A Semi-empirical MO Theory of σ Electron Systems.* II. Bond Polarity and Electronegativity

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In a previous paper,[1] we outlined a first and second order semi-empirical MO theory for σ electron systems. In the first order theory each σ bond is represented by a bonding orbital, and the wave function of a saturated molecule is obtained as an anti-symmetrized product of doubly-occupied bonding or lone-pair orbitals. We then discussed the polarity of the bond orbitals by introducing the bond polarity parameters, Q_p. It was shown that the bond polarity parameter is determined not only by the electronegativity difference but also by the inductive effect. This enables us to make theoretical predictions of experimental properties on the basis of bond polarity parameters. Many experimental quantities, such as dipole moments, nuclear quadrupole coupling constants,[2,3] and fluorine chemical shifts,[4,5] may be approximately calculated from the bond polarity parameters. In this paper we wish to apply our previous first order theory to a calculation of these properties for several organic molecules.

It has been shown that our definition of electronegativity includes the Moffitt[6] or Mulliken[7] scales as special cases. In addition, several other methods[3,8-11] have been proposed for obtaining the electronegativity constants from either experimental or theoretical atomic quantities. However the important question, why such a crude model based on atomic electronegativity constants can so successfully describe bond properties, has never been properly investigated theoretically. In this paper, we will attempt to answer this question by means of our first order theory. In connection with this problem, we will also investigate how the electronegativity scale of Pauling,[8] which was obtained empirically, fits into our theory.

I. The Electronegativity Scale and the Ionic Character of Bonds. — In this section we wish to discuss the connection between the various electronegativity scales and the ionic character of the bonds. We will take Eq. 39 of reference 1, $Q_p = Q_p^\circ + Q_p'$, as a starting point for this discussion. The Q_p° and Q_p' are the specific and induced bond polarities respectively

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[1] Part I of this series, This Bulletin, 37, 1574 (1964).

[2] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

[3] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley & Sons, Inc., N. Y. (1953).

[4] A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

[5] For the hydrogen chemical shifts, this is not true often; the contribution of the excited states are then important.

[6] W. Moffitt, *Proc. Roy. Soc.*, **A202**, 548 (1950).

[7] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

[8] L. Pauling, "The Nature of Chemical Bond," Cornell Univ. Press, N. Y. (1945).

[9] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

[10] J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **28**, 335 (1958).

[11] K. Oohata, *Prog. Theor. Phys. Japan*, **25**, 215 (1961).

defined by Eqs. 40 and 41 of Ref 1. If we considered the bond polarities on the basis only of the atomic electronegativity differences, we could construct a crude model in which bond polarity is regarded as specific for the bond, independent of the surroundings. Fortunately, the contribution of the induced polarity, Q'_{p}, based on the inductive effect to total bond polarity, Q_{p}, will not change our conclusions significantly.[12] It has already been recognized empirically that such a seemingly crude approximation may lead to useful conclusions. Therefore, only each specific bond is discussed here; the inclusion of the inductive effect will be presented in the following section. In addition, since we will consider atomic electronegativities only, we may neglect the homopolar inductive effect,[1] which is generally small. We thus obtain the following simple relation:

$$Q_{\mathrm{p}} = K_{\mathrm{p}}(\chi^{\circ}_{\mathrm{B,p}} - \chi^{\circ}_{\mathrm{A,p}}) \tag{1}$$

where $\chi^{\circ}_{\mathrm{B,p}}$ and $\chi^{\circ}_{\mathrm{A,p}}$ are defined as the Moffitt scale[6] of the electronegativity of atoms B and A respectively.

Let us now consider the bond polarity on the basis of of the atomic properties. Moffitt[6,13,14] has shown that this is roughly equivalent with the situation where the two atoms, A and B, are an infinite distance apart, but still in the same valence states as they would be at their equilibrium distance. If we adopt the approximation[15], $-\varepsilon^{\circ}_{\mathrm{A,pA,p}} \sim I_{\mathrm{A,p}}$, $J^{\circ}_{\mathrm{A,pA,p}} \sim I_{\mathrm{A,p}} - E_{\mathrm{A,p}}$, etc., where the I and E are the corresponding ionization potential and electron affinity respectively, the Moffitt scale[6] of the electronegativity may then be reduced to the Mulliken scale[7] and the Q_{p} at the infinite distance may be written as:

$$Q^{\infty}_{\mathrm{p}} = K^{\infty}_{\mathrm{p}}(\chi^{\circ}_{\mathrm{B,p}} - \chi^{\circ}_{\mathrm{A,p}}) = K^{\infty}_{\mathrm{p}}[1/2(I_{\mathrm{B,p}} + E_{\mathrm{B,p}}) - 1/2(I_{\mathrm{A,p}} + E_{\mathrm{A,p}})] \tag{2}$$

where

$$K^{\infty}_{\mathrm{p}} = 2[(I_{\mathrm{B,p}} - E_{\mathrm{A,p}}) + (I_{\mathrm{A,p}} - E_{\mathrm{B,p}})]^{-1} \tag{3}$$

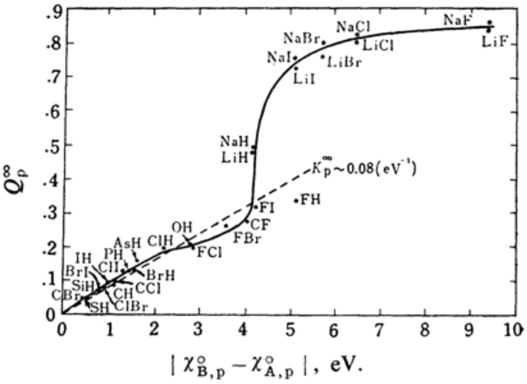

Fig. 1. Relalion between Q^{∞}_{p} and $|\chi^{\circ}_{\mathrm{B,p}} - \chi^{\circ}_{\mathrm{A,p}}|$.

Table I. Values of bond parameters

Bond[a]	$\lvert\chi^{\circ}_{\mathrm{B,p}} - \chi^{\circ}_{\mathrm{A,p}}\rvert$, eV.	K^{∞}_{p}, eV^{-1}	Q^{∞}_{p}
Li(s)-H(s)	4.21	0.113	0.48
Na(s)-H(s)	4.23	0.116	0.49
C(sp^3)-H(s)	1.13	0.084	0.09
Si(sp^3)-H(s)	0.51	0.100	0.05
O(p)-H(s)	2.82	0.073	0.21
F(p)-H(s)	5.15	0.066	0.34
Cl(p)-H(s)	2.28	0.083	0.19
Br(p)-H(s)	1.53	0.087	0.13
I(p)-H(s)	0.91	0.091	0.08
S(p)-H(s)	0.43	0.088	0.04
P(p)-H(s)	1.45	0.092	0.13
As(p)-H(s)	1.67	0.095	0.16
C(sp^3)-F(p)	4.02	0.071	0.28
C(sp^3)-Cl(p)	1.15	0.090	0.10
C(sp^3)-Br(p)	0.40	0.095	0.04
F(p)-Cl(p)	2.87	0.070	0.20
F(p)-Br(p)	3.62	0.073	0.26
F(p)-I(p)	4.24	0.076	0.32
Cl(p)-Br(p)	0.75	0.094	0.07
Cl(p)-I(p)	1.37	0.098	0.13
Br(p)-I(p)	0.62	0.105	0.06
Li(s)-F(p)	9.36	0.090	0.84
Na(s)-F(p)	9.38	0.092	0.86
Li(s)-Cl(p)	6.49	0.124	0.81
Na(s)-Cl(p)	6.51	0.128	0.83
Li(s)-Br(p)	5.74	0.134	0.77
Na(s)-Br(p)	5.76	0.139	0.80
Li(s)-I(p)	5.12	0.144	0.74
Na(s)-I(p)	5.14	0.149	0.76

a) The parentheses indicate the corresponding valence state.

