σ Electronic Structures and Some Physicochemical Properties of Halogenated-conjugated Hydrocarbons

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Researches of the electronic structures of large organic compounds have been carried out, with the molecular orbital and the valence bond methods, almost exclusively on the electronic states of conjugated molecules; these examinations have dealt with electronic spectra, chemical reactivities, π dipole moments and so on. In these discussions no attention has been paid to the behavior of σ electrons in making an unchangeable framework for π electrons to move on. However, some of the physicochemical properties—σ moments, coupling constants *eqQ* in PQR spectra, proton shifts in NMR spectra, etc.—cannot be interpreted theoretically without an explicit consideration on the σ electronic structures.

Recently, in order to discuss the σ electronic structures of conjugated compounds, the present authors have developed a simple molecular orbital method which had previously been successfully adopted for the computation of the electronic structures of saturated hydrocarbons and their derivatives[1-3]; they have published some results of their calculations on the σ electrons of aromatic and olefinic hydrocarbons[4]. In this paper a numerical calculation is performed on the σ electronic structures of halogenated olefins and benzenes, and on this basis the *eqQ* of halogens and the dipole moments of these compounds are discussed.

It would be interesting to compare this paper's calculated results on conjugated halides with those on saturated halides in Refs. 2 and 3.

Method of the Calculation and Evaluation of Parameters

The method of the theoretical calculation of the σ electronic structures of conjugated systems was explained in detail in Ref. 4. In this paper, therefore, it will be repeated only

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[1] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, 34, 442, 1111 (1961).

[2] K. Fukui, T. Yonezawa and H. Kato, *Progress Reports on Electronic Processes in Chemistry*, 3, 55 (1961).

[3] T. Yonezawa, H. Kato, H. Saito and K. Fukui, This Bulletin, 35, 1814 (1962).

[4] K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, ibid., 35, 38 (1962).

briefly. Molecular orbitals are linear combinations of all σ atomic orbitals (LCAO) of all the atoms present—sp^2 hybridized orbitals of carbons, 1 s orbitals of hydrogens, and σ atomic orbitals of halogens. Electronic interactions and overlap integrals are completely disregarded. The parameters of the Coulomb and of the resonance integrals employed are given in Table I. Those for carbon atoms and for hydrogen atoms are the same as were given in Ref. 4. The Coulomb integrals for halogen atoms have been chosen so as to fit Mulliken's electronegativity scale and to be consistent with the integrals in saturated compounds, and the resonance integrals between carbon and halogen have been proportionated to the overlap integrals of the bonds.

TABLE I. PARAMETERS OF COULOMB AND RESONANCE INTEGRALS OF σ AO'S

Coulomb integral:	q_{rr}*	Resonance integral:	q_{rs}**
C_{sp^2}	0	C_{sp^2}–C_{sp^2} (σ bonding)	1
		C_{sp^2}–C_{sp^2} (on the same carbon) m	≡0.38
H	−0.2	C_{sp^2}–H	0.94
F	0.7	C_{sp^2}–F	0.45
Cl	0.3	C_{sp^2}–Cl	0.6
Br	0.25	C_{sp^2}–Br	0.5
I	0.2	C_{sp^2}–I	0.45

* Coulomb integral α_r is expressed as follows:

$$\alpha_r=\alpha+q_{rr}\beta$$

where α and β are the standard Coulomb and the standard resonance integrals in sp^2 system.

** Resonance integral β_{rs} is expressed as follows:

$$\beta_{rs}=q_{rs}\beta$$

The effects of the variation of parameters and those of neglecting overlap integrals will be discussed in the following paragraphs.

General Properties of the Results of Calculations

A few examples of the results of our calculations are shown in Tables II and III and in Figs. 1, 2, 3 and 4. The general propeties of these results for halogenated conjugated systems may be summarized as follows:

1) As is seen in Tables I and II and Fig. 1, each orbital has a large distribution on two certain atomic orbitals which form a bond. This tendency seems to reflect the localized nature of the σ electrons.

2) The lowest unoccupied σ orbital of halides lies much lower than that of mother hydrocarbons, and it is localized on carbon-halogen bonds with a negative and large (in magnitude) bond order. Moreover, the lowering of the level becomes more and more notable with the increased number of halogen atoms. This result comes from the electronegativity of the halogen atoms and the small overlap (the small absolute value of the resonance integral) between the carbon and the halogen.

