Extended Hückel Method Charge Distributions and the Chemical Shift

J. M. Sichel and M. A. Whitehead

Theoretical Chemistry Laboratory, McGill University Montréal 2, Québec

The extended Hückel theory (EHT) is used to calculate the charge distributions in alkanes, halogenated alkanes, and molecules containing methyl and vinyl groups. The charge densities are correlated with ^{13}C, ^{31}P, ^{19}F, ^{35}Cl and ^1H, chemical shifts. The correlations are discussed in terms of the α and β used in the extended Hückel method, and are compared to the results of the self-consistent group orbital and bond electronegativity (SGOBE) method.

La théorie Hückel étendue (EHT) est employée pour calculer les distributions de charge des alcanes, des alcanes halogénés, et des molécules avec des groupes méthyle et vinyle. Les densités de charge sont corrélées avec les "chemical shifts" de ^{13}C, ^{31}P, ^{19}F, ^{35}Cl et ^1H. Les corrélations sont décrites en termes du α et du β employés dans la méthode Hückel étendue, et elles sont comparées aux résultats de la méthode autocohérente des orbitales de groupe et de l'électronégativité des liaisons (SGOBE).

Die erweiterte Hückel-Theorie (EHT) wird benutzt, um Ladungsverteilungen in Alkanen, halogenierten Alkanen und Molekülen mit Vinyl- und Methylgruppen zu berechnen. Beziehungen zwischen Ladungsdichte und chemischer Verschiebung von ^{13}C, ^{31}P, ^{19}F, ^{35}Cl und ^1H werden aufgestellt. Die Beziehungen werden in den Größen α und β der erweiterten Hückel-Methode diskutiert und mit den Ergebnissen der SGOBE-Methode verglichen.

I. Introduction

Recently, simple calculations of the σ-charge distribution, in polyatomic molecules, have been made by two fundamentally different methods: the Extended Hückel Theory [9] (EHT) method, and the Self-Consistent Group Orbital and Bond Electronegativity [44] (SGOBE) method. Both methods are drastic approximations from full self-consistent molecular orbital calculations. The approximations involved in the EHT method are similar to those in the Hückel method for π-systems [29], while the relationship of the SGOBE method to a MO treatment will be discussed in another paper [1]. Since SGOBE charge distributions have been successfully correlated with carbon [44], proton [11, 43] and chlorine [45] nuclear magnetic resonance chemical shifts, it was decided to examine the validity of the EHT charge distributions by attempting to correlate the charge on atoms, in several series of molecules, with the chemical shifts of the corresponding nuclei. Although chemical shifts depend on other factors besides charge distribution, accepted theories of chemical shift indicate that within certain series of molecules, the charge distribution should be the dominant factor determining shifts, which may therefore be used as a measure of "experimental" charge distribution.

II. Extended Hückel Theory

"Extended Hückel" [9] is the term applied to Hückel-like calculations extended to include both σ and π electrons. The method has been extended in this paper and both the original method and the changes will be described.

LCAO–MO calculations on saturated molecules [3, 37, 47] were performed prior to HOFFMANN [9], but the interactions between non-neighbouring atoms, as represented by the overlap and resonance integrals between pairs of atoms not directly bonded, were omitted.

The EHT method is an LCAO–MO theory with a basis set consisting of a $1s$ Slater orbital on each hydrogen atom in the molecule, and $2s$ and $2p$ Slater orbitals on each carbon, boron and nitrogen atom [9]. The complete overlap matrix S for this basis set is computed using the overlap integral formulae [28] for Slater orbitals. The coulomb integral H_{rr} for each atomic orbital is taken as the valence state ionization potential (VSIP) of that orbital in the free atom, and the resonance integrals H_{rs} as

$$H_{rs} = 1.75 \, S_{rs} \, (H_{rr} + H_{ss})/2 \, ,$$

where S_{rs} is the overlap integral between the rth and s^{th} atomic orbitals. All neighbour and non-neighbour interactions S_{rs} and H_{rs} are included so that conformational effects can be computed. The variational matrix equation

$$HC = SCE$$

is solved by LÖWDIN's method [21]. The solution of this equation provides orbital energies and LCAO coefficients of the molecular orbitals, subject to the assumptions of the Hückel approximation [29].

An estimate of the molecular charge distribution is obtained by performing a Mulliken population analysis [27]. In this method of analysing LCAO–MO wave functions, the gross atomic charge on the kth atom is defined as

$$Q_k = N_k^0 - \sum_i^{occ} \sum_{r_k} \sum_{s_l, l} N(i) \, c_{ir_k} \, c_{is_l} \, S_{r_k \, s_l}$$

and the overlap population between the kth and l^{th} atoms, a measure of covalent bond energy [9], as

$$S_{kl} = 2 \sum_i^{occ} \sum_{r_k} \sum_{s_l} N(i) \, c_{ir_k} \, c_{is_l} \, S_{r_k \, s_l} \, .$$

In these definitions N_k^0 is the number of valence-shell electrons on the free neutral atom, c_{ir_k} is the coefficient of the rth atomic orbital on the kth atom in the ith molecular orbital, $S_{r_k \, s_l}$ is the overlap integral between the rth atomic orbital on the kth atom and the sth atomic orbital on the lth atom and $N(i)$ is the occupancy of the ith molecular orbital. The summations extend over all occupied molecular orbitals i, all atomic orbitals r_k on the kth atom, and all atomic orbitals s_l on the lth atom.

This method has been applied to hydrocarbons, both saturated and unsaturated, pyridine, boron-nitrogen analogues of hydrocarbons, and carbonium ions [9], and extended to more polar molecules such as the rare-gas halides [20], the nitro cation, radical and anion [16], and boron hydride derivatives [24, 25]. It has been used to predict the existence of potential energy minima in excited dimers [2], and to study transition states [15] and hydrogen bonding [26].
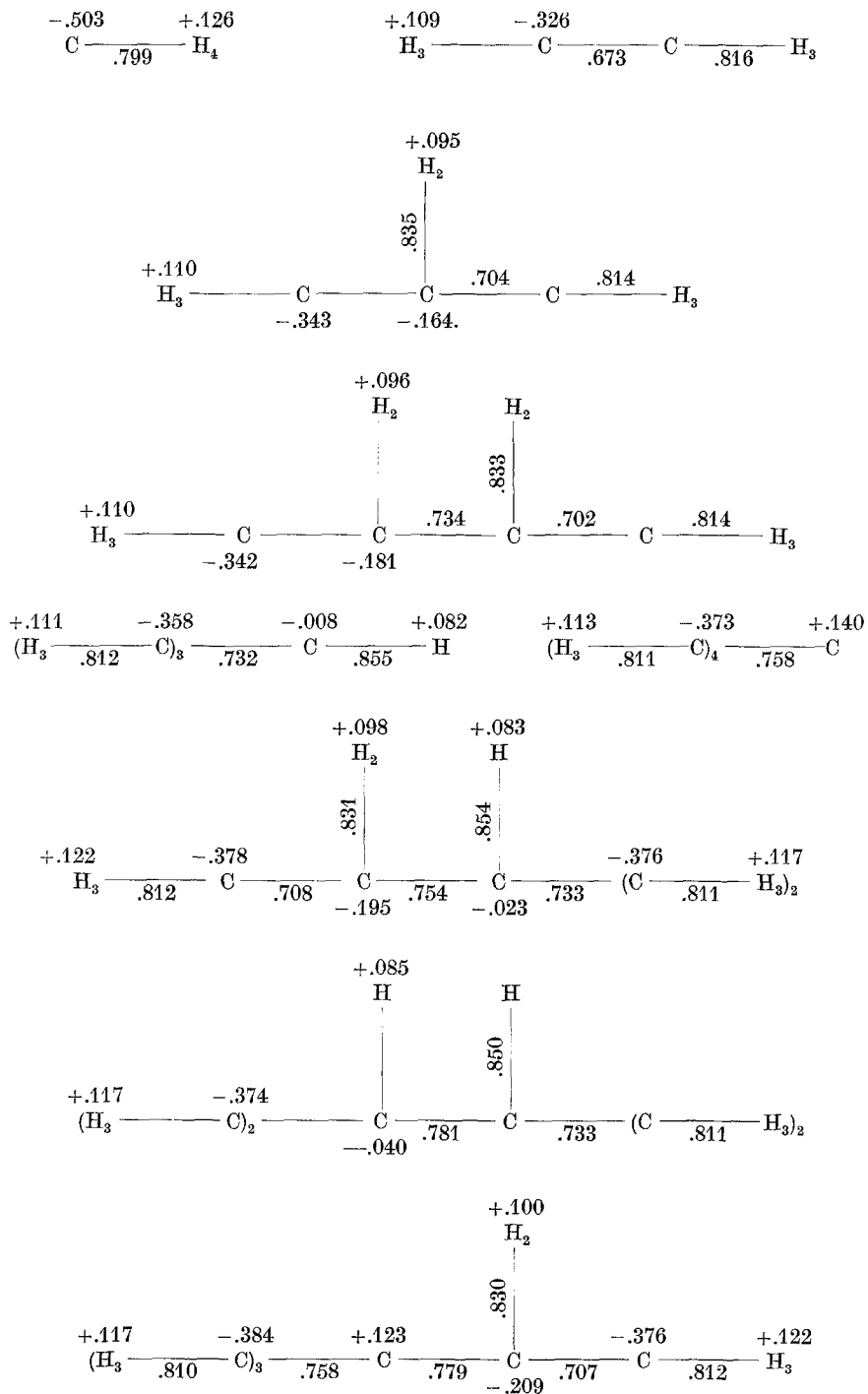
$$-.503 \quad\quad\quad +.126$$
$$C \overline{\quad.799\quad} H_4$$