The Q^{∞}_{p} and K^{∞}_{p} refer to infinite internuclear separation. The values of Q^{∞}_{p}, K^{∞}_{p} and $|\chi^{\circ}_{\mathrm{B,p}} - \chi^{\circ}_{\mathrm{A,p}}|$ for various bonds are tabulated in Table I, and the relation between Q^{∞}_{p} and $|\chi^{\circ}_{\mathrm{B,p}} - \chi^{\circ}_{\mathrm{A,p}}|$ is illustrated in Fig. 1. The values of I and E used are taken from the tables of Pritchard and Skinner.[9] Equation 2 is similar to the definition of ionicity proposed by Wilmshurst[16] or by Hinze et al.[17] The curve in Fig. 1 is similar to the results obtained by

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[12] In fact the values of Π_{pq} are much smaller than unity as will be shown in the following section.

[13] W. Moffitt, *Proc. Roy. Soc.*, **A202**, 534 (1950); **A210**, 245 (1951).

[14] W. Moffitt, *Reports Prog. Phys.*, **17**, 173 (1954).

[15] See Ref. 1 also.

[16] J. K. Wilmshurst, *J. Chem. Phys.*, **30**, 561 (1959).

[17] J. Hinze, M. A. Whitehead and H. H. Jaffe, *J. Am. Chem. Soc.*, **85**, 148 (1963).

Pauling[8] or by Dailey and Townes[18] except for the FH bond.

It may be seen from Table I and Fig. 1 that, for $|\chi^{\circ}_{B,p}-\chi^{\circ}_{A,p}|<4$ eV. or for $Q^{\infty}_{p}<0.3$, the K^{∞}_{p} are nearly constant. In this range, therefore, the Q^{∞}_{p} may be regarded as proportional to the electronegativity differences. The dotted line in Fig. 1 ($K^{\infty}_{p}\sim 0.08\,\mathrm{eV}^{-1}$) seems to confirm this inference. We may say, therefore, that for all covalent bonds $K_p\sim 0.08\,\mathrm{eV}^{-1}$. The fact that the point for the FH bond in Fig. 1 lies very closely to the dotted line seems to indicate that this bond is also essentially covalent. On the other hand, the bonds involving the alkali metals have to be regarded as strongly polar bonds. It follows from Table I that these great polarities are due not only to the large electronegativity difference but also to the large values of K_p which result from the small values of the ionization potentials and the electron affinities of the alkali metals. In general, however, the K_p seem to be insensitive to electronegativity differences. The reasons for this will now be discussed.

At first sight, it appears from Eq. 3 that the values of K_p depend on electronegativity differences. The K_p values, however, depend on the average sum of the energies of the ion pairs A^-B^+ and A^+B^-, and the electronegativity differences, on the difference between them. An inspection of the periodic table will reveal that most polar bonds are formed between metallic elements which have small electronegativities and non-metallic elements which have large electronegativities. Consequently, the average value of the energies of the ion pairs A^-B^+ and A^+B^- is practically independent of the variations in electronegativity between the different metallic elements or between the non-metallic elements. We believe that the general validity and usefulness of the concept of electronegativity may be explained by the above considerations, and also by the fact that the homopolar inductive effect is usually small,[1] so that the differences in electronegativity depend on atomic quantities only.

We will now proceed to discuss the relation between our electronegativity scale and Pauling's scale.[8] Pauling's electronegativity scale has been defined as:

$$|X_B-X_A|=\sqrt{\Delta} \qquad (4)$$

where Δ is the "*ionic-covalent resonance energy*" in terms of eV. On the other hand, anticipating some results of the following paper,[19] we plan to show that, for bonds with small polarities, the ionic-covalent resonance energy, Δ_p, in our theory is given by:

$$\Delta_p=1/2K_p|\chi^{\circ}_{B,p}-\chi^{\circ}_{A,p}|^2 \qquad (5)$$

If the two quantities, Δ and Δ_p, are equivalent, we obtain:

$$|X_B-X_A|=(1/2K_p)^{1/2}|\chi^{\circ}_{B,p}-\chi^{\circ}_{A,p}| \qquad (6)$$

This leads to the following relation:

$$X_P=(1/2K_p)^{1/2}\chi^{\circ}_{M} \qquad (7)$$

where X_P and χ°_{M} stand for Pauling[8] and Mulliken[7] scales of electronegativity in terms of eV. We then have

$$X_P/\chi^{\circ}_{M}=(1/2K_p)^{-1/2}\sim 0.22(\mathrm{eV}^{-1/2}) \qquad (8)$$

where the value $K_p\sim 0.08\,\mathrm{eV}^{-1}$ has been substituted. This value is empirically known to be 0.32 or 0.36 ($\mathrm{eV}^{-1/2}$).[9] The discrepancy between these values may partially be due to our definitions and approximations, especially to the crude evaluation of K_p. This difficulty has been discussed by Mulliken.[20] We will also try to explain it.

Differences in electronegativity are important, not the values themselves; we may thus add an arbitrary constant value to all electronegativities. Pauling's scale[21] has been arbitrarily determined by adjusting it to Eq. 4 under the arithmetic mean assumption, which may often be replaced by the geometrical mean.[22,23] On the other hand, the Mulliken scale may be regarded as an absolute scale of electronegativity. Consequently, the Pauling scale may not be adequately given by Eq. 7. The ionic-covalent resonance energy, Δ_p, in our theory may be defined adequately only for small bond polarities.[19] Therefore, it is not surprising that the value evaluated from Eq. 8 does not agree with the empirical value.

II. Some Applications of the Inductive Effect.—We will now proceed to discuss the case of polyatomic molecules by starting from the complete first order theory. Since this includes a consideration of the inductive effect, we may call it "*an application of the inductive effect.*" In this section, we wish to apply the inductive effect to two types of molecules, namely, MX_n and *n*-alkyl halide molecules (n-$C_mH_{2m+1}X$). We will take Eq. 47 of Ref. 1 as the basic equation for the discussion of this section:

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[18] B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

[19] Part III of this series, This Bulletin, **37**, 1592 (1964).

