812. *A Simple MO–LCAO Method for the Calculation of Charge Distributions in Saturated Organic Molecules.*

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A simple method is presented by which charge distributions can be calculated for saturated molecules. It is checked by use of experimental dipole moments, and its applications and limitations are discussed.

The calculation of charge distributions based on the MO–LCAO theory is useful for the understanding of chemical problems.[1] Unfortunately, so far such calculations have been extensively applied only to the case of π-electrons. We now report an investigation on the possibility of applying this theory, in a very rough approximation, to saturated molecules, intending to calculate charges arising from inductive effects.

The proper meaning of bond charges is, in some respects, a matter of discussion, when one is interested in bonds where overlap and hybridization play an important rôle, because they appear not to be directly correlated with any observed property of molecules. Indeed, theoretical considerations induced Coulson,[2] Mulliken,[3] and others to conclude that dipole moments arise from both bond charges and other effects—core polarization, hybridization, overlap, and lone-pair dipoles. Now it has usually been assumed that the

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* In the frame of the simple MO–LCAO theory, if a localized bond is described by an MO of the form $c_\mu\psi_\mu + c_\nu\psi_\nu$, the bond charge is given (see ref. 3) by $Q_{\mu\nu} = c_\nu^2 - c_\mu^2$, and may be considered to represent the net amount of electrons either in excess or in defect on atom μ, to which an equal defect or excess on atom ν corresponds.

[1] *E.g.*, Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 31; Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 285; Orgel, *Trans. Faraday Soc.*, 1942, **38**, 433.

[2] Coulson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 63.

[3] Mulliken, *J. Chem. Phys.*, 1949, **46**, 539.

total contribution of effects other than that of bond charges to dipole moments is not negligible, but if this is so a direct comparison of calculated charges with dipole moments becomes impossible, especially as the other contributions to dipole moments cannot be exactly calculated because the use of Slater's functions—at least with effective charges corresponding to neutral, non-bonded atoms—is probably not correct [4] and because in many cases the extent to which hybridization takes place is uncertain (*e.g.*, for alkyl halides in connection with quadrupole coupling constants [5]).

In spite of this, which would make it impossible to test results by means of dipole moments, the calculation of charges would be interesting if a reliable set of parameters could be found. Even this is difficult, for many well-known reasons, especially if a simple method is to be applied, but although the situation appears hopeless, especially for polyatomic molecules, we think it worth while to try to apply some simplified calculations by using observed dipole moments both as a source of information about parameters and as a test for calculated charges. The tendency has recently grown to think of hybridization as a general phenomenon, which should be considered as the rule, from which special effects cause deviations.[6] Because of hybridization, lone-pair moments are often produced which, according to many calculations,[7, 8] are usually much larger than bond moments, whose polarity may even oppose that of the dipole moment of the whole molecule. Now, one might consider the appearance of atomic moments, if non-bonding electrons are present, as the counterpart of hybridization and overlap moments, which may be thought to correspond roughly to the polarization of, say, atom A, induced by the neighbouring atoms B, C, etc. In other words, the appearance of lone-pair moments might be interpreted as an attempt, on the part of atom A, to restore electrical symmetry around its nucleus. A similar and even more easily acceptable consideration might be applied to conclude that in atoms like carbon, hybridization and overlap moments cancel. In particular, hybridization moments depend only upon the atomic orbitals of each atom used to build the molecular eigenfunctions, and not, at least directly, upon the kinds of bond formed by the atom in question, the only dependence on the nature of the bonds being through the form one gives to the atomic orbitals. We conclude that, in atoms where four tetrahedral equivalent orbitals are used to build the molecular orbitals of four bonds, we get four equal contributions from hybridization moments, which, because of their spatial arrangement, cancel. The same will happen in general, at least approximately, if atomic orbitals slightly different from tetrahedral are assumed.

If such a view were accepted, one might be induced to think that the dipole moment of a whole molecule can be described essentially in terms of bond charges. Naturally, this would leave the general features of the MO–LCAO treatment for bond moments unchanged because, when only one bond is considered, such contributions as hybridization and overlap must be taken into account. There are some indications supporting this tentative view. First, the possibility of using some properly chosen " bond moments " additively to predict moments of saturated compounds, even if approximate, appears very strange in molecules containing lone pairs if the above suggestion does not hold at least to some extent. Secondly, Smith, Magee, Ree, and Eyring [9] applied a semi-classical model to predict inductive effects in paraffin halides in which method it was implicitly assumed that atomic charges, centred on the nuclei, could be defined from which the entire dipole moment arose. Thirdly, Mulliken [3,10] calculated the primary moment of hydrogen

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[4] See, *e.g.*, Coulson, *Trans. Faraday Soc.*, 1937, **33**, 1479.