$$+.109 \quad\quad\quad -.326$$
$$H_3 \overline{\quad\quad\quad} C \overline{\quad.673\quad} C \overline{\quad.816\quad} H_3$$

$$+.095$$
$$H_2$$
$$| \; .835$$
$$+.110 \quad\quad\quad\quad\quad\quad\quad .704 \quad\quad\quad .814$$
$$H_3 \overline{\quad\quad\quad} C \overline{\quad\quad\quad} C \overline{\quad\quad\quad} C \overline{\quad\quad\quad} H_3$$
$$-.343 \quad\quad -.164.$$

$$+.096$$
$$H_2$$
$$\vdots$$
$$H_2$$
$$| \; .833$$
$$+.110 \quad\quad\quad\quad\quad\quad .734 \quad\quad .702 \quad\quad\quad .814$$
$$H_3 \overline{\quad\quad\quad} C \overline{\quad\quad\quad} C \overline{\quad\quad\quad} C \overline{\quad\quad\quad} C \overline{\quad\quad\quad} H_3$$
$$-.342 \quad\quad -.181$$

$$+.111 \quad\quad -.358 \quad\quad -.008 \quad +.082$$
$$(H_3 \overline{\quad.812\quad} C)_3 \overline{\quad.732\quad} C \overline{\quad.855\quad} H$$

$$+.113 \quad\quad -.373 \quad\quad +.140$$
$$(H_3 \overline{\quad.811\quad} C)_4 \overline{\quad.758\quad} C$$

$$+.098 \quad\quad +.083$$
$$H_2 \quad\quad\quad H$$
$$| \; .831 \quad\quad | \; .854$$
$$+.122 \quad\quad -.378 \quad\quad\quad\quad\quad\quad\quad\quad -.376 \quad\quad +.117$$
$$H_3 \overline{\quad.812\quad} C \overline{\quad.708\quad} C \overline{\quad.754\quad} C \overline{\quad.733\quad} (C \overline{\quad.811\quad} H_3)_2$$
$$-.195 \quad\quad\quad -.023$$

$$+.085$$
$$H \quad\quad\quad H$$
$$| \quad\quad | \; .850$$
$$+.117 \quad\quad -.374 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad +.117$$
$$(H_3 \overline{\quad\quad\quad} C)_2 \overline{\quad\quad\quad} C \overline{\quad.781\quad} C \overline{\quad.733\quad} (C \overline{\quad.811\quad} H_3)_2$$
$$-.040$$

$$+.100$$
$$H_2$$
$$| \; .830$$
$$+.117 \quad\quad -.384 \quad\quad +.123 \quad\quad\quad\quad -.376 \quad\quad +.122$$
$$(H_3 \overline{\quad.810\quad} C)_3 \overline{\quad.758\quad} C \overline{\quad.779\quad} C \overline{\quad.707\quad} C \overline{\quad.812\quad} H_3$$
$$-.209$$

Fig. 1. Population analyses of alkanes. Signed numbers are gross atomic charges [27], unsigned numbers are overlap populations [27]

$$+.091$$
$$H_2$$
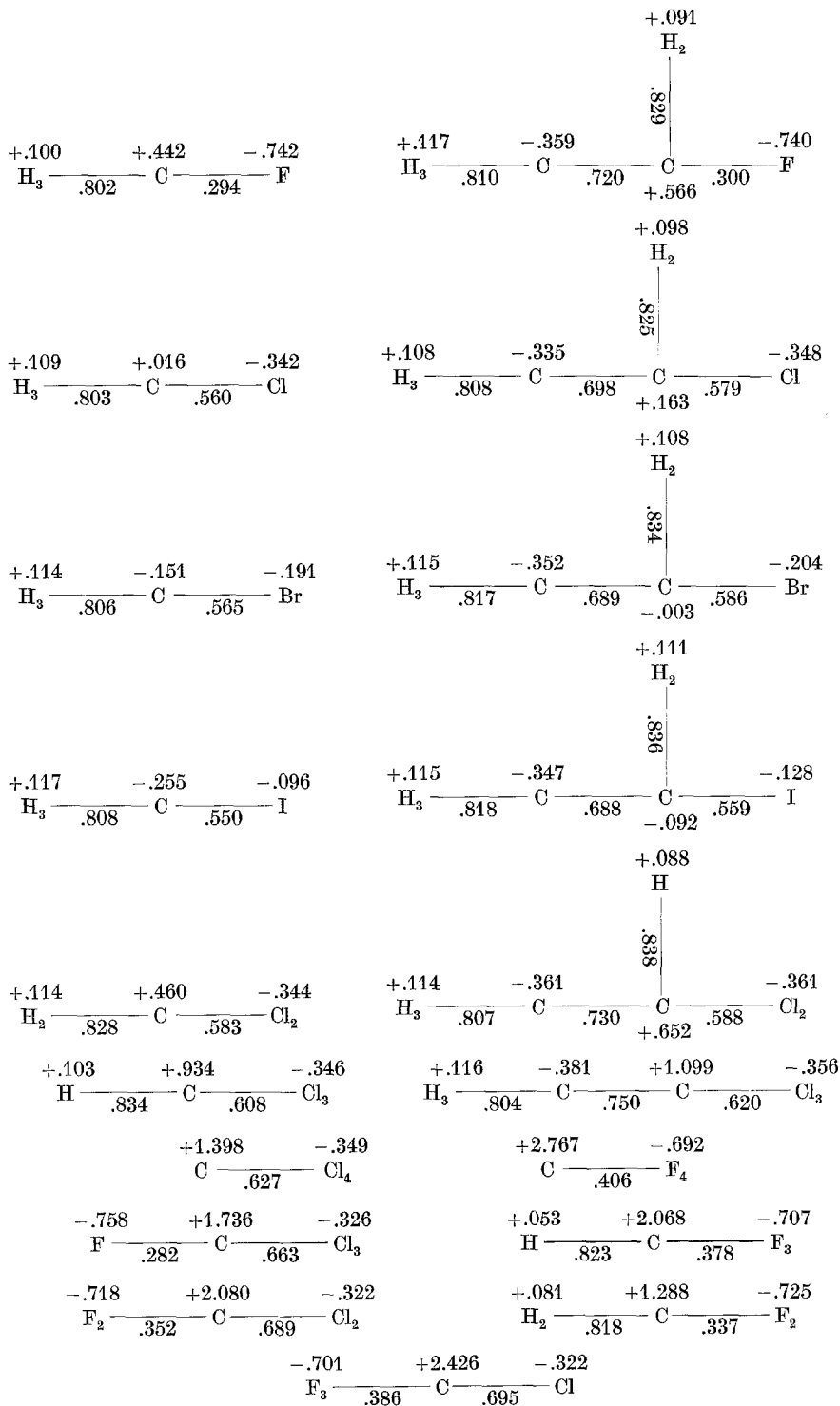$$.829$$

$$\overset{+.100}{H_3} \underset{.802}{——} \overset{+.442}{C} \underset{.294}{——} \overset{-.742}{F}$$