[20] R. S. Mulliken, ibid., 3, 573 (1935).

[21] Pauling arbitrarily adopted $X_H=2.1$ and $X_F=4.0$.

[22] T. L. Cottrell and L. E. Sutton, *Proc. Roy. Soc.*, **A207**, 49 (1951).

[23] A. C. Hurley, ibid., **A218**, 333 (1953).

$$\overline{Q}_{\mathrm{p}}=\sum_{\mathrm{q}}\overline{\Pi}_{\mathrm{pq}}Q_{\mathrm{p}}^{\circ} \qquad (9)$$

where $\overline{Q}_{\mathrm{p}}$ is the SCF bond polarity of the bond p and the $\overline{\Pi}_{\mathrm{pq}}$ values are the SCF polarizabilities which are defined by Eq. 46 of Ref. 1.

A) MX_n-type Molecules.—Let us consider a molecule with *n* equivalent bonds MX. From Eq. 9, we obtain for the bond MX;

$$\overline{Q}_{\mathrm{MX}}=Q_{\mathrm{MX}}^{\circ}/[1-(n-1)\Pi_{(\mathrm{MX,p})(\mathrm{MX,q})}] \qquad (10)$$
$$(\mathrm{p}\neq\mathrm{q})$$

Since $\Pi_{(\mathrm{MX,p})(\mathrm{MX,q})}$ is taken as negative here, it may be concluded that the bond polarities of the MX bonds in the MX_n-type molecules generally decrease with an increase in the number of MX bonds. We are led to believe, therefore, that the small CH bond polarity of methane is due not only to the original small polarity of the CH bond itself, but also to the inductive effect. This conclusion may also be extended to the CH_3 and CH_2 radicals of saturated hydrocarbons. Consequently, it follows that the CH bonds in saturated hydrocarbons may be almost homopolar, which is in agreement with the general opinion and all available experimental information. Another example we wish to consider is the series of the halomethanes, CH_3X, CH_2X_2, CHX_3 and CX_4 (X= halogen). It has been empirically shown that, in the above order, the dipole moments decrease, the magnitudes of halogen nuclear quadrupole coupling constants $|eQq_X|$ increase (as Table II shows), and the fluorine chemical shifts, δ_F,[24] increase as −21.00, −8.09, −1.82 and 0. By making use of the above conclusion together with the gradual decreasing *s* characters of the halogen bonding orbitals in the above order, which will be shown in the next subsection, apart from the induced polarity of the CH bonds,[25,26] the dipole moments may be explained by the decreasing CX bond moments,[27] and the eQq_X and δ_F values, by means of the Townes-Dailey[2] and Saika-Slichter[4,28] formulas respectively. These formulas are shown in Appendices A and B respectively.

TABLE II. MOLECULAR DIPOLE MOMENTS μ AND HALOGEN NUCLEAR QUADRUPOLE COUPLING CONSTANTS $|eQq_X|$ OF HALOMETHANES

Molecule	μ, D[a]	$\|eQq_X\|$, Mc.[a,b]
CH_3Cl	1.87[c,d]	68.4
CH_2Cl_2	1.62[c]	72.47
$CHCl_3$	1.06[c]	76.98
CCl_4	—	81.85
CH_3Br	1.80[d]	529
CH_2Br_2	1.43[e]	563
$CHBr_3$	1.3;[f] 0.99[g]	601
CH_3I	1.65[d]	1766
CH_2I_2	(1.10)[h]	1897
CHI_3	(0.99)[h]	2047
CI_4	—	2130

a) The values of μ are for the gaseous phase except for the values between parentheses. The values of $|eQq_X|$ are for the solid state.
b) H. Robinson, H. G. Dehmelt and W. Gordy, *J. Chem. Phys.*, **22**, 511 (1954).
c) G. A. Barlay and R. J. W. LeFevre, *J. Chem. Soc.*, **1950**, 556.
d) Ref. 3.
e) H. A. Stuart, "Die Struktur des Freien Moleküls," Springer (1952), p. 290.
f) *Trans. Faraday Soc.*, **30**, Appendix (1934).
g) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Intersci. Publ., New York (1950).
h) A. E. van Arkel and J. L. Snoek. *Rec. trav. chim.*, **52**, 719 (1933).

The chlorine nuclear quadrupole coupling constants of some chloro-compounds which are listed in Table III may also be interpreted on this basis. The present conclusion agrees with previous findings.[29,30]

TABLE III. CHLORINE NUCLEAR QUADRUPOLE COUPLING CONSTANTS OF SOME CHLORO-COMPOUNDS

Molecule	$\|eQq_{Cl}\|$, Mc.[a]	
$CCl_3\cdot CHCl_2$	79.9	($-CCl_3$)
	77.7	($-CHCl_2$)
$CH_2Cl\cdot COOH$	73.15	
$CHCl_2\cdot COOH$	76.79	
$CCl_3\cdot COOH$	80.25	

a) Ref. 3

B) n-Alkyl Halide Molecules. — The *n*-alkyl halide molecules (n-$C_mH_{2m+1}X$) may be re-

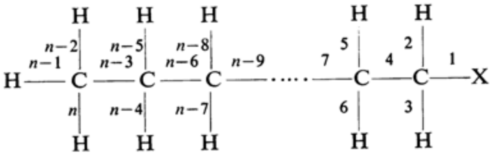

Fig. 2. Numbers of each bond in the $C_mH_{2m+1}X$ molecules.

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24) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953). The reported values have been multiplied by 10^5.

25) S. Maeda, This Bulletin, **31**, 260 (1958).

26) The experimental data cannot be explained by considering the induced polarity of the CH bonds only. Fortunately, however, this effect seems to be small from a theoretical viewpoint also.[25]

27) The bond moment here includes the lone pair moments of the corresponding atoms. See Ref. 19 also.

28) This argument is based on the assumption that the excitation energies ΔE, as will be given in Eq. B-2, would be of the same order of the magnitudes in this series. The validity of this is not obvious, but it would not be too bad an approximation.[4]

29) E. Warhurst, *Trans. Faraday Soc.*, **45**, 461 (1949).

30) H. Hamano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 746 (1956); **79**, 362 (1958).

garded as typical examples of the inductive effect. The numbers of each bond are defined as shown in Fig. 2: For the CX and CH bonds, the AO of the carbon atoms are taken as valence AO A_{CX} and A_{CH}, and those of the halogen and hydrogen atoms, as valence AO B_{CX} and B_{CH} respectively; for the CC bonds, the AO of the carbon atoms closer to the CX bond are taken as A_{CC}. For the sake of simplicity, the following assumptions are made:

1) It is assumed that $Q_2^\circ = Q_3^\circ = Q_4^\circ = \ldots\ldots = Q_n^\circ = 0$, which means that we take all bonds originally homopolar except for the CX bond.