[5] Orville-Thomas, *Quart. Rev.*, 1957, **11**, 162.

[6] *E.g.*, Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **202**, 548; Lennard-Jones and Pople, *ibid.*, p. 155.

[7] *E.g.*, Narasimha Rao, *Trans. Faraday Soc.*, 1957, **53**, 1160.

[8] Cohan and Coulson, *Trans. Faraday Soc.*, 1956, **52**, 1163.

[9] Smith, Magee, Ree, and Eyring, *J. Amer. Chem. Soc.*, 1951, **73**, 2263; 1952, **74**, 229; 1953, **75**, 5183; 1956, **78**, 3922.

[10] See also Benedict, Herman, Moore, and Silverman, *J. Chem. Phys.*, 1957, **26**, 1671.

chloride which agreed fairly well with the observed value, although if no hybridization was introduced the total moment was radically different from, and indeed opposite to, that observed. Finally, Tomiie[11] has compared *X*-ray data for diformylhydrazine with bond charges which he calculated using σ charges found from Hannay and Smith's formula,[12] which is based on the well-known relation between electronegativities and bond moments used in additive calculations. The good agreement further supports our suggestion.

A careful theoretical investigation, in some simple cases, is possible. In ammonia, treated in the usual manner,[8] there appears to be an extremely high value of the atomic dipole of nitrogen, which is not likely to be preserved in a more elaborate calculation,[13] perhaps because the effective charges of atoms in valence states should be much higher than Slater's values,[4] and the strongly directional field of electrons in hybrid orbitals should considerably modify the spatial symmetry of orbitals in favour of electrical symmetry. A rough SCF calculation carried out by evaluating the potential produced by electrons in each hybrid orbital on the other orbitals led us, in the case of tetrahedral orbitals, to conclude that the radial parts of atomic orbitals, when lone pairs are present, should be modified largely in the same way as if we chose a larger value of Z_{eff} for the lone-pair orbitals than for the bonding orbitals. A method for the study of molecules based on similar considerations was recently suggested.[14]

An attempt to see whether our suggestion is reasonable can be made either by very elaborate theoretical calculations or by less sound rough semi-empirical methods. We chose the latter way because it can provide a general procedure to determine approximate bond charges and is applicable to many molecules, so that results can be compared not only with dipole moments, but with other molecular properties.

Procedure.—The application of the simple MO–LCAO method to the calculation of bond charges implies, at least in principle, the solution of the secular equation which, for a localized bond between atoms μ and ν, is:

$$\begin{vmatrix} H_{\mu\mu} - E & H_{\mu\nu} - ES_{\mu\nu} \\ H_{\mu\nu} - ES_{\mu\nu} & H_{\nu\nu} - E \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In order to solve this equation, the values of four parameters, $H_{\mu\mu}$, $H_{\nu\nu}$, $H_{\mu\nu}$, and $S_{\mu\nu}$ are needed. Apart from $S_{\mu\nu}$, which is often neglected, and at any rate is unimportant in our connection, the nature of the simple MO–LCAO method requires that such parameters be evaluated empirically on the basis of the nature of the atoms involved in the bonds and of their surroundings. If, for each bond in a molecule, we apply eqn. (1), we must consequently vary our parameters not only according to the type of bond but also according to the structure of the rest of the molecule. Our procedure was very simple: we started from the usual positions:

$$\begin{aligned} H_{\mu\mu} &= \alpha + \delta_\mu\beta \\ H_{\nu\nu} &= \alpha + \delta_\nu\beta \\ H_{\mu\nu} &= \varepsilon_{\mu\nu}\beta \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

with α and β two basic parameters whose values need not be known. We assumed that, to a first approximation $\varepsilon_{\mu\nu}$ was independent of the surroundings, while δ_μ and δ_ν were influenced only by atoms directly bound to μ and ν respectively. Consequently, we assumed that a correct expression for, say, δ_μ should be:

$$\delta_\mu = \delta_\mu{}^\circ + \sum_{\lambda \text{ adj. to } \mu} \gamma_{\mu(\lambda)}\delta_\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\delta_\mu{}^\circ$ and $\gamma_{\mu(\lambda)}$ are two suitable empirical parameters, one depending only upon the nature of atom μ, the other upon atom μ and each adjacent atom λ. Eqn. (3) is one of

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[11] Tomiie, unpublished work.
[12] Hannay and Smith, *J. Amer. Chem. Soc.*, 1946, **68**, 171.
[13] Hamilton, *J. Chem. Phys.*, 1957, **26**, 435.
[14] Arai, *J. Chem. Phys.*, 1957, **26**, 435.

the n equations giving the δ's for the n atoms on the molecule under study. The whole set of these equations gives a linear system in the unknowns δ_μ, δ_ν, ..., which can easily be solved. In order to calculate charges, one can either proceed in the usual manner or (usually a very good approximation) use the equation [3]

$$Q_{\mu\nu} = (\delta_\nu - \delta_\mu)/2\varepsilon_{\mu\nu} \qquad . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

Provided that δ's, γ's, and ε's are known, eqn. (4) gives the bond charges, whose sum over all bonds formed by an atom gives the total apparent charge of that atom in the molecule.