$$\overset{+.117}{H_3} \underset{.810}{——} \overset{-.359}{C} \underset{.720}{——} \overset{C}{\underset{+.566}{}} \underset{.300}{——} \overset{-.740}{F}$$

$$+.098$$
$$H_2$$
$$.825$$

$$\overset{+.109}{H_3} \underset{.803}{——} \overset{+.016}{C} \underset{.560}{——} \overset{-.342}{Cl}$$

$$\overset{+.108}{H_3} \underset{.808}{——} \overset{-.335}{C} \underset{.698}{——} \overset{C}{\underset{+.163}{}} \underset{.579}{——} \overset{-.348}{Cl}$$

$$+.108$$
$$H_2$$
$$.834$$

$$\overset{+.114}{H_3} \underset{.806}{——} \overset{-.151}{C} \underset{.565}{——} \overset{-.191}{Br}$$

$$\overset{+.115}{H_3} \underset{.817}{——} \overset{-.352}{C} \underset{.689}{——} \overset{C}{\underset{-.003}{}} \underset{.586}{——} \overset{-.204}{Br}$$

$$+.111$$
$$H_2$$
$$.836$$

$$\overset{+.117}{H_3} \underset{.808}{——} \overset{-.255}{C} \underset{.550}{——} \overset{-.096}{I}$$

$$\overset{+.115}{H_3} \underset{.818}{——} \overset{-.347}{C} \underset{.688}{——} \overset{C}{\underset{-.092}{}} \underset{.559}{——} \overset{-.128}{I}$$

$$+.088$$
$$H$$
$$.838$$

$$\overset{+.114}{H_2} \underset{.828}{——} \overset{+.460}{C} \underset{.583}{——} \overset{-.344}{Cl_2}$$

$$\overset{+.114}{H_3} \underset{.807}{——} \overset{-.361}{C} \underset{.730}{——} \overset{C}{\underset{+.652}{}} \underset{.588}{——} \overset{-.361}{Cl_2}$$

$$\overset{+.103}{H} \underset{.834}{——} \overset{+.934}{C} \underset{.608}{——} \overset{-.346}{Cl_3}$$

$$\overset{+.116}{H_3} \underset{.804}{——} \overset{-.381}{C} \underset{.750}{——} \overset{+1.099}{C} \underset{.620}{——} \overset{-.356}{Cl_3}$$

$$\overset{+1.398}{C} \underset{.627}{——} \overset{-.349}{Cl_4}$$

$$\overset{+2.767}{C} \underset{.406}{——} \overset{-.692}{F_4}$$

$$\overset{-.758}{F} \underset{.282}{——} \overset{+1.736}{C} \underset{.663}{——} \overset{-.326}{Cl_3}$$

$$\overset{+.053}{H} \underset{.823}{——} \overset{+2.068}{C} \underset{.378}{——} \overset{-.707}{F_3}$$

$$\overset{-.718}{F_2} \underset{.352}{——} \overset{+2.080}{C} \underset{.689}{——} \overset{-.322}{Cl_2}$$

$$\overset{+.081}{H_2} \underset{.818}{——} \overset{+1.288}{C} \underset{.337}{——} \overset{-.725}{F_2}$$

$$\overset{-.701}{F_3} \underset{.386}{——} \overset{+2.426}{C} \underset{.695}{——} \overset{-.322}{Cl}$$

Fig 2. Population analyses of halogenated alkanes

$$
\begin{array}{cccc}
+.102 & +.242 & -1.131 & +.583 \\
\text{H}_3 \!\!\underset{.809}{\text{---}}\!\! \text{C} \!\!\underset{.446}{\text{---}}\!\! \text{O} \!\!\underset{.532}{\text{---}}\!\! \text{H}
\end{array}
\qquad
\begin{array}{cccc}
+.114 & -.280 & -.195 & +.132 \\
\text{H}_3 \!\!\underset{.809}{\text{---}}\!\! \text{C} \!\!\underset{.622}{\text{---}}\!\! \text{S} \!\!\underset{.810}{\text{---}}\!\! \text{H}
\end{array}
$$

+.106   +.231   −1.097
(H₃ —.812— C)₂ —.480— O

+.120   −.306   −.111
(H₃ —.809— C)₂ —6.54— S

−1.073   +.358
N —.685— H₃

+.161   −.054
P —.802— H₃

+.104   −.038   −1.006   +.366
H₃ —.814— C —.602— N —.686— H₂

+.123   −.572   +.353   −.075
H₃ —.817— C —.604— P —.822— H₂

+.110   −.057   −.884   +.341
(H₃ —.819— C)₂ —.638— N —.727— H

+.124   −.591   +.534   −.095
(H₃ —.814— C)₂ —.631— P —.844— H

+.104   −.044   −.809
(H₃ —.812— C)₃ —.667— N

+.125   −.608   +.700
(H₃ —.811— C)₃ —.660— P

+.102   −.063   +.028
[(H₃ —.819— C)₄ —.725— N]+

+.127   −.750   +.895   −.176
H₃ —.816— C —.595— Si —.828— H₃

+.127   −.787   +1.625
(H₃ —.805— C)₄ —.629— Si

+.129   −.767   +1.159   −.198
(H₃ —.812— C)₂ —.611— Si —.832— H₂

+.131   −.783   +1.561
(H₃ —.801— C)₄ —.613— Ge

+.129   −.785   +1.404   −.214
(H₃ —.810— C)₃ —.619— Si —.839— H

+.126   −.914   +2.146
(H₃ —.809— C)₄ —.486— Sn

+.150   −.083   +1.829   −1.098
H₃ —.777— C —.771— N —.820— O₂

+.077
H
| .825
+.144   −.334   −1.312
H₃ —.783— C —.838— C =.791= O
+1.136

+.146   −.198   +.985   −1.226
H₃ —.757— C —.902— C ≡1.595≡ N

+.132   −.234   +.089   −.400   +.150
H₃ —.773— C —.842— C ≡1.913≡ C —.809— H

Fig. 3. Population analyses of methyl derivatives
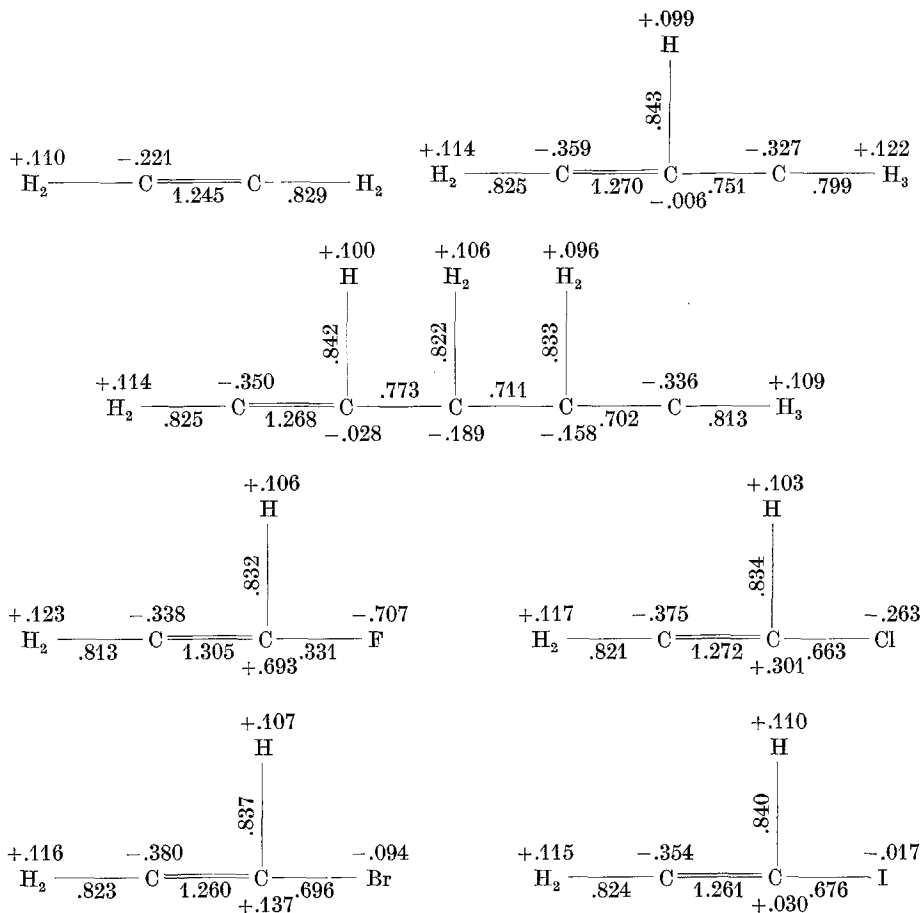
Fig. 4. Population analyses of vinyl derivatives

In the present work this method is used with a computer subroutine written to calculate overlap integrals between $1s$, $2s$, $2p$, $3s$, $3p$, $5s$ and $5p$ Slater orbitals using standard formulae [28]. Since the effective quantum number [39] n^* for Slater $4s$ and $4p$ orbitals is 3.7, overlap integrals involving these orbitals cannot be calculated in closed form, and were approximated by a linear interpolation, i.e.

$$S\ (na,\ 4b) = 0.3\ S\ (na,\ 3b) + 0.7\ S\ (na,\ 5b)$$

where a and b are the Slater orbitals of any two given types. A plot of $S\ (1s,\ n^*s)$ against n^* shows that this approximation is unlikely to be in error by more than 0.01 for the value of S for this case. In view of the approximations made in the EHT method, this further approximation does not seem to be serious.