3) The electronegativity of the halogen atoms causes them to attract a considerable amount of electron density to the carbon-halogen (C–X) bonds from other near-by bonds, so that the sum of the σ charge density

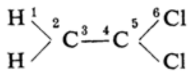
TABLE II. CALCULATED σ ELECTRONIC STRUCTURE OF VINYLIDENE CHLORIDE

Symmetry*			Energy** λ_j	Electron distribution on each AO***					
				H_1	C_2	C_3	C_4	C_5	Cl_6
Unoccupied	10	S	−1.2765	0.05763	0.07558	0.36551	0.31672	0.02242	0.00325
	9	A	−1.2143	0.22617	0.27383	0	0	0	0
	8	S	−0.8173	0.24699	0.10654	0.04037	0.16999	0.03205	0.00924
	7	A	−0.7296	0	0	0	0	0.37325	0.12675
	6	S	−0.2285	0.02004	0.00002	0.11787	0.00668	0.18248	0.23519
Occupied	5	S	+0.6387	0.05870	0.04673	0.20443	0.20529	0.04585	0.14386
	4	A	+0.6496	0	0	0	0	0.12675	0.37325
	3	A	+0.6543	0.27383	0.22617	0	0	0	0
	2	S	+1.0866	0.07398	0.13858	0.00037	0.06859	0.15991	0.09305
	1	S	+1.4570	0.04266	0.13255	0.27145	0.23274	0.05729	0.01541

* Symmetry about the C-C axis

** λ_j is the coefficient in $\varepsilon_j=\alpha+\lambda_j\beta$, where ε_j is the jth molecular orbital energy.

*** Nomenclature of AO's:



And $(C_{ir})^2$ is given in the table.

on the bond (the σ bond density) exceeds 2 and the net charge on the bond becomes negative.

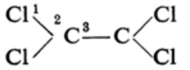
4) Because of the polarity of a C–X bond, X being negative and C being positive, a similar but weakened polarity is caused in adjacent

TABLE III. CALCULATED σ ELECTRONIC STRUCTURE OF TETRACHLOROETHYLENE

	Symmetry	Energy λ_i	Electron distribution on each AO** Cl₁	C₂	C₃
Unoccupied	A	−1.2131	0.00523	0.03326	0.42302
	AA	−0.7296*	0.12675	0.37325	0
	S	−0.3690	0.10267	0.12766	0.03934
	A	−0.1286	0.14669	0.07484	0.05693
Occupied	S	+0.6395	0.12307	0.03939	0.17506
	AA	+0.6496*	0.37325	0.12675	0
	A	+1.0217	0.09808	0.14189	0.02005
	S	+1.4096	0.02425	0.08295	0.28560

* Doubly degenerate orbital being localized on C-Cl bonds

** Nomenclature of AO's:



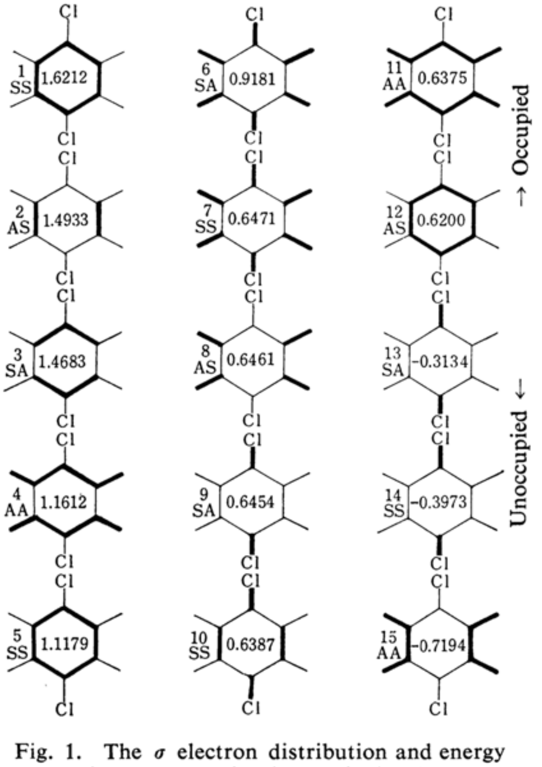
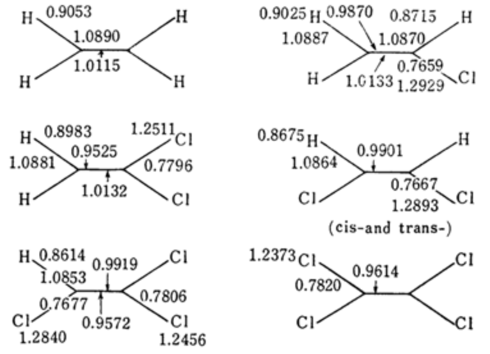
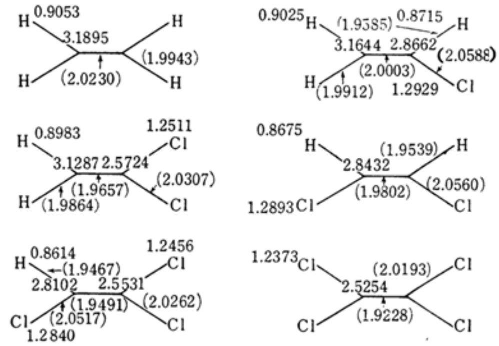