For example, let us suppose that $\delta_H{}^\circ = 0{\cdot}00$, $\delta_C{}^\circ = 0{\cdot}07$, $\delta_N{}^\circ = 0{\cdot}24$; $\varepsilon_{CH} = 1{\cdot}00$, $\varepsilon_{CN} = 1{\cdot}00$, $\varepsilon_{NH} = 0{\cdot}45$; $\gamma_{H(C)} = \gamma_{H(N)} = 0{\cdot}4$; $\gamma_{C(C)} = \gamma_{C(N)} = \gamma_{N(C)} = 0{\cdot}1$; $\gamma_{C(H)} = \gamma_{N(H)} = 0{\cdot}3$; and let us calculate the charge distribution of dimethylamine, $(CH_3)_2NH$. To find the δ's we must solve the system:

$$\begin{aligned}
\delta_{H_1} &= \delta_H{}^\circ + \gamma_{H(C)}\delta_C \\
\delta_C &= \delta_C{}^\circ + 3\gamma_{C(H)}\delta_{H_1} + \gamma_{C(N)}\delta_N \\
\delta_N &= \delta_N{}^\circ + 2\gamma_{N(C)}\delta_C + \gamma_{N(H)}\delta_{H_2} \\
\delta_{H_2} &= \delta_H{}^\circ + \gamma_{H(N)}\delta_N
\end{aligned}$$

where H_1 is a hydrogen atom of the methyl group and H_2 that of the amino-group. There should really be 10 equations, but the six hydrogen atoms of the methyl groups are equivalent, as are the two carbon atoms. Substitution of the numerical values leads to:

$$\delta_{H_1} = 0{\cdot}063; \quad \delta_C = 0{\cdot}158; \quad \delta_N = 0{\cdot}309; \quad \delta_{H_2} = 0{\cdot}123$$

By use of eqn. (4) one immediately deduces that:

$$Q_{HC} = 0{\cdot}047; \quad Q_{CN} = 0{\cdot}075; \quad Q_{HN} = 0{\cdot}206$$

Correspondingly, the charges of the atoms are:

$$Q_{H_1} = 0{\cdot}047; \quad Q_C = -0{\cdot}066; \quad Q_N = -0{\cdot}356; \quad Q_{H_2} = 0{\cdot}206$$

where, for instance,

$$Q_C = -3Q_{HC} + Q_{CN}$$

From bond charges bond moments can also be deduced, by multiplying them by the experimental bond distances. A suitable choice of the bond angles very easily gives the total expected moment by vectorial addition. In our example, if all angles are taken as tetrahedral, the calculated moment is 0·9 D, while the experimental value is 1·0 D.

Before describing how parameters were chosen, and some results, we suggest one possible theoretical interpretation of our assumptions. Consider a monoelectronic bicentric LCAO–MO of the form $C_\mu\psi_\mu + C_\nu\psi_\nu$, with ψ_μ and ψ_ν appropriate atomic orbitals. Let the total Hamiltonian be of the form:

$$\mathrm{H} = \mathrm{H}_\mu - \sum_{\lambda \neq \mu} \frac{Z_\lambda}{r_\lambda} = \mathrm{H}_\nu - \sum_{\lambda \neq \nu} \frac{Z_\lambda}{r_\lambda} \qquad . \ . \ . \ . \ . \ . \ . \quad (5)$$

the Z_λ's being appropriate " effective charges " and H_μ and H_ν the Hamiltonians for atoms μ and ν. The matrix elements of H will be:

$$\left.\begin{aligned}
H_{\mu\mu} &= E_\mu - \sum_{\lambda \neq \mu} \int \frac{Z_\lambda \psi_\mu{}^2}{r_\lambda}\,\mathrm{d}v \\
H_{\nu\nu} &= E_\nu - \sum_{\lambda \neq \nu} \int \frac{Z_\lambda \psi_\nu{}^2}{r_\lambda}\,\mathrm{d}v
\end{aligned}\right\} \qquad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

$$H_{\mu\nu} = \beta_{\mu\nu} - \sum_{\lambda \neq \mu,\nu} \int \frac{Z_\lambda \psi_\mu \psi_\nu}{r_\lambda}\,\mathrm{d}v \qquad . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

with $\quad E_\mu = \int \psi_\mu \mathrm{H}_\mu \psi_\mu \mathrm{d}v,\ E_\nu = \int \psi_\nu \mathrm{H}_\nu \psi_\nu \mathrm{d}v,\ \beta_{\mu\nu} = \int \psi_\mu \left(\mathrm{H}_\mu - \frac{Z_\nu}{r_\nu}\right) \psi_\nu \mathrm{d}v$