In setting the coulomb integral of an atomic orbital equal to the VSIP of the orbital in the free atom, the VSIP values of HINZE and JAFFÉ [7] were used, rather than those of SKINNER and PRITCHARD [38], since the former are the result of a more complete and systematic examination of atomic spectral data, and systematic calculation of non-observable states.

The charge distributions of several alkanes, halogenated alkanes, methyl derivatives and vinyl derivatives have been calculated in this way. The population analyses of these molecules are shown in Fig. 1 — 4. The small differences from HOFFMANN's results [9] for the alkanes are due entirely to the changes in the coulomb integral values for carbon. Since this work is concerned with the correlation of computed charges with chemical shifts, atoms which are equivalent over the time required for an NMR transition are regarded as equivalent, even though their instantaneous environments differ, so that, for example, only the average charge of the six hydrogen atoms in dimethyl ether is reported; the methly groups rotate quickly enough so that all six protons have the same chemical shift, although the instantaneous distances of each proton from the carbon in the other methyl group are not identical.

III. Relation of chemical shift to charge distribution

The use of chemical shifts as a measure of the charge distribution for comparison with the calculated results is naturally suggested by the elementary concept that the magnetic shielding of a nucleus by the electronic currents should vary linearly with the electron density near that nucleus. In fact, chemical shifts depend on factors other than electron density, so that detailed theories of chemical shift must be examined to determine when the chemical shifts can be expected to indicate the actual charge distribution in a molecule.

The total screening of a nucleus can be divided [35] into a diamagnetic and a paramagnetic contribution from local currents associated with the given atom, and contributions from local currents on other atoms. (Ring current effects are neglected here as ring compounds are not considered in this work). For all nuclei, except protons, the local paramagnetic term is dominant in determining chemical shifts [33]. This conclusion, first reached for fluorine shifts [35], is based on calculations which show that the local diamagnetic term, as given by the Lamb formula [17], is much too small to account for the observed range of shifts. Neighbour anisotropy effects from the local currents on neighbouring atoms are also considered to be negligible [33, 35] compared to the local paramagnetic effects, although the work of SPIESECKE and SCHNEIDER [41] shows that neighbour anisotropy effects on the carbon chemical shifts in the methyl halides may be as large as 54 ppm for methyl iodide. This conclusion is based on deviations from linear dependence of the carbon chemical shifts of methyl derivatives on the substituent Pauling atomic (not orbital) electronegativity. Nevertheless, chemical shifts of nuclei other than protons are usually primarily attributed to the local paramagnetic term.

POPLE [32] formulated an LCAO–MO theory of chemical shifts, assuming zero-differential overlap. Recently [33], applying this theory to carbon shifts, he considered the dominant local paramagnetic term, and indicated three effects on the chemical shift:

(i) a charge dependence,

(ii) an electronic excitation energy dependence, and

(iii) a multiple bond effect.

(i) The variation of chemical shift with charge for an approximately neutral atom, such as carbon, is dominated by the dependence of the paramagnetic shift

on the mean inverse cube radius of the $2p$ orbitals, $\langle r^{-3} \rangle_{2p}$ [19]. The atomic orbitals of an atom expand with increased negative charge due to interelectronic repulsion, and $\langle r^{-3} \rangle_{2p}$ decreases. Assuming linear dependence of the Slater screening constant on the atomic charge, this factor is proportional to the charge to first-order [33], so that a linear charge dependence is expected from this effect alone.

(ii) The shift also depends on the mean inverse electronic excitation energy, for which POPLE [33] chose one value in ethane and lower values for unsaturated molecules to allow for the lower energies of the unoccupied orbitals.

(iii) Finally POPLE noted the existence of a multiple-bond effect due to the presence, in the expression for the local paramagnetic shift, of terms involving combinations of LCAO coefficients which are not directly charge-dependent and which are non-zero only when multiple bonds are present. This analysis refers to localized MO wave functions and not to completely delocalized wave functions such as those of the EHT method.

The low carbon chemical shifts of unsaturated compounds have been attributed to the last two effects [33]. Carbon chemical shifts are therefore expected to indicate charge density trends only within a series of saturated molecules, or perhaps within a series of unsaturated molecules with the same type of multiple bonding, but not between the two series.

Fluorine shifts in aromatic molecules have been discussed by KARPLUS and DAS [13] and by WU and DAILEY [46], who express the shifts in terms of σ and π charge density and π bond order. The computations in this work are restricted to series of saturated molecules with fluorine bonded to tetrahedral carbon, so that π bonding is negligible and fluorine chemical shifts, like carbon shifts, are expected to increase with charge density on fluorine atoms. A linear dependence is expected for small variations in C–F bond polarity [46].

For proton shifts [31, 34] the local paramagnetic currents on the hydrogen atom are negligible due to the unavailability of low-lying p orbitals, so that the local diamagnetic term is dominant. This term is given by the Lamb formula [17] and is proportional to the electron population on the hydrogen atom. However paramagnetic currents on neighbouring atoms, the neighbour anisotropy effects, are important in determining proton shifts [34], as:

(i) few electrons are localized close to a given proton to screen distant electrons, so that the latter have a larger effect,

(ii) H–X bonds are shorter than other bonds so that the distant electrons are closer, and

(iii) the total range of proton chemical shifts is much smaller, due to the absence of local paramagnetic effects, than the ranges of shifts of other nuclei, so that neighbour anisotropy effects are relatively larger. The linear charge dependence of proton shifts, predicted from the local diamagnetic term, is therfore expected to be reliable only in series of molecules with similar geometries, in which the anisotropy effects are constant throughout the series.

These general predictions are confirmed by empirical correlations of chemical shifts in various series of molecules against substituent atomic electronegativities [18] and against calculated π-charge densities [19, 40].

IV. Results

Two general trends are apparent when the atomic charges of various series of molecules, calculated as described in Section II, are plotted against the chemical shift of a given nucleus.

It is found that in a series of molecules in which one atom, or group, is substituted and the rest of the molecule held constant (e.g. the methyl derivatives), or in which successive substitution of a given atom or group occurs at a given point (e.g. the chloromethanes),

(i) the computed charge on the atom next to the substituent varies approximately linearly with the chemical shift;

(ii) the computed charges on the second atom from the substituent fail to correlate in general.

Examples of both trends are given below. All graphs in this paper are drawn so that a positive slope indicates increased magnetic shielding with increased electron population, as expected if the computed charges show the correct trend. The lines drawn are fitted by a least-squares analysis.

(i) The successful correlations at the point of substitution are illustrated in Fig. 5 — 9. Fig. 5 and 6 show carbon chemical shifts plotted against gross atomic charges for the chloromethanes [18] and methylmethanes [41] respectively. The correlations are approximately linear. It is noted (Fig. 6) that methyl groups in alkanes are electron-withdrawing relative to hydrogen. It has been shown [12, 43] by electronegativity equalization calculations that methyl groups are electron-withdrawing in alkanes, in agreement with the EHT results, but electron-releasing in some alkyl derivatives as evidenced by reactivity trends.