2) Only the values of Π_{pq} between adjacent bonds are considered; the others are taken to be zero.

From Eq. 9 we then obtain:

$$ {}^m\overline{Q}_j = {}^m\overline{\Pi}_{j1} Q_1^\circ, \quad (j = 1, 2, 3, \ldots\ldots, n) \tag{11} $$

where the superscript m indicates the number of carbon atoms in each molecule, and ${}^m\overline{\Pi}_{j1}$ is given by:

$$ {}^m\overline{\Pi}_{j1} = (-1)^{j+1}\, {}^m\Delta_n^{j1} / {}^m\Delta_n \tag{12} $$

where ${}^m\Delta_n$ is the determinant of n rows and columns given by:

$$ {}^m\Delta_n = \left|\begin{array}{cccccccccccccccccccc}
1 & \Pi_{\mathrm{XH}} & \Pi_{\mathrm{XH}} & \Pi_{\mathrm{XC}} &&&&&&&&&&&&&&&& \\
\Pi_{\mathrm{HX}} & 1 & \Pi_{\mathrm{HH}} & \Pi_{\mathrm{HC}} &&&&&&&&&&&&&&&& \\
\Pi_{\mathrm{HX}} & \Pi_{\mathrm{HH}} & 1 & \Pi_{\mathrm{HC}} &&&&&&&&&&&&&&&& \\
\Pi_{\mathrm{CX}} & \Pi_{\mathrm{CH}} & \Pi_{\mathrm{CH}} & 1 & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CC}} &&&&&&&&&&&&& \\
&&& -\Pi_{\mathrm{HC}} & 1 & \Pi_{\mathrm{HH}} & \Pi_{\mathrm{HC}} &&&&&&&&&& 0 &&& \\
&&& -\Pi_{\mathrm{HC}} & \Pi_{\mathrm{HH}} & 1 & \Pi_{\mathrm{HC}} &&&&&&&&&&&&& \\
&&& -\Pi_{\mathrm{CC}} & \Pi_{\mathrm{CH}} & \Pi_{\mathrm{CH}} & 1 & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CC}} &&&&&&&&&& \\
&&&&&& -\Pi_{\mathrm{HC}} & 1 & \Pi_{\mathrm{HH}} & \Pi_{\mathrm{HC}} &&&&&&&&&& \\
&&&&&& -\Pi_{\mathrm{HC}} & \Pi_{\mathrm{HH}} & 1 & \Pi_{\mathrm{HC}} &&&&&&&&&& \\
&&&&&& -\Pi_{\mathrm{CC}} & \Pi_{\mathrm{CH}} & \Pi_{\mathrm{CH}} & 1 & -\Pi_{\mathrm{CH}} &&&&&&&&& \\
&&&&&&&&& -\Pi_{\mathrm{HC}} &&&&&&&&&& \\
&&&&&&&&&&& \ddots &&&&&&&& \\
&&&&& m-1 &&&&&&&& \Pi_{\mathrm{HC}} &&&&&& \\
&&&&&&&&&&&& \Pi_{\mathrm{CH}} & 1 & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CC}} &&& \\
&&&&&&&&&&&&& -\Pi_{\mathrm{HC}} & 1 & \Pi_{\mathrm{HH}} & \Pi_{\mathrm{HC}} &&& \\
&&&&&&&&&&&&& -\Pi_{\mathrm{HC}} & \Pi_{\mathrm{HH}} & 1 & \Pi_{\mathrm{HC}} &&& \\
&& 0 &&&&&&&&&&& -\Pi_{\mathrm{CC}} & \Pi_{\mathrm{CH}} & \Pi_{\mathrm{CH}} & 1 & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CH}} & -\Pi_{\mathrm{CH}} \\
&&&&&&&&&&&&&&&& -\Pi_{\mathrm{HC}} & 1 & \Pi_{\mathrm{HH}} & \Pi_{\mathrm{HH}} \\
&&&&&&&&&&&&&&&& -\Pi_{\mathrm{HC}} & \Pi_{\mathrm{HH}} & 1 & \Pi_{\mathrm{HH}} \\
&&&&&&&&&&&&&&&& -\Pi_{\mathrm{HC}} & \Pi_{\mathrm{HH}} & \Pi_{\mathrm{HH}} & 1
\end{array}\right| \tag{13} $$

Here for each Π we take its absolute value. The subscripts X, H and C refer to the CX, CH and CC bonds respectively. Since the inductive effect is only important for the CH and CC bonds adjacent to the CX bond, only the ${}^m\overline{Q}_2 = {}^m\overline{Q}_3$ and ${}^m\overline{Q}_4$ will be considered. The inductive effect between the CX bond and the non-adjacent CC and CH bonds may be treated in a similar fashion, but it will not be explicitly considered here. The ${}^m\overline{\Pi}_{11}$, ${}^m\overline{\Pi}_{21} = {}^m\overline{\Pi}_{31}$ and ${}^m\overline{\Pi}_{41}$ (except for CH_3X when $m=1$) may be written explicitly as:

$$ {}^m\overline{\Pi}_{11}(c\rho_{m-1}+d)/(e\rho_{m-1}+f), \quad (m \geqq 2) \tag{14} $$

$$ {}^m\overline{\Pi}_{21} = {}^m\overline{\Pi}_{31} = (-\Pi_{\mathrm{HX}}\rho_{m-1} + \Pi_{\mathrm{HC}}\Pi_{\mathrm{CX}}) / (e\rho_{m-1}+f), \quad (m \geqq 2) \tag{15} $$

$$ {}^m\overline{\Pi}_{41} = [2\Pi_{\mathrm{HX}}\Pi_{\mathrm{CH}} - \Pi_{\mathrm{CX}}(1+\Pi_{\mathrm{HH}})] / (e\rho_{m-1}+f), \quad (m \geqq 2) \tag{16} $$

where

$$ \rho_m = {}^m\tilde{\Delta}_n^{11} / {}^m\Delta_n^{11} = (a\rho_{m-1}+b)/(c\rho_{m-1}+d), \quad (m \geqq 2) \tag{17} $$

$$ a = 1 + \Pi_{\mathrm{HH}} - 2\Pi_{\mathrm{CH}}\Pi_{\mathrm{HC}} = c + d $$
$$ b = \Pi_{\mathrm{CC}}(4\Pi_{\mathrm{HC}}\Pi_{\mathrm{CH}} - \Pi_{\mathrm{CC}} - \Pi_{\mathrm{CC}}\Pi_{\mathrm{HH}}) - 2\Pi_{\mathrm{CH}}\Pi_{\mathrm{HC}} $$
$$ c = 1 + \Pi_{\mathrm{HH}} $$
$$ d = -2\Pi_{\mathrm{CH}}\Pi_{\mathrm{HC}} $$
$$ e = 1 + \Pi_{\mathrm{HH}} - 2\Pi_{\mathrm{HX}}\Pi_{\mathrm{XH}} $$
$$ f = 2\Pi_{\mathrm{HC}} $$

Here ${}^m\tilde{\Delta}_n^{11}$ is the determinant obtained by replacing the first row and column of ${}^m\Delta_n$ by the row $(1, -\Pi_{\mathrm{CH}}, -\Pi_{\mathrm{CH}}, -\Pi_{\mathrm{CC}}, 0, 0, \cdots\cdots, 0)$ and the column $(1, -\Pi_{\mathrm{HC}}, -\Pi_{\mathrm{HC}}, -\Pi_{\mathrm{CC}}, 0, 0, \cdots\cdots, 0)$ respectively.

