπ</i>	1.069			

Table 4. The ¹³C nuclear magnetic resonance shifts compared to the charge on the ¹³C atom, n_r

Molecule	n_r	δ (ppm)	
CCl ₄	3.706	26 ^a	35 ^b
CHCl ₃	3.786	48 ^a	52 ^b
CH ₂ Cl ₂	3.872	74 ^a	76 ^b
CH ₃ Cl	3.964		107 ^b
CH ₄	4.060		130.8 ^c
CH ₃ CH ₃	4.054		122.8 ^c
(\dot{C} H ₃) ₂ CH ₂	4.052		111.3 ^c
(CH ₃) ₂ \dot{C} H ₂	4.048		110.9
\dot{C} H ₃ CH ₂ Cl	4.017		110.8 ^c
CH ₃ \dot{C} H ₂ Cl	4.006		89.3 ^c

The dotted carbon is the one for which δ is reported.

^a LAUTERBUR, P. C.: J. chem. Physics **26**, 217 (1957).

^b HOLM, C. H.: J. chem. Physics **26**, 707 (1957).

^c SPIESECKE, H., and W. G. SCHNEIDER: J. chem. Physics **35**, 722 (1961).

Table 5. *The hybridization of the chlorine bonding orbital and the charge distributions in several alkyl chlorides*

Molecule	s_{Cl}	n_{Cl}	n_H	$n_{Cl^{35}}$		
CCl_4	0.201	1.073		0.7406 ^a		
$CHCl_3$	0.203	1.124	0.843	0.6981 ^a		
CH_2Cl_2	0.204	1.176	0.888	0.6559 ^a		
CH_3Cl	0.197	1.228	0.936	0.6207 ^a		
CH_4			0.985			
CH_3CH_3			0.982			
CH_2ClCH_2Cl	0.199	1.217	0.923	0.6262 ^b		
$CHCl_2CHCl_2$	0.194	1.147	0.870	0.6873 ^c		
CCl_3CCl_3	0.189	1.087		0.7413 ^a		

	S_{Cl}	n_A	n_B	n_C	n_D	$Q_{Cl^{35}}$
$\begin{array}{c} Cl_A \\ \\ H_3^D-C-C-BH_2 \\ \\ Cl_2 \end{array}$	0.215	1.240	0.926	1.079	0.968	0.5960 ^c
$\begin{array}{c} H_3^D-C-C-BH \\ \\ Cl_2 \end{array}$	0.210	1.183	0.890	1.133	0.955	0.6453 ^b
$\begin{array}{c} H_3^D-C-C-A \\ \\ Cl_3 \end{array}$	0.204	1.131		1.193	0.943	0.6914 ^b

^a LIVINGSTON, R.: J. Physic. Chem. **57**, 496 (1953).

^b LIVINGSTON, R.: J. chem. Physics **20**, 1170 (1952).

^c HOOPER, H. O., and P. J. BRAY: J. chem. Physics **33**, 335 (1960).

A second plot of i versus s can be made from eq. (11), and this is a curve; the two curves cross at a unique i and s for the system. This value of s is then used to determine the charge distributions of the remaining orbitals. Charge distributions and orbital hybridizations for some alkyl halides are given in Tab. 5.

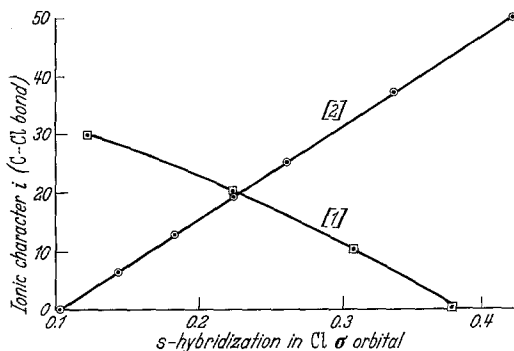


Fig. 4. Plots of ionic character, i versus the amount of s -hybridization in the chlorine σ orbitals. [1] is calculated from nuclear quadrupole resonance data and $e = (1 - i)(1 - s)$ where $i = |n_{Cl} - 1|$. [2] is calculated from the electronegativity equation

$$x_j^A = b_j^A + 2c_j^A n_j^A$$

with various assumed hybridizations. Where the curves [1] and [2] cross the i and s values are unique; the charge distributions are calculated using these values of i and s

Hydrocarbons

The charge distributions of the hydrocarbons (Tab. 3) indicate that the polarity of the C-H bond is 2%, 7% and 12%, for aliphatic, ethylenic and acetylenic carbon atoms respectively; in each case the carbon atom bears a small negative charge relative to the free atom, agreeing with the experimental evidence of increased acidity in this series.