Eqns. (6) and (7) are valid only for the monoelectronic case, and they depend strongly upon the actual form of ψ_μ and ψ_ν, and, in a second-order approximation, upon the ψ_λ's. However, we can suppose that monoelectronic orbitals are correct, provided we do not take in explicitly the forms of the atomic orbitals, do not evaluate E and β on the basis of free-atom properties, and consider the Z's as involving also the contributions to the potential energy of electrons other than the one we are considering. Now, eqns. (6) and (7) can be written as:

$$H_{\mu\mu} = \alpha + \delta_\mu{}^\circ\beta - \sum_\lambda I_{\mu(\lambda)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$H_{\mu\nu} = \beta_{\mu\nu} - \sum_\lambda I_{\mu\nu(\lambda)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

with $I_{\mu(\lambda)}$ and $I_{\mu\nu(\lambda)}$ the integrals which appear explicitly in eqns. (6) and (7). Thus, our previous assumptions are equivalent to putting (*a*) $I_{\mu(\lambda)} = -\gamma_{\mu(\lambda)}\delta_\lambda$ for μ and λ adjacent, (*b*) $I_{\mu(\lambda)} = 0$ for μ, λ not adjacent, and (*c*) $I_{\mu\nu(\lambda)} = 0$. Therefore, let us consider $I_{\mu(\lambda)}$ and $I_{\mu\nu(\lambda)}$, and assume that Z_λ does not depend upon whether atom λ forms the bond we are interested in, but only depends upon whether atom λ is adjacent to atom μ, whose coulombian integral we are considering. (This assumption amounts only to introducing an "average potential" produced by atom λ on atom μ.) Let us assume, too, that Z_λ is centred on the nucleus of atom λ. A rough approximation, obtained by considering the orbital ψ_μ as a finite sphere centred on the nucleus of atom μ, gives:

$$\int \frac{Z_\lambda\psi_\mu{}^2}{r_\lambda} \mathrm{d}v = \frac{Z_\lambda}{R_{\mu\lambda}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Similarly, the mixed integral of eqn. (7) might be approximated as:

$$\int \frac{Z_\lambda\psi_\mu\psi_\nu}{r_\lambda} \mathrm{d}v = \frac{2Z_\lambda S_{\mu\nu}}{R_{\mu\lambda} + R_{\nu\mu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In the case of eqn. (11) both Z_λ and $S_{\mu\nu}$ may be supposed to be small enough to make it possible to neglect the mixed integral $I_{\mu\nu(\lambda)}$. This corresponds to the assumption that $\delta_{\mu\nu}$ should not be much influenced by the surroundings of the bond under study. As to eqn. (10), it is far too rough to be used directly, especially if hybrid orbitals are involved. However, it shows that $I_{\mu(\lambda)}$ should depend principally upon the apparent charge of atom λ at a distance $R_{\mu\lambda}$, and upon the reciprocal of the distance itself, so that it should rapidly decrease when $R_{\mu\lambda}$ increases. This justifies approximation (*b*). As to (*a*), eqn. (10) suggests that $I_{\mu(\lambda)}$ should be apt to be split into two factors, one of which should depend only upon atom μ while the other should represent something like a "polarizability" of atom μ on the part of atom λ.

Determination of Parameters.—In order to determine parameters, an obvious procedure might be to introduce eqn. (4) into the equations giving the dipole moments of a properly chosen set of molecules. However, this would be useless because there are not enough molecules for which dipole moments corresponding to definite conformations are known to allow, after use of some of them to determine parameters, a check of the calculated charges by use of the rest. This is because in most saturated compounds the possibility of hindered internal rotation makes their dipole moments uncertain in connection with our problem. Therefore, we culled all possible sources of information for values of the parameters, a procedure which also gives a sounder foundation to our calculations.

In the determination of the values of δ° we started from electronegativities (x), with the obvious equation:

$$\delta_\mu{}^\circ = k(x_\mu - x_{\mathrm{H}})/x_{\mathrm{H}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If this equation were used as such, k would obviously be the only parameter determinable from dipole moments. However, δ, and not δ°, should be directly correlated with electronegativities, so that, especially in the case of univalent atoms to which large values of γ correspond, some minor changes, after determination of k, were found necessary. k was calculated simply by adjusting $\varepsilon_{\mathrm{CH}}$ to unity.