Let us now examine the variations in the polarities of the bonds with an increase in the number of carbon atoms. For this purpose, we consider that the first derivatives $\mathrm{d}^{\mathrm{m}}\overline{\Pi}_{11}/\mathrm{d}m=(\partial^{\mathrm{m}}\overline{\Pi}_{11}/\partial\rho_{\mathrm{m}-1})(\mathrm{d}\rho_{\mathrm{m}-1}/\mathrm{d}m)$, etc. Since $\Pi\ll 1$,[31] we may limit ourselves to a consideration of the terms quadratic in Π. We then obtain :[32]

$$\partial^{\mathrm{m}}\overline{\Pi}_{11}/\partial\rho_{\mathrm{m}-1}\sim(-\Pi_{\mathrm{XC}}\Pi_{\mathrm{CX}})(e\rho_{\mathrm{m}-1}+f)^{-2}<0 \tag{18}$$

$$\partial^{\mathrm{m}}\overline{\Pi}_{21}/\partial\rho_{\mathrm{m}-1}\sim(-\Pi_{\mathrm{CX}}\Pi_{\mathrm{HC}})(e\rho_{\mathrm{m}-1}+f)^{-2}<0 \tag{19}$$

$$\partial^{\mathrm{m}}\overline{\Pi}_{41}/\partial\rho_{\mathrm{m}-1}\sim(\Pi_{\mathrm{CX}})(e\rho_{\mathrm{m}-1}+f)^{-2}>0 \tag{20}$$

Next let us examine the properties of the series ρ_{m}. From Eq. 17 we obtain the recurrent formula

$$\mathrm{d}\rho_{\mathrm{m}-1}/\mathrm{d}m=(ad-bc)(c\rho_{\mathrm{m}-2}+d)^{-2}\mathrm{d}\rho_{\mathrm{m}-2}/\mathrm{d}m \tag{21}$$

We know, by considering Eq. 21 and the numerical values[31] of Π_{CC}, Π_{CH} and Π_{HC}, that the ρ_{m} and $(\mathrm{d}\rho_{\mathrm{m}-1}/\mathrm{d}m)$ are monotonously decreasing and increasing functions of m respectively and that $\lim_{\mathrm{m}\to\infty}(\mathrm{d}\rho_{\mathrm{m}-1}/\mathrm{d}m)=0$. From the above results, we obtain the following :

$$\mathrm{d}^{\mathrm{m}}\overline{\Pi}_{11}/\mathrm{d}m>0, \qquad \mathrm{d}^{\mathrm{m}}\overline{\Pi}_{21}/\mathrm{d}m>0$$
$$\mathrm{d}^{\mathrm{m}}\overline{\Pi}_{41}/\mathrm{d}m<0 \tag{22}$$

$$\mathrm{d}^{2\mathrm{m}}\overline{\Pi}_{11}/\mathrm{d}m^2<0, \qquad \mathrm{d}^{2\mathrm{m}}\overline{\Pi}_{21}/\mathrm{d}m^2<0$$
$$\mathrm{d}^{2\mathrm{m}}\overline{\Pi}_{41}/\mathrm{d}m^2>0 \tag{23}$$

$$\lim_{\mathrm{m}\to\infty}(\mathrm{d}^{\mathrm{m}}\overline{\Pi}_{11}/\mathrm{d}m)=\lim_{\mathrm{m}\to\infty}(\mathrm{d}^{\mathrm{m}}\overline{\Pi}_{21}/\mathrm{d}m)=\lim_{\mathrm{m}\to\infty}(\mathrm{d}^{\mathrm{m}}\overline{\Pi}_{41}/\mathrm{d}m)=0 \tag{24}$$

Since the signs of ${}^{\mathrm{m}}\overline{Q}_1$, ${}^{\mathrm{m}}\overline{Q}_2={}^{\mathrm{m}}\overline{Q}_3$ and ${}^{\mathrm{m}}\overline{Q}_4$ are positive, negative and negative respectively, it may be concluded that the polarity of the CX bonds increases with an increase in the number of carbon atoms and that the induced polarities of the CC and CH bonds increase and decrease with an increase in the number of carbon atoms respectively. If the number of carbon atoms becomes very large, all these quantities reach a saturation value asymptotically. It follows from Eqs. 18—20 that, in the present approximation, the ratios of the variations of the CX, CH and CC bond polarities are given by :

$$|\mathrm{d}^{\mathrm{m}}\overline{Q}_1/\mathrm{d}m|:|\mathrm{d}^{\mathrm{m}}\overline{Q}_2/\mathrm{d}m|:|\mathrm{d}^{\mathrm{m}}\overline{Q}_4/\mathrm{d}m|=\Pi_{\mathrm{XC}}:\Pi_{\mathrm{HC}}:1 \tag{25}$$

Equation 25 indicates that the variation in the induced polarity of the CC bond is most significant of all. Our conclusions may also be extended to the more distant CC and CH bonds, but they are not valid for the case of $\mathrm{CH_3X}$ molecules.

For $\mathrm{CH_3X}$ molecules, we have :

$${}^1\overline{\Pi}_{11}=[1-(3\Pi_{\mathrm{XH}}\Pi_{\mathrm{HX}})(1+2\Pi_{\mathrm{HH}})^{-1}]^{-1} \tag{26}$$

$${}^1\overline{\Pi}_{21}=(-\Pi_{\mathrm{HX}})(1+2\Pi_{\mathrm{HH}}-3\Pi_{\mathrm{XH}}\Pi_{\mathrm{HX}})^{-1} \tag{27}$$

We will now attempt to compare the ${}^1\overline{\Pi}_{11}$ for $\mathrm{CH_3X}$ with the ${}^2\overline{\Pi}_{11}$ for $\mathrm{C_2H_5X}$. The ${}^2\overline{\Pi}_{11}$ may be approximated by

$${}^2\overline{\Pi}_{11}\sim[1-(2\Pi_{\mathrm{XH}}\Pi_{\mathrm{HX}}+\Pi_{\mathrm{XC}}\Pi_{\mathrm{CX}})\times(1+\Pi_{\mathrm{HH}}-5\Pi_{\mathrm{CH}}\Pi_{\mathrm{HC}})^{-1}]^{-1} \tag{28}$$

By comparing the second terms of Eqs. 26 and 28, it may be concluded that ${}^2\overline{\Pi}_{11}>{}^1\overline{\Pi}_{11}$. Therefore, the previous argument is valid for all molecules of the series $\mathrm{C_mH_{2m+1}X}$ except for the ${}^1\overline{\Pi}_{21}$.