Fig. 1. The σ electron distribution and energy λ_i of some MO's in *p*-dichlorobenzenes (thick lines denote the most densely populated bonds).



(a) σ Electron density on each AO



(b) Total σ electron density on each atom and bond σ density (in parentheses)

Fig. 2. Electron distributions of ethylene and chloroethylenes.

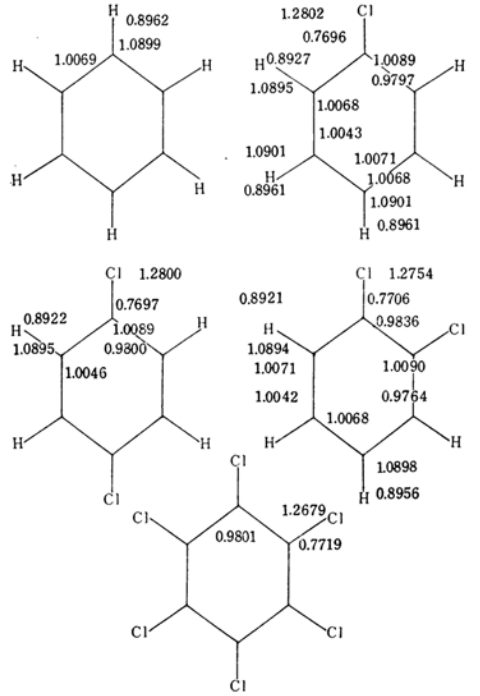


Fig. 3. Total σ electron density of benzene and chlorobenzenes.

TABLE IV. CALCULATED σ ELECTRONIC STRUCTURE OF HEXACHLOROBENZENE

	j	Symmetry xy	Energy λ_j	Electron distribution on each AO		
				Cl_1	C_2	C_3(ring)
Unoccupied	24	AA	−1.38000	0	0	0.08333
	22, 23	SA, AS	−1.27825	0.00209	0.01448	0.15838
	20, 21	SS, AA	−1.08869	0.01299	0.06956	0.12539
	19	SA	−1.01172	0.01128	0.05391	0.05074
	18	SS	−0.56479	0.05150	0.10699	0.00408
	16, 17	SA, AS	−0.52114	0.10496	0.19659	0.01589
	14, 15	SS, AA	−0.34699	0.11312	0.13154	0.04434
	13	SA	−0.15872	0.07009	0.04097	0.02780
Occupied	12	AS	+0.62000	0	0	0.08333
	10, 11	SS, AA	+0.63931	0.16148	0.05164	0.06011
	8, 9	SA, AS	+0.64524	0.21223	0.07026	0.02542
	7	SS	+0.64622	0.11026	0.03671	0.00985
	6	SA	+0.85044	0.08529	0.07178	0.00479
	4, 5	SS, AA	+1.09637	0.04575	0.08059	0.10350
	2, 3	SA, AS	+1.45415	0.01405	0.05200	0.13364
	1	SS	+1.59857	0.00490	0.02296	0.06940