Fig. 7 shows the chemical shifts [10, 41] of methyl carbon atoms in methyl derivatives, CH_3X, plotted against the computed charges on the same carbon atoms. The methyl carbon charges in the saturated molecules correlated approximately linearly with chemical shift, so that unreported chemical shifts of methyl carbons in similar molecules can be predicted, e.g. $CH_3SH = 128$, $CH_3PH_2 = 154$, and $CH_3SiH_3 = 170$ ppm relative to benzene.

The observed methyl carbon shifts [41] of acetaldehyde and nitromethane, two methyl derivatives with multiply-bonded substituents, are 34 and 40 ppm lower respectively than would be expected from the line in Fig. 7 for saturated methyl derivatives. Pople's theory of carbon chemical shifts [33] predicts that in multiply-bonded compounds the lower electronic excitation energy (ΔE) and multiple-bond effect cause low-field shifts. If it is assumed that the π molecular orbitals of the multiple bonds are delocalized to some extent so that those atomic orbitals on the methyl carbons which have the correct symmetry participate in them (hyperconjugation), then the low-field shifts may be attributed to these effects. On the other hand, the methyl carbon shift in methyl cyanide is only 3 ppm higher than that predicted from the computed methyl carbon charge and Fig. 7. The multiple bond effect is substantial for double bonds, but is zero for a symmetrical triple bond [33], and therefore presumably small for other triple bonds. In methyl cyanide the ΔE effect is present, and the multiple-bond effect virtually absent; the absence of a low-field shift shows that the ΔE effect is small enough to be virtually cancelled by the positive anisotropy effect of the cyanide group. It is therefore concluded that the multiple bond effect and/or anisotropy

Fig. 7

Gross atomic charge on methyl carbon in methyl derivatives CH_3X

Carbon chemical shift (ppm rel. to C_6H_6)

Fig. 6

Gross atomic charge on central carbon in methylmethanes

Carbon chemical shift (ppm rel. to C_6H_6)

Fig. 5

Gross atomic charge on carbon in chloromethanes

Carbon chemical shift (ppm rel. to C_6H_6)

Fig. 9

Gross atomic charge on phosphorus in methylphosphines

Phosphorus chemical shift (ppm rel. to 85% aq. H_3PO_4)

Fig. 8

Gross atomic charge on methyl carbon in methyl derivatives $(CH_3)_nX$

Carbon chemical shift (ppm rel. to C_6H_6)

Fig. 5. Plot of ^{13}C chemical shift against gross atomic charge on carbon, as computed by the Extended Hückel Theory as described in the text, for CCl_4 (1), $CHCl_3$ (2), CH_2Cl_2 (3), CH_3Cl (4), CH_4 (5). The line drawn was determined by a least-squares fit

Fig. 6. Plot of chemical shift against gross atomic charge on central carbon for CMe_4 (1), $CHMe_3$ (2), CH_2Me_2 (3), CH_3Me (4), CH_4 (5)★

Fig. 7. Plot of ^{13}C chemical shift against gross atomic charges on carbon for saturated ⊙ and unsaturated △ methyl derivatives CH_3X. CH_3F (1), CH_3OH (2), CH_3Cl (3), CH_3NH_2 (4)' CH_3Br (5), CH_3I (6), C_2H_6 (7), CH_4 (8), CH_3NO_2 (9), CH_3CHO (10), CH_3CN (11). The unsaturated points were ignored in fitting the line

Fig. 8. Plot of ^{13}C chemical shift against gross atomic charge on carbon in methyl derivatives $(CH_3)_nX$. The dashed line for $n = 1$ is taken from Fig. 7. $n = 2$, $(CH_3)_2O$ (1), $(CH_3)_2S$ (2), $(CH_3)_2CH_2$ (3). $n = 3$, $(CH_3)_3N$ (4), $(CH_3)_3CH$ (5). $n = 4$, $[(CH_3)_4N]^+$ (6). $(CH_3)_4C$ (7), $(CH_3)_4Si$ (8), $(CH_3)_4Ge$ (9), $(CH_3)_4Sn$ (10)★

Fig. 9. Plot of ^{31}P chemical shift against gross atomic charge on phosphorus for PMe_3 (1), $PHMe_2$ (2), PH_2Me (3), PH_3 (4)
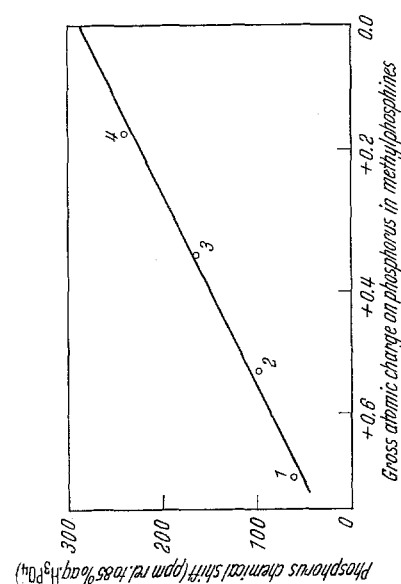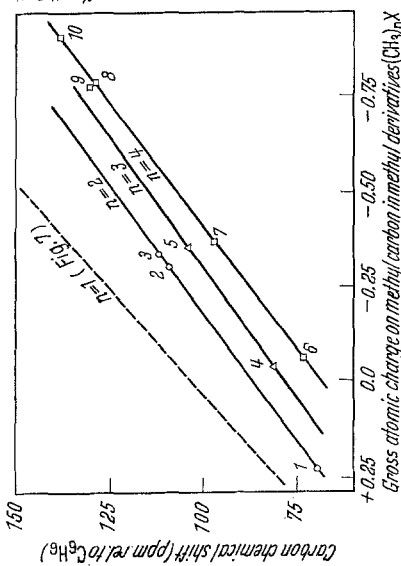
★ The dotted carbon atom in each molecule is the one considered

contribution is much more important than the ΔE effect in causing the low-field shifts of the other two molecules. This can be understood from the fact that $\pi \longleftrightarrow \pi^*$ transitions do not contribute to the ΔE term for symmetry reasons [14], so that the difference between the $\sigma \longleftrightarrow \pi^*$ effective excitation energies in unsaturated molecules and the $\sigma \longleftrightarrow \sigma^*$ excitations in saturated molecules is not important enough to cause large chemical shifts. Since the chemical shift of the methyl carbon in methyl cyanide corresponds to that which would be expected from the computed charge, the chemical shift of methyl carbons in other molecules with triply bonded substituents may be predicted. For example, the chemical shift of the methyl carbon in methylacetylene is predicted to be 127 ppm relative to benzene, assuming the same deviation from the line in Fig. 7 as for methyl cyanide.

Fig. 8 shows correlations of the computed charge with the chemical shift [41] of methyl carbons in methyl derivatives with several methyl groups, $(CH_3)_nX$, with the line from Fig. 7 drawn in as a dotted line. The lines for different n are approximately parallel. The difference between the lines for different n may be attributed to the varying anisotropy of the central atom X; for $n = 4$ the X atom is isotropic, while for $n < 4$ it is not, so that increasing positive anisotropy contributions to the chemical shift with decreasing n are expected (cf. Fig. 3 of Ref. [41]). This explanation of the occurrence of different lines is reasonable since the difference in chemical shift between the most anisotropic and the isotropic line, about $30 - 40$ ppm, is of the same order of magnitude as the anisotropy effects in methyl halides [41].

Fig. 9 shows that the phosphorus chemical shifts [42] of the methylphosphines vary almost linearly with the calculated charges on phosphorus. This indicates that chemical shifts in this series are dominated by the charge-dependent term, in contrast to nitrogen chemical shifts where changes in the $n \longleftrightarrow \pi^*$ transition energy are the dominant factor [5]. The observed nitrogen shifts [5] in the methylamines failed to show any systematic trend in terms of the calculated charges for nitrogen (Fig. 3).

(ii) Fig. 10 — 15 illustrate the failure of the calculated charges on the second atom from a substituent to correlate with the chemical shift. In the halomethanes, as discussed in Part III, the halogen chemical shifts should vary linearly with the true charge on the halogen atoms, because multiple bonding in these saturated molecules is negligible. However they do not vary linearly as the charges calculated by the EHT method. Fig. 10 shows that for the system $F-C-X_3$, the calculated charges follow the correct order as indicated by fluorine chemical shifts [23] when X=F is successively replaced by X=H, but the wrong order when X=H is successively replaced by X=Cl. Neither plot is even approximately linear. In Fig. 11 the recently measured chlorine chemical shifts [36] of the chloromethanes are used to show that the calculated charges on chlorine also follow the wrong order when hydrogen atoms are successively substituted by chlorine atoms.