So far we have disregarded changes in the valence states of the stoms, especially for the halogenes. In principle, a variation in the bond polarity is accompanied by a change in the hybridization of the corresponding AO. However, a complete calculation would be difficult, so we will discuss the problem qualitatively on the following assumptions :

1) All the valence AO of carbon atoms are assumed to be the usual sp^3 hybrids ; only the hybridization of the valence AO of the halogens will be considered explicitly.

2) The *s* character in the halogen bonding orbitals is assumed to be small. The empirical data[2,3,18] on the nuclear quadrupole coupling constants of the halogens support this assumption.

3) The interaction between the halogen atom and the non-adjacent alkyl group may be accounted for by means of the CX bond polarity, $\overline{Q}_1$, only.

If the valence AO of the halogens are represented by Eqs. A-4 and A-5 in Appendix A, the electronic energy, W_{e}°, of these molecules may be written as :

$$\begin{aligned}W_{\mathrm{e}}^{\circ}=&\,a^2\Delta W(1-\overline{Q}_1)-\overline{Q}_1E_{\mathrm{X}}+W_{\mathrm{x}}(a=0)\\&+1/4(1-\overline{Q}_1)^2(J_{\mathrm{CC}}+J_{\mathrm{X(b\sigma)X(b\sigma)}})\\&+(1-\overline{Q}_1)H_{\mathrm{C}}+2F_1\gamma_1+1/2(1-\overline{Q}_1^2)J_{\mathrm{CX(b\sigma)}}\\&+4(1-\overline{Q}_1)J_{\mathrm{C}\Pi}+(1+\overline{Q}_1)H'_{\mathrm{X(b\sigma)}}\\&+4H'_{\Pi}+2H'_{\mathrm{X(b\sigma)}}+R_{\mathrm{r}}\end{aligned} \tag{29}$$

where

$$\begin{aligned}W_{\mathrm{X}}(a=0)=&\,2I(\mathrm{s})+5I(\mathrm{p})+F^{\circ}(\mathrm{ss})+10F^{\circ}(\mathrm{pp})\\&-10/25F^2(\mathrm{pp})+10F^{\circ}(\mathrm{sp})-5/3\mathrm{G}^1(\mathrm{sp})\end{aligned} \tag{30}$$

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[31] The values calculated from simple Slater AO are $\Pi_{\mathrm{CC}}=0.16$, $\Pi_{\mathrm{CH}}=0.10$, $\Pi_{\mathrm{HC}}=0.12$ and $\Pi_{\mathrm{HH}}=0.08$, respectively so that this approximation seems to be reasonable.

[32] In Eq. 20, we have also neglected the small term $2(\Pi_{\mathrm{CX}}\Pi_{\mathrm{HH}}\text{-}\Pi_{\mathrm{HX}}\Pi_{\mathrm{CH}})$.

$$\Delta W = I(\mathrm{p}) - I(\mathrm{s}) - F^\circ(\mathrm{ss}) - 4F^\circ(\mathrm{sp}) + 2/3G^1(\mathrm{sp}) + 5F^\circ(\mathrm{pp}) - 10/25F^2(\mathrm{pp}) \tag{31}$$

$$E_\mathrm{X} = -I(\mathrm{p}) - 2F^\circ(\mathrm{sp}) + 1/3G^1(\mathrm{sp}) - 5F^\circ(\mathrm{pp}) + 10/25F^2(\mathrm{pp}) \tag{32}$$

and where the subscripts 1, C and Π stand for the CX bond, the carbon AO associated with it, and the halogen Π orbitals respectively. The a^2 values describe the amount of *s* character in the halogen bonding orbitals. R_r is the energy of the alkyl group (except for the CX bond), including the interaction energy with the CX bond. $W_\mathrm{X}(a=0)$, ΔW and E_X are the valence state energy of the halogens for the configuration $(n\mathrm{s})^2(n\mathrm{p}\sigma)(n\mathrm{p}\Pi)^4V_1$, its promotion energy to the $(n\mathrm{s})(n\mathrm{p}\sigma)^2(n\mathrm{p}\Pi)^4\cdot V_1$, and the electron affinity of halogens for the p orbital respectively. *I*, *F* and *G* are Slater parameters,[33] where s and p stand for the *n*s and *n*p orbitals of the halogen respectively. The variational procedure for Eq. 29, neglecting small terms, yields:

$$\begin{aligned} a \sim {} & [(1+S_1)^{-2}S_{\mathrm{Cs}}\gamma_1 - F_1\{H_{\mathrm{Cs}} - 1/2S_{\mathrm{Cs}}(H_{\mathrm{X(b}\sigma)} \\ & + H_\mathrm{C})\}] - 1/2(1-\overline{Q}_1^2)(\mathrm{CC}|\mathrm{sp}) + (1-\overline{Q}_1 \\ & + F_1S_1)(\mathrm{C:sp})/[[\Delta W(1-\overline{Q}_1) \\ & + 1/2(1-\overline{Q}_1)^2\{-F^\circ(\mathrm{pp}) - 4/25F^2(\mathrm{pp}) \\ & + F^\circ(\mathrm{sp}) + 2/3G^1(\mathrm{sp})\} + [(1+S_1)^{-2}S_{\mathrm{Cp}}\gamma_1 \\ & - F_1\{H_{\mathrm{Cp}} - 1/2S_{\mathrm{Cp}}(H_{\mathrm{X(b}\sigma)} + H_\mathrm{C})\}] \\ & - F_1S_1\{I(\mathrm{s}) - I(\mathrm{p})\}]] \end{aligned} \tag{33}$$

where

$$S_{\mathrm{Cs}} = \langle \mathrm{C}|\mathrm{s}\rangle, \qquad S_{\mathrm{Cp}} = \langle \mathrm{C}|\mathrm{p}\rangle$$

$$(\mathrm{CC}|\mathrm{sp}) = \langle \mathrm{C}(1)\mathrm{s}(2)|r_{12}^{-1}|\mathrm{C}(1)\mathrm{p}(2)\rangle$$

$$(\mathrm{C};\ \mathrm{sp}) = \langle \mathrm{s}|-1/r_\mathrm{C}|\mathrm{p}\rangle$$

The first terms of the numerator and denominator are both positive and greater than the following terms. From Eq. 33, neglecting small terms, we have

$$\mathrm{d}a^2/\mathrm{d}\overline{Q}_1 \sim 2a^2/(1-\overline{Q}_1) \tag{34}$$

This shows that the variation of a^2 is less than that of $\overline{Q}_1$ and the corresponding derivative is positive.