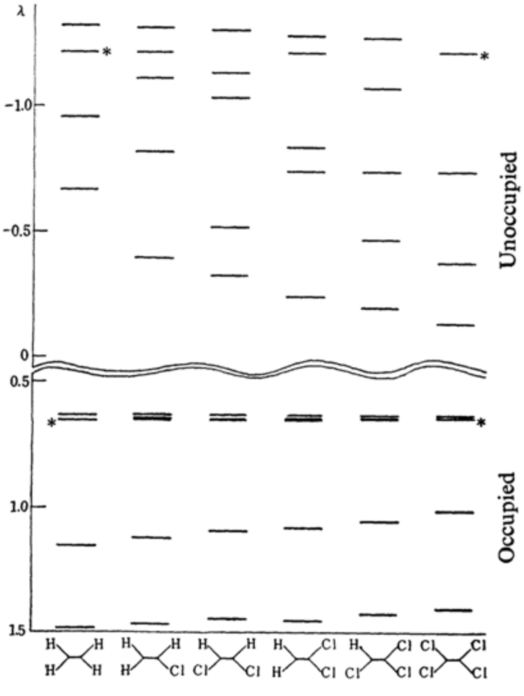


Fig. 4. σ Energy levels of ethylene and chloroethylenes. (*: Doubly degenerate)

C–C bonds and is transmitted to farther bonds with, however, a rapid decrement.

Results 3 and 4 seem to correspond to the so-called inductive effect in organic chemistry.

Effects of Parameters.—In order to see the effects of parameters on the results, some calculations on various compounds have been carried out with varied parameters; a few examples are shown in Tables V and VI. For the sake of brevity, only a summary of the calculated results will be given here. A change in the Coulomb integral of chlorine atoms causes a change in their σ electron density; the bond moment of the C–Cl bond is well explained with its value near 0.3 (as has been adopted) or less, though its influence is little on the qualitative results of calculation.

TABLE V. VARIATION OF PARAMETERS (1)

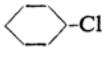
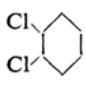
1,2-Dichloroethylene

q_{Cl}	q_{Cl}	q_H
0.25	1.2488	0.8721
0.28	1.2733	0.8692
0.30	1.2893	0.8675

Vinyl chloride

q_{Cl}	q_{Cl}	q_{H1}	q_{H2}
0.25	1.2522	0.8754	0.9028
0.28	1.2765	0.8730	0.9027
0.30	1.2929	0.8715	0.9025
0.32	1.3088	0.8699	0.9024

TABLE VI. VARIATION OF PARAMETERS (2): CHANGE OF q_{Cl}

q_{Cl}	m			
0.6	0.38	1.2802	1.2800	1.2754
0.6	0.42	1.2914	1.2910	1.2851
0.6	0.45	1.3010	1.3005	1.2935
0.8	0.42	1.2206	1.2205	—

Effects of Overlap Integrals.—In σ electron systems where neighboring atomic orbitals are mutually deeply overlapping, the neglect of

TABLE VII. ELECTRON DISTRIBUTION OF TETRACHLOROETHYLENE WITH OVERLAP INCLUDED

Energy λ_i	Electron distribution (a)**					Electron distribution (b)***		
	Cl_1	C_2Cl_1	C_2	C_3	C_3C_4	Cl_1	C_2	C_3
+0.42935	0.10799	0.03193	0.01115	0.11179	0.17216	0.12395	0.02712	0.19787
+0.47204*	0.30954	0.12796	0.06250	0	0	0.37352	0.12648	0
+0.76116	0.03989	0.06772	0.13586	0.05683	−0.08752	0.07375	0.16972	0.01307
+0.90885	0.00814	0.02505	0.09111	0.14205	0.21875	0.02066	0.10363	0.25143
q	0.93109	0.50531	0.60123	0.62134	0.60678	1.18375	0.85389	0.92473

* Doubly degenerate orbital

** Electron distribution on the atom A is $(C_{iA})^2$, while on the bond AB it is calculated as $2C_{iA}C_{iB}S_{AB}$.

*** In this calculation distribution on the bond AB is divided by two and added to those on the atom **A** and on the atom **B.**

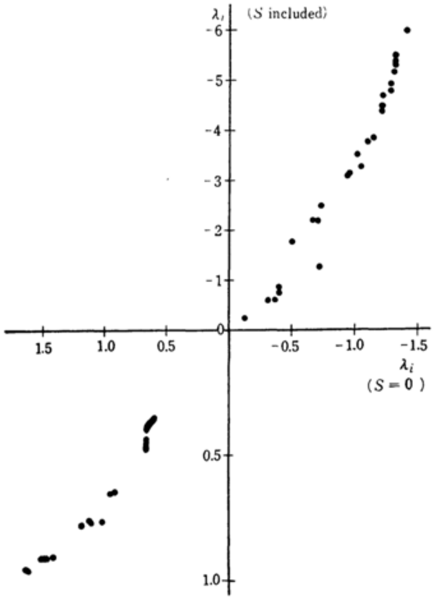


Fig. 5. Energy levels with overlap included and neglected.