Fig. 12 shows that the trend of methyl proton shifts [41] in methyl derivatives is also incorrectly predicted by the EHT method. A linear correlation of proton chemical shifts with charges on hydrogen would not be expected even if the calculated charge distribution were completely accurate, due to varying anisotropy effects in the methyl derivatives chosen. Nevertheless the fact that the whole

trend of calculated hydrogen charges is in the wrong direction as indicated by the chemical shifts emphasizes the unreliability of the EHT method for predicting charge trends two atoms removed from the substituent.

Fig. 13 shows both the successful correlation at the point of substitution and the failure at the next atom in the case of substituted ethanes. Fig. 13a shows that the chemical shifts [41] of the methylene carbons in the ethyl halides vary approximately linearly with the calculated charges on these carbons. In contrast to this, when the methyl carbon chemical shifts of the ethyl halides are plotted against the computed carbon charges in Fig. 13b, it is found that ethyl chloride is out of line. Furthermore the calculated electron populations of the methylcarbons in the
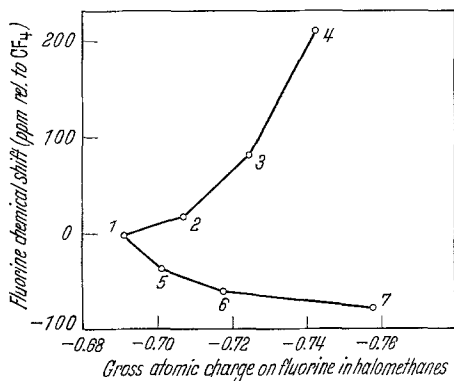
Fig. 10

Fig. 11

Fig. 10. Plot of ^{19}F chemical shift against gross atomic charge on fluorine for CF_4 (1), CHF_3 (2), CH_2F_2 (3), CH_3F (4), $CClF_3$ (5), CCl_2F_2 (6), CCl_3F (7)
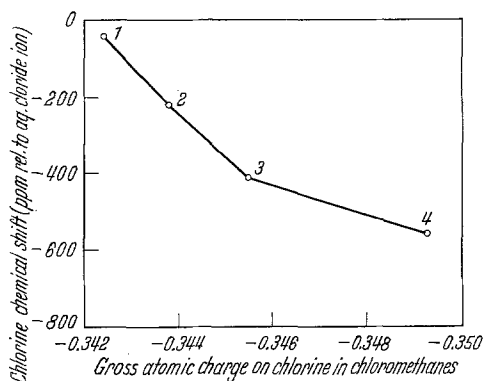
Fig. 11. Plot of ^{35}Cl chemical shift against gross atomic charge on chlorine for CH_3Cl (1), CH_2Cl_2 (2), $CHCl_3$ (3), CCl_4 (4)

1-multichloroethane series increase with successive chlorine substitution, in opposition to the trend shown by the chemical shifts [18]. That is, for ethane substituted by one or more halogens on the same carbon atom, the EHT method predicts the correct charge trends for the substituted carbon but not always for the methyl carbon.

Carbon atoms participating in multiple bonds have lower chemical shifts than those in saturated molecules [33]. In a series of molecules with the same type of multiple bonding, however, the multiple-bond effects should be similar, so that the carbon chemical shifts should approximately indicate the true charge density trends within the series. Fig. 14a and 14b show that in a series of vinyl halides, the calculated charges on the substituted carbon follow the order indicated by the chemical shift data [22], but those on the methylene carbon do not. This is analogous to the situation for substituted ethanes. The poorer fit for the point of substitution compared to that for a series of saturated molecules may be attributed to the fact that the effect of the double bond is not exactly constant throughout the series.

Finally, Fig. 15 shows the charge trends predicted by EHT for branching alkanes. The theory predicts that substitution of methyl groups for hydrogen atoms results in electron withdrawal at the point of substitution, and electron
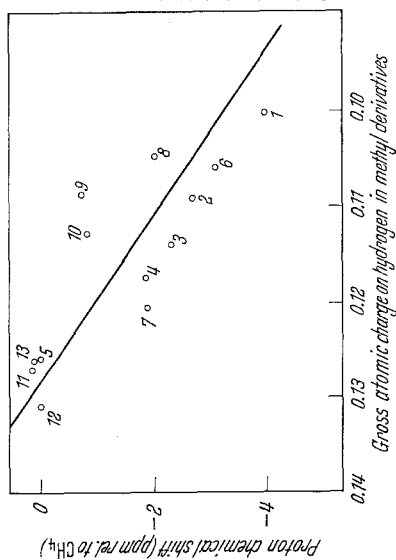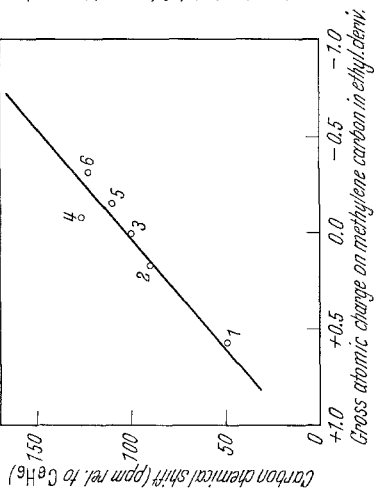
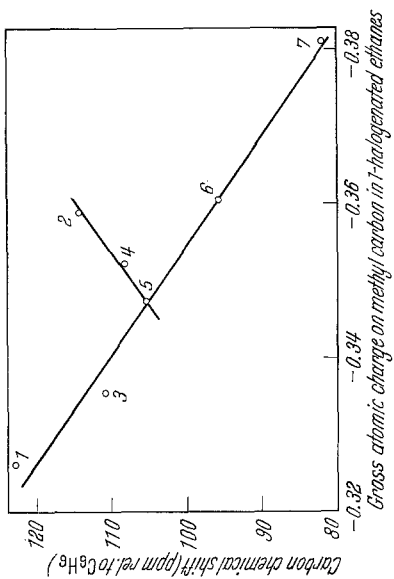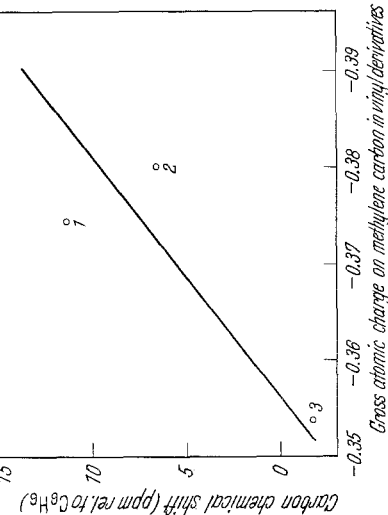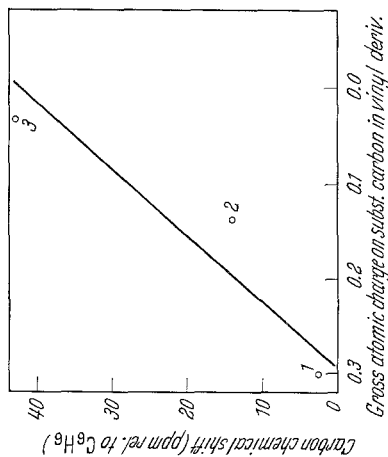Fig. 12. Plot of ¹H chemical shift against gross atomic charge on hydrogen for CH₃F (1), CH₃Cl (2), CH₃Br (3), CH₃I (4), CH₄ (5), (CH₃)₂O (6), (CH₃)₂S (7), (CH₃)₃N (8), C₂H₆ (9), (CH₃)₄C (10), (CH₃)₄Si (11), (CH₃)₄Ge (12), (CH₃)₄Sn (13)

Fig. 13a and b. a Plot of ¹³C chemical shift against gross atomic charge on carbon for CH₃CH₂F (1), CH₃CH₂Cl (2), CH₃ĊH₂Br (3), CH₃CH₂I (4), CH₃ĊH₂CH₃ (5), ĊH₃CH₃ (6)★. b Plot of ¹³C chemical shift against gross atomic charge on carbon for CH₃ĊH₃ (1), ĊH₃CH₂F (2), ĊH₃CH₂Cl (3), ĊH₃CH₂Br (4), ĊH₃CH₂I (5), ĊH₃CHCl₂ (6), ĊH₃CCl₃ (7)★

Fig. 14a and b. a Plot of ¹³C chemical shift against gross atomic charge on carbon for CH₂=CHCl (1), CH₂=ĊHBr (2), CH₂=ĊHI (3)★. b Plot of ¹³C chemical shift against gross atomic charge on carbon for ĊH₂=CHCl (1), ĊH₂=CHBr (2), ĊH₂=CHI (3)★

─────────

★ The dotted carbon atom in each moleculeis the one considered

Fig. 13b

Fig. 13a

Fig. 12

Fig. 14b

Fig. 14a

donation to the next carbon atom. The chemical shift data [4] indicate, however, that substitution of methyl for hydrogen in the alkanes shown results in electron withdrawal from both these positions, so that again the theory is correct at the point of substitution but not at the next atom.