Now we will consider the same relation from a different point of view. Clearly we hope that the results thus obtained agrees with Eq. 34. The variation in the electronegativity, χ_X°, of the halogen as a function of a^2 is given by:

$$\mathrm{d}\chi_\mathrm{X}^\circ/\mathrm{d}a^2 = \Delta W + Y \tag{35}$$

where

$$\begin{aligned} Y = {} & F^\circ(\mathrm{sp}) + 2/3G^1(\mathrm{sp}) - F^\circ(\mathrm{pp}) - 4/25F^2(\mathrm{pp}) \\ & + a^2[F^\circ(\mathrm{ss}) + F^\circ(\mathrm{pp}) + 4/25F^2(\mathrm{pp}) \\ & - 2F^\circ(\mathrm{sp}) - 4/3G^1(\mathrm{sp})] \end{aligned}$$

Since, for $a^2 \ll 1$, the *Y* value will generally be positive, Eq. 35 shows that χ_X° increases with an increase in the amount of *s* character. The ${}^\mathrm{m}\Pi_{11}$ are insensitive to variations in a^2 and are closed to unity, as may be seen from the definition. We have then

$$\mathrm{d}\overline{Q}_1/\mathrm{d}a^2 \sim (\mathrm{d}K_{\mathrm{CX}}/\mathrm{d}a^2)(\chi_\mathrm{X}^\circ - \chi_\mathrm{C}^\circ) + K_{\mathrm{CX}}(\mathrm{d}\chi_\mathrm{X}^\circ/\mathrm{d}a^2) \tag{36}$$

where

$$\begin{aligned} \mathrm{d}K_{\mathrm{CX}}/\mathrm{d}a^2 & = K_{\mathrm{CX}}{}^2[-Y + \mathrm{d}(J_{\mathrm{CX(b}\sigma)} + 2\gamma_1)/\mathrm{d}a^2] \\ & \sim -0.01Y(\mathrm{eV}^{-1}) \end{aligned} \tag{37}$$

The second term of Eq. 37, which is connected with the strength of the bond, is much smaller than the first term, so it may be neglected and the approximate value, $K_{\mathrm{CX}} \sim 0.1$ (eV.$^{-1}$), substituted. The substitution of Eqs. 35 and 37 into Eq. 36 yields

$$\mathrm{d}\overline{Q}_1/\mathrm{d}a^2 \sim 0.1\Delta W + (0.06 \sim 0.1)Y \tag{38}$$

where the fact that $|\chi_\mathrm{X}^\circ - \chi_\mathrm{C}^\circ|$ is 4 eV. or less for all the halogens is used. Experimental data on ΔW are, unfortunately, not available, but the estimated values of Pritchard and Skinner[9] are F: 21 eV.; Cl: ~11 eV.; Br: ~11 eV.; I: ~8 eV. The exact values of *Y* are not known, but they are probably compatible with or less than ΔW. It follows, therefore, that the derivative of $\overline{Q}_1$ with respect to a^2 is always larger than unity. This agrees qualitatively with Eq. 34.

It may be concluded that both the polarity of the CX bond and the amount of *s* character in the bonding orbital of the halogen increase with an increase in the number of carbon atoms, but that the first effect is more important than the second. (For the CI bond, however, they are probably equally important.) The previous conclusion should, therefore, be modified as follows: The increasing polarities in the CX bonds are caused not only by the increasing polarizability, ${}^\mathrm{m}\overline{\Pi}_{11}$, but also by the increasing electronegativity, χ_X°, in connection with the increasing amount of *s* character. Both the amount of *s* character and the polarities of the CX bonds reach saturation values if the carbon atoms become very numerous.

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[33] J. C. Slater, *Phys. Rev.*, **34**, 1293 (1929).

[34] H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957).

TABLE IV. DIPOLE MOMENTS OF ALKYL HALIDES (IN DEBYE UNITS)

Chloride	μ	Bromide	μ	Iodide	μ
CH_3Cl	1.87[a]	CH_3Br	1.80[a]	CH_3I	1.65[a]
C_2H_5Cl	1.98[b]	C_2H_5Br	1.99[c]	C_2H_5I	1.93[c]
	2.00[c]		2.01[d]		1.87[d]
n-C_3H_7Cl	2.04[c]	n-C_3H_7Br	2.01[e]	n-C_3H_7I	1.97[c]
			2.15[d]		2.01[d]
n-C_4H_9Cl	2.11[d]	n-C_4H_9Br	2.15[d]	n-C_4H_9I	2.08[d]
	2.04[f]				

a) Ref. 3.
b) J. C. Jelatis, *Tech. Rep.*, **7**, O. N. R. Contract N5 ori-78 T. O. I. Lab. Ins. Res. Mass. Inst. Tech. (1947).
c) P. C. Mahanti, *Phil. Mag.*, (7) **20**, 274 (1935).
d) L. G. Groves and S. Sugden, *J. Chem. Soc.*, **1937**, 158.
e) R. Sanger, O. Steiger and K. Gachter, *Helv. Phys. Acta*, **5**, 200 (1932).
f) C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **3**, 347 (1935).
g) R. H. Wiswall and C. P. Smyth, ibid., **9**, 356 (1941).

TABLE V. NUCLEAR QUADRUPOLE COUPLING CONSTANTS OF ALKYL HALIDES $|eQq_X|$ (IN Mc. UNITS)

Chloride	$\lvert eQq_{Cl}\rvert$[a]	Bromide	$\lvert eQq_{Br}\rvert$[b]	Iodide	$\lvert eQq_I\rvert$[b]
CH_3Cl	68.1	CH_3Br	528.9	CH_3I	1753
C_2H_5Cl	65.4	C_2H_5Br	497.0	C_2H_5I	1647
n-C_3H_7Cl	65.9	n-C_3H_7Br	503.0	n-C_3H_7I	1672
n-C_4H_9Cl	66.5	n-C_4H_9Br	499.9	n-C_4H_9I	1660

a) H. O. Hooper and P. J. Bray, *J. Chem. Phys.*, **33**, 334 (1960).
b) S. Kojima, K. Tsukada, S. Ogawa and A. Shimauchi, ibid., **21**, 1415 (1953).

These conclusions may be extended to similar halogen compounds, for example, the halomethanes, because the behavior of molecules is accounted for only by the CX bond polarity here. This has already been shown in Subsection II-A).

It has been shown that the dipole moments of alkyl halides increase with an increase in the number of carbon atoms and that they also tend to a saturation value,[35] as Table IV shows. This fact may be interpreted as follows: Both the induced dipole moments of the CC bonds and the moments of the CX bonds increase with an increase in the number of carbon atoms, while the lone pair moment of the halogens behaves similarly. The CH bond moments decrease, and they oppose the increase in molecular dipole moments, but this effect is small.[25] The saturation of the dipole moment may be explained by the saturation of all the quantities involved.