This charge, 0.061e in methane, is appreciably smaller than those calculated by HOFFMANN [5] using MULLIKEN's concept of gross atomic populations. In this approach the charge resid-

ing on the carbon atoms Q_k is

$$Q_k = [\text{Gross Atomic Population}]_{\text{Atom}} - [\text{Gross Atomic Population}]_{\text{Molecule}}$$

where the Gross Atomic Population is given by

$$\sum_i \sum_{r_k} N(i, r_k) = \sum_i \sum_{r_k} N(i) C_{ir_k} (C_{ir_k} + \sum_{l=k} C_{is_1} S_{r_k s_1})$$

where there is the i th molecular orbital (M.O)

the r th atomic orbital (A.O)

and k th atom

and the first term of the bracket refers to orbitals specific to the k th atom, and the second term shares equally with the k th and l th atom. Thus in methane

$$Q_{\text{C}} = -0.532$$

$$Q_{\text{H}} = +0.133 \text{ from the extended Huckel treatment of}$$

HOFFMANN, while

$$Q_{\text{C}} = -0.061$$

$$Q_{\text{H}} = +0.015 \text{ from the modified}$$

SGOBE method. The bond polarity, or ionic characters, from the two methods, in methane and ethane, are 13.3% and 17.8% compared to 1.5% and 1.8%. Both methods agree qualitatively in that the hydrogen bears a positive charge in these molecules, and that replacement of H by CH_3 results in a net decrease in the charge Q_{H} , and both show the uniformity of Q_{C} and alternation along a chain.

Both methods are drastic approximations from a full selfconsistent field molecular orbital treatment of the molecules; it is difficult to state which series of results best approximates the true quantitative charge distributions of a molecule.

The extended Huckel method suffers from several deficiencies, which cause high bond polarities, the most important of which is the neglect of all electron-repulsion terms in the Coulomb integrals. This deficiency of the extended Huckel method could possibly be overcome by using a method similar to the "ω-technique" [11] of the Huckel method for π electron systems.

The charge distributions of benzene and acetylene permit I_{vj} , the π ionization potentials of the bonded orbitals, to be calculated using eq. (8) and Tab. 2. The values are

$$\text{acetylene} \quad 9.85 \text{ eV}$$

$$\text{benzene} \quad 10.40 \text{ eV}$$

compared to 11.16 eV for the atomic configuration used in M.O calculations. This variation of I_{vj} shows that the effective charges of the σ bonded orbitals differs appreciably from unity, and the effect of this on I_{vj}^{π} must be considered before any accurate M.O calculations, using I_{vj}^{π} as a parameter, can be made.

Inorganic hydrides

The orbital charge distributions of the inorganic hydride molecules (Tab. 3) were calculated assuming that the extent of s - p hybridization of the bonding orbitals, of the central atom, could be calculated from bond angles, using

$$s = \cos \Theta / (\cos \Theta - 1) .$$

The same hybridizations were assumed to hold for the methyl derivatives of these hydrides. The order of the R-H bond polarities for both the hydrides and their methyl derivatives is the same as that derived from the AEC using Pauling's electronegativity values [6], namely

$$\chi_{\text{eff}}^{\text{R}} \text{ order is } \text{O} > \text{N} > \text{S} > \text{C} > \text{Si} .$$

Comparing the polarity of the R-H bonds with the corresponding methyl derivatives, shows that for R, N, O or S replacing hydrogen by a $-\text{CH}_3$ group results in a *smaller* positive charge on the hydrogen atom of the R-H bond. This corresponds to the positive inductive effect of the methyl group in organic chemistry [2]. The only exception to this effect is in methane, where replacement of $-\text{H}$ by $-\text{CH}_3$ results in a very small withdrawal of electron density from the hydrogen orbital.

This slight electron-feeding ability is also encountered in the alkyl chlorides (Tab. 4). Thus in CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$; CH_2Cl_2 and CH_3CHCl_2 the bond polarity of the CH bond illustrates this effect. The SGOBE method's prediction this effect shows that it overcomes the defects of previous approximate group electronegativity treatments, which usually assume [13] that

$$\chi_{\text{CH}_3}^{\text{At}} = \frac{1}{2} \chi_{\text{C}}^{\text{At}} + \frac{1}{6} [\chi_{\text{H}}^{\text{At}} + \chi_{\text{H}}^{\text{At}} + \chi_{\text{H}}^{\text{At}}]$$

and $\chi_{\text{CH}_3}^{\text{At}} > \chi_{\text{H}}^{\text{At}}$ since $\chi_{\text{C}}^{\text{At}} > \chi_{\text{H}}^{\text{At}}$. This leads to a larger bond polarity in any *polarity versus change in electronegativity* relationship, and the $-\text{CH}_3$ possesses a negative inductive effect.

General

Although no direct method is available to check these calculated molecular charge distributions, it is possible to correlate them qualitatively with empirical methods, which measure physical properties dependent, in part, on the orbital charges.

a) Molecular Dipole Moments: the paraffin hydrocarbons possess zero, or almost zero, dipole moments [2] whether symmetrical or unsymmetrical; this is substantiated by the present results where the charge distributions for atoms in the molecule are finite but small in their difference from the free atomic state; the extended Huckel results are rather difficult to fit into this low dipole moment picture, since the large deviation of orbital charge from unity would yield rather large dipole moments in some unsymmetrical paraffin hydrocarbons.