It has been assumed in this paper that the gross atomic charge is analogous to the chemical concept of charge an an atom. Actually, the question of what constitutes the best measure of atomic charge for correlation with chemical shift may become important. In view of this, attempts were made to correlate chemical shift with two measures of charge;

(i) the gross atomic population [27] as in the EHT method, and

(ii) the net atomic population [27], in which overlap populations are neglected completely.
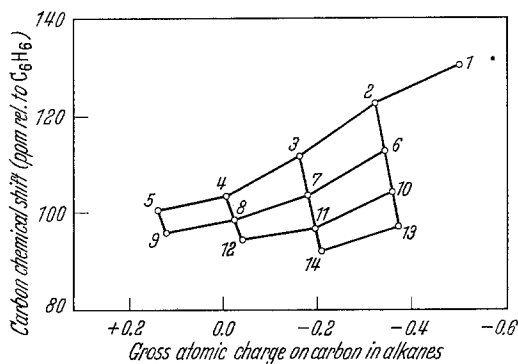
Fig. 15. Effect of branching in alkanes. CH_4 (1), CH_3Me (2), $\overset{\cdot}{C}H_2Me_2$ (3), $\overset{\cdot}{C}HMe_3$ (4), $\overset{\cdot}{C}Me_4$ (5), $\overset{\cdot}{C}H_3CH_2Me$ (6), $Me\overset{\cdot}{C}H_2CH_2Me$ (7), $Me_2\overset{\cdot}{C}H\,CH_2Me$ (8). $Me_3\overset{\cdot}{C}\,CH_2Me$ (9), $\overset{\cdot}{C}H_3CHMe_2$ (10), $Me\overset{\cdot}{C}H_2CHMe_2$ (11), $Me_2\overset{\cdot}{C}H\,CHMe_2$ (12), $\overset{\cdot}{C}H_3CMe_3$ (13), $Me\overset{\cdot}{C}H_2CMe_3$ (14). The dotted carbon atom in each molecule is the one considered.

When the populations were computed from EHT wave functions, the same overall correlation trends with chemical shift were found for both types of population. Therefore only the results of method (i) have been presented in detail, and an explanation of the trends is sought in an analysis of the EHT method.

V. Discussion

The main feature of EHT charge distributions is that while the predicted charges in a series of molecules correlate successfully with the chemical shift at the point of substitution, they fail to correlate at the next atom. Most of the chemical shift trends at the second atom from the substituent can be explained by the chemical concept of the inductive effect, although there are exceptions such as the chlorofluoromethanes. In most of the series of molecules whose computed charge distributions are shown in Fig. 1 — 4, the inductive effect is not predicted. However the chemical shift trends, well-known chemical evidence and calculations by the SGOBE method [43] all indicate that the inductive effect does in fact exist. The failure of the EHT at the second atom from the substituent may be expressed therefore as a failure to predict the inductive effect, a failure which must be due to the assumptions of EHT.

Another feature of the charge distributions predicted by EHT is that they are much more polar than those predicted by the SGOBE method. For example, the

charge on each chlorine atom in carbon tetrachloride is computed as -0.349 by EHT, compared to -0.073 by the SGOBE method. Since the actual polarity cannot be determined experimentally, the assumptions of both methods must be examined in an attempt to determine on a theoretical basis which method is more likely to predict correct polarities, or whether the true polarity is intermediate between the predictions of the two theories.

A qualitative analysis of the assumptions will be made, in which those approximations which are likely to cause the features mentioned above will be indicated, guided by the actual results of the computations.

The results of an LCAO–MO calculation depend on the choice of coulomb and resonance integrals. The EHT parametrization is that the coulomb integral, H_{rr}, is the VSIP of an atomic orbital in the free atom, and the resonance integral, H_{rs}, between two atomic orbitals with overlap integral S_{rs} is

$$H_{rs} = 1.75 \, S_{rs} \, (H_{rr} + H_{ss})/2 \, .$$

It is reasonable to assume that coulomb and resonance integrals corresponding to those used in self-consistent field method would give better results. Since an SCF–LCAO–MO method has not yet been applied to σ orbitals in molecules such as those treated in this paper, it will be assumed that the relation of the coulomb and resonance integrals in such a method to those used in EHT would be analogous to the relation of the parameters used in Pople's SCF–LCAO–MO method for π orbitals [30] to those in the Hückel method for π orbitals [29].

The coulomb integral of a π orbital on a given atom in the Hückel method is assigned a constant value regardless of the molecule in which the atom is located. In contrast to this, POPLE's expression [30] for the coulomb integral H_{rr} of an atomic orbital in a π system is,

$$H_{rr} = U_{rr} + \tfrac{1}{2} \, P_{rr} \, G_{rr} + \sum_{s \neq r} (P_{ss} - Z_s) \, G_{rs}$$

where

(i) U_{rr} is the diagonal matrix element of the rth orbital with respect to the one-electron Hamiltonian containing only the kinetic energy and the interaction with the core of its own atom,

(ii) P_{rr} is the charge-density in the rth atomic orbital under the zero-differential-overlap approximation.

(iii) Z_r is the occupancy of the rth atomic orbital in the free atom, and

(iv) G_{rs} is the electrostatic interaction energy between an electron in the rth atomic orbital and one in the sth.

This expression depends on the actual charge distribution in the molecule, since

(i) the second term represents an intraatomic repulsion term in the rth orbital dependent on the charge density P_{rr}, and

(ii) the third term represents interatomic electrostatic interactions dependent on the charge densities P_{ss} in the orbitals of the other atoms. Pople and Hückel coulomb integrals differ by intraatomic and interatomic electrostatic interaction terms, both of which vary with the molecular charge distribution.

Similarly SCF–LCAO–MO coulomb integrals for σ systems are expected to differ from EHT coulomb integrals by intraatomic electrostatic interaction terms

dependent on the molecular charge distribution. However in calculations involving more than one atomic orbital per atom, the intraatomic repulsion term is divided into a term involving repulsion between two electrons in the orbital concerned, and terms involving electrostatic repulsions by electrons in other orbitals on the same atom. Thus the SCF and EHT coulomb integrals should differ by three types of terms dependent on the charge distribution of the molecule: *intraorbital repulsion, interorbital repulsions* on the same atom, and *interatomic electrostatic interactions*.

The effect of neglecting each of these terms in EHT may now be considered. In an SCF calculation, a transfer of electrons in a molecule to an atom or atoms with higher coulomb integrals in the neutral state than other atoms results in a reduction of the originally higher coulomb integrals and an increase in the originally lower coulomb integrals due to the intraorbital repulsion term in the coulomb integral expression. This term therefore has the effect of reducing the polarity of the various bonds in the molecule, so that its neglect is probably responsible for the high polarities predicted by the EHT. Since there are also theoretical reasons [1] for believing that the polarities predicted by the SGOBE method are too low, it is probable that the true polarity of a given bond in a given molecule lies in between the values predicted by the EHT and SGOBE methods.

The neglect of *interorbital repulsions* is probably responsible for the failure of the EHT to predict the inductive effect. Consider, for example, methyl fluoride in terms of a basis set with tetrahedral hybrid orbitals on carbon directed along its bonds. (Although this is not the basis set used in the EHT method, it is an equivalent basis set since the orbitals in one basis are linear combinations of those in the other). From the viewpoint of an SCF method, the transfer of electrons from the carbon orbital directed toward the fluorine atom to the fluorine orbital results in a decrease of electrostatic repulsion between this carbon orbital and the carbon orbitals directed toward the hydrogen atoms. The carbon orbitals directed toward the hydrogens therefore have a higher coulomb integral than in a methyl derivative in which the substituent bond orbital has a lower coulomb integral than for fluorine. This results in a charge transfer from the hydrogen atom to these carbon orbitals. This represents a molecular-orbital description of the inductive effect. The failure of the EHT to predict the inductive effect is due to the neglect of the interorbital electrostatic repulsion terms in the coulomb integral on which the inductive effect depends.