Information on the CX bonds may also be obtained from a consideration of the molecular quadrupole coupling constants, eQq_X of the halogens. They show an oscillating decrease with an increase in the number of carbon atoms, as is listed in Table V. This behavior is caused by crystal fields; it may be explained by considering the different unit cells[35] for compounds with even and odd numbers of carbon atoms. The saturation effect may be obscured, especially by this influence. In this connection, it may be of interest to observe that the boiling points[36] of these molecules or paraffins increase monotonously with an increase in the carbon numbers, whereas the melting points[36] increase in an oscillatory fashion. We may expect, therefore, the eQq_X values for free molecules to decrease monotonously. This inference seems to be confirmed if they are interpreted by the Townes-Dailey formula in Appendix A.

Discussion

We have shown that the first order theory, which contains the electronegativity and the inductive effect, is particularly valuable for a discussion of the bond polarity; it makes it possible to give a qualitative interpretation of the experimental dipole moments, nuclear quadrupole coupling constants, etc. It may then be noticed that the SCF procedure is indispensable to the interpretation of the above experimental data. The physical meaning of the SCF procedure may be explained in connection with the inductive effect as follows: The polarities induced in the other bonds by a certain polar bond may also polarize the

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[35] A. Mueller, *Proc. Roy. Soc.*, **A120**, 437 (1928).

[36] N. A. Lange, "Handbook of Chemistry," Handbook Publ. Inc., Ohio (1956).

original bond.[37] We can then determine the accurate charge distribution in the molecule by considering all the correlations among the intra-molecular bonds. This corresponds to the exact solution of the many-body problem on the assembly of charged particles; it corresponds to our SCF procedure also. In fact, the correspondence between the quantum-mechanical and classical inductive effects has been pointed out. A close inspection of the examples shown in Section II will confirm the above explanation. Furthermore, the theory may be extended even to infinite polymers, as has been shown in Subsection II-B). This suggests that the present theory may be applicable to very large molecules. Although in the present treatment, the second order theory has been omitted, it ought to be taken into account in the quantitative discussion; the delocalization of the lone pair electrons on the halogen atoms—they attribute to the highest occupied orbitals in saturated molecules—may be especially important.

In Section I, the validity of the electronegativity scale has been discussed on the assumption that the polarity of bonds may be inferred from the valence state of the atoms in the infinite separation. This seems to confirm the idea of "*atoms in molecules*" developed by Moffitt.[13,14] It is not true for the inductive effect; however, the valence state of atoms is important even then.

Summary

A previously proposed theory is applied to a study of the electronegativity scale and the ionic character of bonds. The general validity of the electronegativity scale and also the relation between the Mulliken and Pauling scales are discussed. The previously defined inductive effect is used as a basis for calculations on MX_n-type molecules and on *n*-alkyl halide molecule. The results are then used for the qualitative interpretation of the experimental dipole moments, nuclear quadrupole coupling constants and fluorine chemical shifts.

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Appendix A. The Derivation of the Townes-Dailey Formula.—The electronic contributions to the nuclear quadrupole coupling constants, eQq, for axially symmetric molecules are represented by:

$$eQq=eQ\langle\Phi^{\circ}|r^{-3}(3\cos^2\theta-1)|\Phi^{\circ}\rangle \qquad \text{(A-1)}$$

where e and Q are the electronic charge and the nuclear quadrupole moment of the coupled atom respectively; Φ° is the molecular wave function which is given by Eq. 16 of Ref. 1. The contribution of the inner-shell electrons of the coupled atom may be neglected.[2,3,18] Because of the rapid decrease of the function r^{-3}, we will consider only the contribution of the coupled atom. In this approximation, we obtain

$$eQq=2eQ\sum_{\mathrm{p}}\langle\varphi_{\mathrm{p}}|r^{-3}(3\cos^2\theta-1)|\varphi_{\mathrm{p}}\rangle \qquad \text{(A-2)}$$

where φ_{p} refers to the bonds connected with the coupled atom or its lone pairs.

Now let us consider the case of a halogen atom. For the MX bond (X=halogen), we have

$$\varphi_{\mathrm{MX}}=c_{\mathrm{M}}M+c_{\mathrm{X}}X(\mathrm{b}\sigma) \qquad \text{(A-3)}$$

where

$$X(\mathrm{b}\sigma)=a(n\mathrm{s})+(1-a^2)^{1/2}(n\mathrm{p}\sigma) \qquad \text{(A-4)}$$

$$X(\mathrm{l}\sigma)=(1-a^2)^{1/2}(n\mathrm{s})-a(n\mathrm{p}\sigma) \qquad \text{(A-5)}$$

The M refers to the AO of the atom M, and $X(\mathrm{b}\sigma)$ and $X(\mathrm{l}\sigma)$ are the bonding and lone pair orbitals respectively of the halogen with σ symmetry, together with the lone pair orbitals, $n\Pi$ and $n\overline{\Pi}$, with Π symmetry. The parameter a is the hybridization factor, and n can take the values 3, 4 and 5 for Cl, Br and I. The substitution of Eqs. A-3, A-4 and A-5 into Eq. A-2 yields:

$$eQq_{\mathrm{X}}=(1-a^2)(-1+Q_{\mathrm{MX}}-F_{\mathrm{MX}}S_{\mathrm{MX}})eQq_{\mathrm{np}\sigma} \qquad \text{(A-6)}$$

If we neglect the overlap S_{MX}, we have the following simple formula:

$$eQq_{\mathrm{X}}=-(1-a^2)(1-Q_{\mathrm{MX}})eQq_{\mathrm{np}\sigma} \qquad \text{(A-7)}$$

This is equivalent to the Townes-Dailey formula,[2] which was derived from a valence bond treatment. It may be rewritten:

$$eQq_{\mathrm{X}}=-2/5eQ(1-a^2)(1-Q_{\mathrm{MX}})\langle n\mathrm{p}|r^{-3}|n\mathrm{p}\rangle \qquad \text{(A-8)}$$

where the integral is the mean value of r^{-3} for the np orbital of the free halogen atom.

Appendix B. The Derivation of the Saika-Slichter Formula. — On the assupmtion that the second (paramagnetic) term in Ramsey's equation[38] is mainly responsible for the chemical shifts in fluorine, the chemical shift may be approximated by

$$\Delta\sigma=-(4/3\Delta E)(0|\sum_{\mathrm{jk}}\boldsymbol{m}_{\mathrm{j}}\boldsymbol{m}_{\mathrm{k}}\boldsymbol{r}_{\mathrm{k}}{}^{-3}|0) \qquad \text{(B-1)}$$

The various quantities in this formula are defined in Ramsey's paper.[38] In the same way as in Appendix A, we obtain

$$\Delta\sigma=-(2/3\Delta E)(e^2\hbar^2/m^2c^2)(1-a^2)(1-Q_{\mathrm{MF}}) \times\langle 2\mathrm{p}|r^{-3}|2\mathrm{p}\rangle \qquad \text{(B-2)}$$

This corresponds to the Saika-Slichter formula.[4] It resembles the Townes-Dailey formula given by Eq. A-8, as has already been predicted by Saika and Slichter.[4]

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37) It is called "*reaction field*" in classical theory.

38) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).