Similarly in the alkyl chlorides, inorganic halides and methyl derivatives, the charge distributions agree with the current qualitative picture for the molecular dipole moments [2]:

1. In all carbon-chlorine bonds the chlorine is more negative and the carbon more positive than in the free atomic case

$$n_{\text{T}}^{\text{Mol}} > n_{\text{T}}^{\text{At}}]_{\text{Cl}} ; \quad n_{\text{T}}^{\text{Mol}} < n_{\text{T}}^{\text{At}}]_{\text{C}} .$$

2. The charge density on atoms or groups bound to a chlorinated carbon will be drawn slightly toward the positive centre, carbon, resulting in a higher separation of positive and negative charge centres, and increased dipole moment, as in the molecules CH_4 and CH_3Cl where the 1s orbitals of hydrogen have an effective charge of 0.985 and 0.936 respectively; thus in CH_3Cl there is a charge transfer to the central carbon atomic orbitals, from the H 1s orbitals.

3. The valence electrons associated with a methyl group are more easily distorted by the nearby positive charge than are valency electrons of a hydrogen atom. In $\text{CH}_3\text{CH}_2\text{Cl}$ each of the hydrogen $1s$ orbitals in the $-\text{CH}_2\text{Cl}$ segment has an effective charge of 0.926; in the CH_3 group this is 0.921 for the carbon orbital joining to CH_2Cl . When CH_3CHCl_2 is considered, the results are 0.890 and 0.867. It can be concluded that a methyl group is more effective in removing the positive charge of the halogenated carbon atom orbital than is a hydrogen atom.

4. The effect described above falls off rapidly as the distance from the C-Cl bond increases; hence the dipole moment change from ethyl to propyl chloride is small, and further changes as the chain length increases are negligible, as shown by CH_3CH_3 and $\text{CH}_3\text{CH}_2\text{Cl}$. The change in orbital charges of the hydrogen atoms

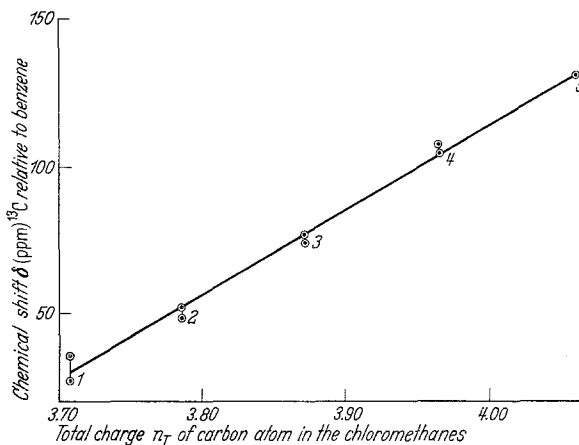


Fig. 5. Plot of the ^{13}C n.m.r. chemical shift, δ , in parts per million, relative to benzene, CCl_4 (1); CHCl_3 (2); CH_2Cl_2 (3); CH_3Cl (4) and CH_4 (5), against n_T , the total charge density on the carbon atom

bound to the chlorinated carbon atom from those in ethane is -5.6% ; the change in the charges of the hydrogen atoms bound to the non-halogenated carbon is only -1.4% .

b) Nuclear Magnetic Resonance chemical shifts: the chemical shift in n. m. r. has been shown [7] to be dependent upon the orbital charges. The chemical shift δ is defined so that it increases as the field increases. There should be a proportionality between δ and the net electron charge at the nucleus concerned. This is shown in Tab. 4 to be a linear relationship for the ^{13}C chemical shift and the total charge n_T for the chloromethanes (Fig. 5).

c) Nuclear Quadrupole Resonance frequencies: the results for the alkyl chlorides show that successive replacement of H by Cl increases the C-H bond polarity, (with C always the negative end of the bond), makes the C-Cl bonds less polar, and the n_T of carbon smaller.

In all the aliphatic chlorides considered, the combined SGOBE and n. q. r. plots indicate the extent of s hybridization in the orbital to be $20.0 \pm 1.5\%$. This is remarkably close to the value predicted by TOWNES and DAILEY [12]; that the extent of s hybridization in a chlorine orbital in a bond for which the atomic electronegativities differed by more than 0.2 is 15% .

With such a fixed hybridization of the chlorine bonding orbital, it is possible to predict unknown n.q.r. frequencies for ^{35}Cl in alkyl halides, by assuming $s = 0.2$ and calculating, $i_{\text{C-Cl}}$ from the SGOBE method and hence ρ . Thus the n.q.r. ^{35}Cl frequencies of $\text{CHCl}_2\text{CH}_2\text{Cl}$ are expected to be 35.12 and 36.76 Mc/s respectively at 77 °K.

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