Again considering methyl fluoride as an example, the inclusion of *interatomic electrostatic terms* would result in a decrease of the coulomb integrals of the carbon orbitals relative to those of the hydrogens, since the carbon orbitals are closer to the negatively charged fluorine atom than the hydrogen atom is. The neglect of this term should result in a greater positive error in the coulomb integrals of carbon than that of hydrogen, and an electron transfer from hydrogen to carbon. That is, neglect of this term should oppose the effect caused by neglect of interorbital repulsion on carbon and tend to predict an inductive effect. The absence of an inductive effect in the actual computed results shows that neglect of interorbital repulsion on the same atom is the dominant error. In terms of a basis set with tetrahedral orbitals on carbon again, it is clear that the difference between the repulsion of the negatively charged fluorine on an electron in a carbon orbital

directed toward a hydrogen, and that on an electron in the hydrogen valence orbital, is relatively small compared to the change in repulsion of electrons in one carbon orbital on one electron in another so that neglect of the latter effect should be more significant than neglect of the former, as confirmed by the results.

The effect of errors in EHT resonance integrals should also be considered. The resonance integral used in the Pople theory [30] is $H_{rs} = H'_{rs} - \frac{1}{2} G_{rs} P_{rs}$, where H'_{rs} is an offdiagonal element of the core Hamiltonian matrix and P_{rs} is the bond order between the rth and s^{th} orbitals. As is the case for the coulomb integrals, the resonance integrals used in the Pople method differ from those in the Hückel method by terms dependent on the actual charge distribution in the molecule, so that in a calculation involving both σ and π orbitals, the SCF resonance integrals should differ from the EHT resonance integrals by similar terms. It is difficult to predict the effect which inclusion of such terms would have on the results, and since the main features of the computed charge distributions have been explained in terms of the coulomb integrals, a detailed analysis of the neglect of these terms in the resonance integrals will be omitted here.

It is also noted at this point that since the EHT method includes resonance integrals between non-neighbouring atoms, the presence of small resonance integrals between, say, the hydrogen and fluorine orbitals in methyl fluoride allows a direct charge transfer from hydrogen to fluorine (as the latter has the higher orbital coulomb integrals), or an "apparent inductive effect". As the non-neighbour resonance integrals are small, this effect is expected to be quite small and it is not surprising that the computations show that it is dominated by the interorbital repulsions of the carbon atom.

VI. Conclusion

The results of EHT computations show that the most serious approximations in the theory are the neglect of intraatomic repulsion terms, both intra- and interorbital, in the coulomb integrals of the atomic orbitals making up the basis set of the calculations. The neglect of the intraorbital term is responsible for the high polarities predicted by the method, and the neglect of interorbital repulsions is responsible for the failure to predict inductive effects. It is therefore probable that the charge distributions predicted by EHT could be improved by making the coulomb and resonance integrals dependent on the molecular charge distribution as is done in a self-consistent field method. A similar conclusion has been reached from a study of hydrogen bonding by the EHT method [26]. It is worth noting that even such a simplified self-consistent method as the SGOBE method predicts better charge distributions, and predicts inductive effects.

We are currently attempting to apply an SCF–LCAO–MO method to the calculation of charge distributions in saturated molecules, with the object of determining how complete a method can be applied with computation times comparable to those required for the EHT method, so that molecules of similar size can be treated.

References

[1] Baird, N. C., J. M. Sichel, and M. A. Whitehead: (To be published).

[2] Chesnut, D. V., C. J. Fritchie, and H. E. Simmons: J. chem. Physics 42, 1127 (1964).

[3] Fukui, K., H. Kato, and T. Yonezawa: Bull. chem. Soc. Japan 33, 1197, 1201 (1960).

[4] Grant, D. M., and E. G. Paul: J. Am. chem. Soc. 86, 2984 (1964).

[5] Herbison-Evans, D., and R. E. Richards: Mol. Physics 8, 19 (1964).

[6] Hinze, J.: Ph. D. Thesis, University of Cincinnati (1962).

[7] —, and H. H. Jaffe: J. Am. chem. Soc. 84, 540 (1962).

[8] —, M. A. Whitehead, and H. H. Jaffe: J. Am. chem. Soc. 85, 148 (1963).

[9] Hoffmann, R.: J. chem. Physics 39, 1397 (1963); 40, 2745, 2474, 2480 (1964).

[10] Holm, C. H.: J. chem. Physics 26, 707 (1957).

[11] Hruska, F., G. Kotowycz, and T. Schaefer: Canad. J. Chem. 43, 3188 (1965).

[12] Huheey, J. E.: J. physic. Chem. 69, 3284 (1965).

[13] Karplus, M., and T. P. Das: J. chem. Physics 34, 1683 (1961).

[14] —, and J. A. Pople: J. chem. Physics 38, 2803 (1963).

[15] Kato, H., K. Morokuma, T. Yonezawa, and K. Fukui: Bull. chem. Soc. Japan 38, 1749 (1965).

[16] —, T. Yonezawa, K. Morokuma, and K. Fukui: Bull. chem. Soc. Japan 37, 1710 (1964).

[17] Lamb, W. E.: Physic. Rev. 60, 817 (1941).

[18] Lauterbur, P. C.: Ann. N. Y. Acad. Sci. 70, 841 (1958).

[19] — Tetrahedron Letters 1961, 274.

[20] Lohr, L. L., and W. N. Lipscomb: Noble-gas compounds. (Editor: H. H. Hyman). Chicago: Univ. of Chicago Press 1963.

[21] Löwdin, P. O.: J. chem. Physics 18, 365 (1950).

[22] Maciel, G. E.: J. physic. Chem. 69, 1947 (1965).

[23] Meyer, L. H., and H. S. Gutowsky: J. physic. Chem. 57, 481 (1953).

[24] Moore, E. B.: Inorg. Chem. 4, 1084 (1965).

[25] — J. chem. Physics 43, 503 (1965).

[26] Morokuma, K., H. Kato, T. Yonezawa, and K. Fukui: Bull. chem. Soc. Japan 38, 1264 (1965).

[27] Mulliken, R. S.: J. chem. Physics 23, 1833, 1841 (1955).

[28] —, C. A. Rieke, D. Orloff, and H. Orloff: J. chem. Physics 17, 1248 (1949).

[29] Parr, R. G.: Quantum theory of molecular electronic structure. New York: Benjamin 1964.

[30] Pople, J. A.: Trans. Faraday Soc. 49, 1375 (1953).

[31] — Proc. Roy. Soc. A 239, 550 (1957).

[32] — J. chem. Physics 37, 53 (1962).

[33] — Mol. Physics 7, 301 (1964).

[34] —, W. G. Schneider, and H. J. Bernstein: High resolution nuclear magnetic resonance. New York: McGraw-Hill 1959.

[35] Saika, A., and C. P. Slichter: J. chem. Physics 22, 26 (1954).

[36] Saito, Y.: Canad. J. Chem. 43, 2530 (1965).

[37] Sandorfy, C.: Canad. J. Chem. 33, 1337 (1955).

[38] Skinner, H. O., and H. A. Pritchard: Trans. Faraday Soc. 49, 1254 (1953).

[39] Slater, J. C.: Physic. Rev. 36, 57 (1930).

[40] Spiesecke, H., and W. G. Schneider: Tetrahedron Letters 1961, 468.

[41] — — J. chem. Physics 35, 722 (1961).

[42] van Wazer, J. R., C. F. Callis, J. N. Shoolery, and R. C. Jones: J. Am. chem. Soc. 78, 5715 (1956).

[43] Whitehead, M. A., and N. C. Baird: (To be published).

[44] — —, and M. Kaplansky: Theoret. chim. Acta 3, 135 (1965).

[45] —, and M. Kaplansky: (To be published).

[46] Wu, T. K., and B. P. Dailey: J. chem. Physics 41, 2796 (1964).

[47] Yoshizumi, H.: Trans. Faraday Soc. 53, 125 (1957).

Prof. M. A. Whitehead
Theoretical Chemistry Laboratory McGill, University
Montréal 2, Quebec (Canada)