The next step was to chose values for γ. For these, we had only a clue from the parameters used for π-systems: Pauling and Wheland had, indeed, suggested that, for the effect of hetero-atoms on carbon, a value of 0·1 for the quantity corresponding to our γ should be used.[15] Therefore we assumed that the γ's should have that order of magnitude, and proceeded as follows. We considered the cases of CH_3Cl and $(CH_3)_3CCl$, and set down the corresponding sets of equations (5). We imposed the condition that $\delta_{Cl} - \delta_C$ in the latter should be larger than that in the former, because of the known order of inductive effects of the methyl and the *tert.*-butyl group.[16] This led us to conclude that, approximately, the two conditions to be fulfilled were:

$$\gamma_{H(C)}\gamma_{C(H)} > \gamma_{C(C)}\ ; \quad \gamma_{C(Cl)}/\gamma_{Cl(C)} \gg \delta_C{}^{\circ}/\delta_{Cl}{}^{\circ}$$

Consequently, we assumed $\gamma_{C(C)} = 0{\cdot}1$, $\gamma_{C(H)} = 0{\cdot}3$, and $\gamma_{H(C)} = 0{\cdot}4$. For $\gamma_{C(Cl)}$ and $\gamma_{Cl(C)}$ we chose respectively 0·2 and 0·4 on the basis of the probable marked interaction between chlorine and carbon, and checked those values by calculation of dipole moments of some simple molecules. Values of $\varepsilon_{\mu\nu}$, initially chosen on the basis of dissociation energies, were then modified, in a few cases very considerably, by comparison of calculated with observed moments.

In order not to use new parameters, and in spite of the fact that $I_{\mu(\lambda)}$ depends on $R_{\mu\lambda}$, which varies for different couples of atoms, we assumed that for atoms of the same rows γ should be the same, *e.g.*, $\gamma_{C(C)} = \gamma_{C(N)} = \gamma_{N(C)} = \gamma_{N(O)}$, etc.; $\gamma_{C(H)} = \gamma_{N(H)}$, etc. The molecules used for the determination of parameters were H_2O, $CH_3{\cdot}OH$, $CH_3{\cdot}Cl$, $CHCl_3$, CH_3F, NH_3, $CH_3{\cdot}NH_2$. In Table 1 the final choice of parameters is given.

TABLE 1. *Parameters used.*

Bond	C–H	C–C	C–N	C–O	C–F	N–H	O–H	C–Cl
ε_{AB}	1·00	1·00	1·00	0·95	0·85	0·45	0·45	0·65
$\gamma_{A(B)}$	0·3	0·1	0·1	0·1	0·1	0·3	0·3	0·2
$\gamma_{B(A)}$	0·4	0·1	0·1	0·1	0·1	0·4	0·4	0·4
$\delta_A{}^{\circ}$	0·07	0·07	0·07	0·07	0·07	0·24	0·40	0·07
$\delta_B{}^{\circ}$	0·00	0·07	0·24	0·40	0·57	0·00	0·00	0·35

The following must be noted; (1) The results, particularly in the case of dipole moments, are very sensitive both to the second decimal place of the γ's and ε's, and to the third decimal place of the δ°'s. However, given the roughness of our assumptions, and in view of our present purpose to elaborate and test a method, we approximated the values of the parameters to 0·1, 0·05, and 0·01 respectively. (2) There is a degree of arbitrariness in our choice of parameters. However, they are so inter-related that change of one involves change of all so that their "self-consistency" limits very strongly the arbitrariness in question. Moreover, given the fair agreement of calculated moments with experimental data, such a "self-consistency" strongly supports the reliability of our present method.

Results.—Some results for appropriate charge distributions are given in Table 2. In Tables 3, 4, and 5, some comparisons are illustrated. Table 6 gives some results about energies.

Charges. It is important that charges should agree with the variation of inductive effects deduced, from many properties of molecules, for groups such as alkyl. In general, our calculated charges do agree with the usually accepted variation of inductive effects. However, the definition of inductive effects is based not only on physical properties of molecules, but also on their chemical behaviour, so that dipole moments do not always agree with their supposed variation. In those cases also our calculated charges do not agree: *e.g.*, the increment of charge on the nitrogen atom is reproduced, even if weakly, in passing from methyl- to ethyl-amine, but that calculated for passage from methyl- to dimethyl-amine does not correspond to the variation in basicity.

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[15] Wheland and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2086.

[16] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

The latter case will be considered when we speak of energies. Except for these special cases, the well-known [16] sequence of inductive effects $CH_3^- < CH_3{\cdot}CH_2^- < (CH_3)_2CH^- < (CH_3)_3C^-$ is perfectly reproduced, and this shows that eqn. (3), which we contrived to satisfy the relation $CH_3^- < (CH_3)_3C^-$, is at least satisfactory as an interpolation formula: this is important in connection with the feature of the present method which more strictly relates to inductive effects. The fact that, in general, hydrogen does not show an inductive effect feebler than alkyl groups can be interpreted similarly to our interpretation of the anomaly of amines.

TABLE 2. *Atomic charges.*

Compound	1	2	3	4	5	6	7
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{Cl}$	+0·075	−0·058	−0·167				
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{C}\overset{4}{H}_2\overset{5}{Cl}$	+0·043	−0·089	+0·001	+0·068	−0·177		
$\overset{1}{H}\ \overset{2}{C})_2\overset{3}{C}\overset{4}{H}\overset{5}{Cl}$	+0·043	−0·093	+0·053	+0·063	−0·186		
$\overset{2}{C})_3\overset{3}{C}\overset{4}{Cl}$	+0·042	−0·097	+0·106	−0·193			
$CH_2\cdot CH_2\cdot\overset{1}{C}\overset{2}{H}_2\cdot\overset{3}{C}\overset{4}{H}_2\cdot\overset{5}{C}\overset{6}{H}\overset{7}{Cl}$	−0·071	+0·038	−0·051	+0·041	+0·037	+0·063	−0·172
$(\overset{1}{H}_3\overset{2}{C})_2\overset{3}{C}\overset{4}{Cl}_2$	+0·046	−0·077	+0·174	−0·148			
$\overset{1}{H}_2\overset{2}{C}\overset{3}{Cl}_2$	+0·105	+0·024	−0·117				
$\overset{1}{H}\overset{2}{C}\cdot\overset{3}{Cl}_3$	+0·131	+0·056	−0·063				
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{C}\overset{4}{Cl}_3$	+0·051	−0·043	+0·181	−0·097			
$\overset{1}{N}\overset{2}{H}_3$	−0·750	+0·250					
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{N}\overset{4}{H}_2$	+0·049	−0·058	−0·537	+0·225			
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{C}\overset{4}{H}_2\cdot\overset{5}{N}\overset{6}{H}_2$	+0·040	−0·110	−0·011	+0·046	−0·539	+0·224	
$(\overset{1}{H}_3\overset{2}{C})_2\overset{3}{N}\overset{4}{H}$	+0·047	−0·066	−0·356	+0·206			
$(\overset{1}{H}_3\overset{2}{C})_3\overset{3}{N}$	+0·041	−0·058	−0·198				
$\overset{1}{H}_2\overset{2}{O}$	+0·351	−0·702					
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{O}\overset{4}{H}$	+0·055	−0·011	−0·472	+0·318			
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{C}\overset{4}{H}_2\cdot\overset{5}{O}\overset{6}{H}$	+0·041	−0·105	+0·039	+0·052	−0·476	+0·317	
$(\overset{1}{H}_3\overset{2}{C})_3\overset{3}{C}\cdot\overset{4}{O}\overset{5}{H}$	+0·040	−0·109	+0·131	−0·480	+0·314		
$(\overset{1}{H}_3\overset{2}{C})_2\overset{3}{O}$	+0·053	−0·023	−0·272				
$(\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{C}\overset{4}{H}_2)_2\overset{5}{O}$	+0·040	−0·105	+0·024	+0·050	−0·280		
$CH_2\cdot CH_2\cdot\overset{1}{C}\overset{2}{H}_2\cdot\overset{3}{C}\overset{4}{H}_2\cdot\overset{5}{O}$	−0·060	+0·039	+0·023	+0·050	−0·282		
$O\cdot CH_2\cdot\overset{1}{C}\overset{2}{H}_2\cdot\overset{3}{O}\cdot\overset{4}{C}\overset{5}{H}\cdot\overset{6}{C}\overset{7}{H}_3$	+0·120	+0·051	−0·413	+0·263	+0·070	−0·071	+0·040
$\overset{1}{H}_3\overset{2}{C}\cdot\overset{3}{F}$	+0·060	+0·049	−0·229				
$\overset{1}{H}_2\overset{2}{C}\overset{3}{F}_2$	+0·075	+0·256	−0·203				
$\overset{1}{H}\overset{2}{C}\overset{3}{F}_3$	+0·085	+0·470	−0·185				

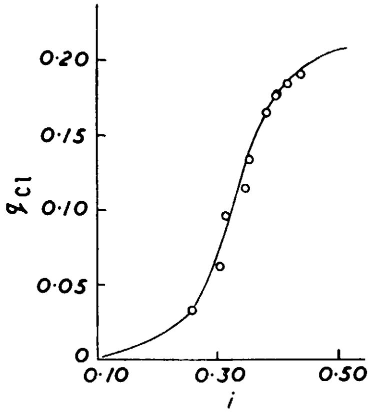
Quadrupole coupling constants. A comparison of calculated charges with quadrupole coupling constants would be valuable. Unfortunately, only a few substances were studied;

most of them were studied in the solid state; and the meaning [5] of eQq^{mol} is still uncertain. However, a qualitative comparison can be made for alkyl halides (Table 3 and Figure). No meaning should be inferred from the shape of the curve, as the values relate [17] to solids where molecules interact in a way dependent on their shape and packing, but charges and quadrupole coupling constants do appear to be correlated.

TABLE 3. *Comparison of calculated charges* (q) *with the function* $i = 1 - (eQq^{\mathrm{mol}}/2eQq^{\mathrm{atom}})$ *for* ^{35}Cl.

Compound.	q	i	Compound	q	i	Compound	q	i
CCl_4	0·034	0·256	$CH_3{\cdot}CHCl_2$	0·135	0·350	$CH_3{\cdot}CH_2{\cdot}CH_2Cl$	0·178	0·395
$CHCl_3$	0·063	0·300	$(CH_3)_2CCl_2$	0·148	—	$(CH_3)_2CHCl$	0·186	0·414
$CH_3{\cdot}CCl_3$	0·097	0·307	CH_3Cl	0·167	0·378	$(CH_3)_3CCl$	0·193	0·434
CH_2Cl_2	0·117	0·341	$CH_3{\cdot}CH_2Cl$	0·177	0·400			

Values are from Gordy, Smith, and Trambarulo, ref. 17.



Dipole moments. Our aim was to test charges by comparison with observed electric dipole moments. In Table 4 we list molecules for which we calculated dipole moments, and it must be noted that: (1) Starred (*) molecules were used for the determination of parameters; we did not try to make their calculated and observed dipole moments coincide perfectly because of the approximations used to obtain values for the parameters. (2) The dipole moments are given only to the first decimal place, because that is the limit of reliability of the approximation. (3) For high-molecular weight compounds, which cannot be vaporized, results may be influenced by association in solvents and by the neglect or arbitrary introduction of atomic polarizations—the large difference for *tert.*-butylamine is probably due to measurements' being made on solutions: ethylamine behaves similarly in that its dipole moment from gas measurements is 0·9 D, from solutions 1·3 D.

TABLE 4. *Observed* (*a*) *and calculated* (*b*) *dipole moments.*

	(a)	(b)		(a)	(b)		(a)	(b)
*NH_3	1·5	1·3	*H_2O	1·8	1·9	*$CH_3{\cdot}Cl$	1·9	1·8
*$CH_3{\cdot}NH_2$	1·3	1·3	*$CH_3{\cdot}OH$	1·7	1·7	CH_2Cl_2	1·6	1·7
$CH_3{\cdot}CH_2{\cdot}NH_2$	0·99	0·85—1·34	$CH_3{\cdot}CH_2{\cdot}OH$	1·7	1·7	*$CHCl_3$	1·0	1·2
			$(CH_3)_3C{\cdot}OH$	1·7	1·7	$(CH_3)_3CCl$	2·1	2·1
$(CH_3)_2NH$	1·0	0·9	$(CH_3)_2O$	1·3	1·4	$CH_3{\cdot}CCl_3$	1·8	1·9
$(CH_3)_3N$	0·6	0·6	$CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$	1·7	1·6	$CH_2{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}CH_2$	2·1	1·8
$(CH_3)_3C{\cdot}NH_2$	1·4	0·9	$CH_2{\cdot}O{\cdot}CH(CH_3){\cdot}O{\cdot}CH_2$	1·2	0·8	*CHF_3	1·6	1·6
						CH_2F_2	1·9	2·0

Values are from Landolt–Börnstein " Tabellen," Berlin, 1950, and Gordy, *et al.*, ref. 17.

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[17] Gordy, Smith, and Trambarulo, " Microwave Spectroscopy," Wiley, New York, 1953.

However, the overall agreement is fair, especially in view of the sensitivity of dipole moments to parameters. It is encouraging that the method still works, even if approximately, for compounds more complex than simple alcohols (*e.g.*, tetrahydrofuran and 2-methyldioxolan, for which the calculations were made by assuming a regular pentagonal ring and tetrahedral angles for carbon orbitals external to it).

Bond moments. According to our calculations, bond moments are often very variable because we tried to take inductive effects into account. However, the mean values of bond moments appear not to be very different from additive bond moment values, as shown in Table 5. This may be thought to represent the connecting link between usual additive calculations of dipole moments and ours.

TABLE 5. *Bond moments.*

(*a*)	(*b*)	(*a*)	(*b*)
μ(CH) from 0·20 to 0·28 D	0·3 D	μ(CO) from 0·93 to 1·14 D	0·86 D
μ(CN) from 0·47 to 0·62 D	0·45 D *	μ(OH) from 1·44 to 1·60 D	1·53 D
μ(NH) from 1·21 to 1·08 D	1·31 D	μ(CCl) from 0·83 to 1·65 D	1·56 D

(*a*) From our calculations. (*b*) Bond moments for vectorial addition, as given by Sutton in Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, except the starred value, taken from Pullman and Pullman, " Les Théories électroniques de la Chimie Organique," Masson et Cie, Paris, 1952.

Energies. In such simplified calculations, we cannot expect to be able to calculate energies. However, some considerations are possible, which are important in that they allow a clearer insight into the meaning of bond charges as calculated by us. Formally, energies are given by

$$E_{\mu\nu} = 2\alpha + [\delta_\mu + \delta_\nu + \varepsilon_{\mu\nu}\sqrt{(1 + Q_{\mu\nu}^2)}]\beta = E_{\text{rep}} \quad . \quad . \quad . \quad (13)$$

where we neglected overlap because, in comparisons, it is not very important. E_{rep} represents the repulsion energy between the cores of atoms, which was not included in our Hamiltonian.

To show the use of eqn. (6), we consider, as an example, amines and their conjugated acids. We chose this because the basicities of amines do not agree with the order in which our charges decrease: indeed, it has been assumed that the electron-repelling nature of the CH_3^- group increases the charge of nitrogen in amines from ammonia through to trimethylamine, and this has been given as an explanation of the basicities, with an exception for trimethylamine itself, which is much less basic than expected.[18] However, a different explanation is as follows. Consider the reaction $NH_3 + H^+ \rightleftharpoons NR_3H^+$, and let us try to calculate the energy variation ΔE for it from eqn. (13). Let us assume that the γ's are the same for bonds formed by N^+ as for bonds formed by N; that $\delta_{N^+}{}^\circ = 0{\cdot}31$ because of the increase in electronegativity in passing from N to N^+, and that $\varepsilon_{N^+X} = 1{\cdot}33\varepsilon_{NX}$ because ε_{NH} is much smaller than ε_{CH}, to whose value ε_{N^+H} should presumably approach. Such a choice is largely arbitrary but is useful to show that there is at least one set of parameters which leads to an inversion of the order of ΔE's with respect to charges of nitrogen for mono-, di-, and tri-methylamine. We thus get Table 6 in which, though repulsion energies are not included, the variations of basicities are correctly

TABLE 6. *Dissociation constants of amines.*

$E = E(NR_3H^+) - E(NR_3) - E(H^+) - \Delta E_{\text{rep}}$ [a].

Amine	$\Delta E/\beta$	$pK_b^{25°}$ [b]
NH_3	3·38	4·75
$CH_3{\cdot}NH_2$	3·52	3·37
$(CH_3)_2NH$	3·72	3·22
$(CH_3)_3N$	4·11	4·20

[a] ΔE_{rep} represents the difference between the core repulsion energies of NR_3H^+ and NR_3. [b] From L. F. Fieser and M. Fieser, " Organic Chemistry, " Reinhold, New York, 1957.

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[18] Brown, Bartolomey, and Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435.

reproduced, except for that of trimethylamine, whose behaviour remains mysterious although its experimental pK_b might correspond to a particularly high repulsion energy.

The preceding calculation is only meant to present an example relating to the possibility of comparing calculated charges with what is usually called " inductive effects," especially when reactivity is concerned.

Discussion.—This work was not intended to provide a final choice of parameters or the best method (even among uncomplicated, quick ones) for the calculation of molecular properties. Some possibly useful aspects and properties were overlooked because we wished only to see whether a simple MO–LCAO method was usable in connection with saturated systems, especially with respect to dipole moments as a check, these, apart from bond lengths and angles, being the only reliable and extensive data upon which to base such a calculation. The charges obtained have the properties required of real charges, and have some right to be considered as such: they give correct dipole moments, correspond to inductive effects, are clearly correlated with quadrupole coupling constants, and the parameters used to calculate them are probably useful to calculate energies, provided one considers only a set of very similar molecules. Therefore whatever the real meaning of the charges calculated, we may reasonably expect that they are somehow connected with other molecular properties. If so, they may be used to compare molecules, and perhaps find for molecular properties interpretations hitherto overlooked because of the lack of a general method for treating saturated systems.

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