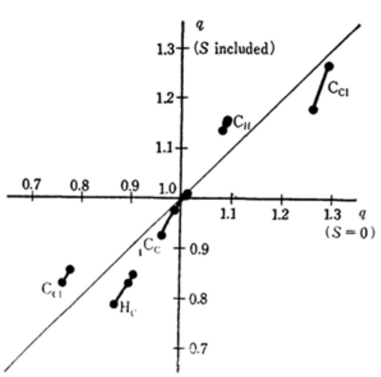


Fig. 6. Total σ electron densities on each kind of AO's with overlap included and neglected (C_H, for example, denotes the carbon AO in a C-H bond.).

the overlap integrals might lead to an erroneous conclusion, even in a qualitative sense. Therefore, some computations have been performed with the inclusion of overlap integrals between adjacent atoms, which have been settled as follows:

$$S_{CH}=0.72$$
$$S_{CC}=0.77$$
$$S_{CCl}=0.46$$

Results with respect to ethylene, 1, 2-dichloroethylene, tetrachloroethylene, benzene and *p*-dichlorobenzene, as shown in Table VII and Figs. 5 and 6, indicate that those energy levels with overlap included are almost completely parallel to those with overlap neglected and that the occupied levels of the former come near to α_σ, while unoccupied levels flee from α_σ. As for the σ electron density, on the basis of Fig. 6, those on similar atomic orbitals on similar bonds (for instance, carbons' AO's on C–Cl bond, as is expressed by C_{Cl} in the figure) very parallel with each other, leading also to an unvaried qualitative conclusion in both calculations.

Dipole Moments

The dipole moment of conjugated compounds is composed of the σ moment and the π moment. Most of the theoretical works have been concerned with only the π moment till now, and in those cases the σ moment was empirically estimated on the basis of bond moments which are assumed to be constant in a series of compounds. In this paragraph, the σ moment of each compound is evaluated by the use of the σ electron distribution given in the tables and the figures. In the evaluation, all the bond angles are assumed to be 120°; the C–Cl bond length, 1.70 Å; C–H, 1.08 Å; C–C (aromatic) 1.40 Å, and C–C (olefinic) 1.34 Å, and the displacement of the center of the charge distribution is taken into

TABLE VIII. DIPOLE MOMENTS OF CHLOROETHYLENES (IN UNITS OF DEBYE)

Substituent	Calculated			Observed
	σ Moment	π Moment	Total Moment	
Cl	1.84	0.36	1.47	1.44
1,2-di-Cl(cis)	3.20	0.65	2.55	1.74
1,1-di-Cl	1.81	0.34	1.47	1.30
tri-Cl	1.84	0.37	1.47	0.94

TABLE IX. DIPOLE MOMENTS OF CHLOROBENZENES

Substituent	Calculated			Observed
	σ Moment	π Moment	Total Moment	
Cl	1.69	0.31	1.39	1.57
o-di-Cl	2.96	0.54	2.41	2.25

account by 0.46 Å in an sp^2 hybridized orbital of carbon and by 0.44 Å in a σ orbital (the s character of 15% is tentatively assumed) of chlorine.

The σ moments obtained are tabulated in Tables VIII and IX, together with the π moments calculated in the simple LCAO MO approximation with parameters $\alpha^{\pi}{}_{\text{Cl}}=\alpha_{\pi}+1.8\beta_{\pi}$, $\alpha^{\pi}{}_{\text{C}'}=\alpha+0.18\beta_{\pi}$ and $\beta_{\text{CCl}}=0.8\beta_{\pi}$, where α_{π} and β_{π} are the standard Coulomb and the standard resonance integrals in the π electron systems, and with the calculated total moments compared with the observed dipole moments.

Generally speaking, the calculated moments are larger than observed ones; this may be attributed to the choice of parameters and also to a disregard of the σ overlaps. However, a calculated σ moment does not seem to be a simple vector sum of bond moments. A part of the so-called ortho effects—a deviation from the additivity of bond moments in ortho-disubstituted compounds—may be understood on the basis of this result. However, the extremely small moment of trichloroethylene cannot so be explained, probably due to the roughness on the electronic repulsions between the neighboring polar groups. On these problems a theoretical paper would be published in the near future[5].

The Coupling Constant of Halogen in the PQR Spectra

In chlorides, bromides and iodides the coupling constants, *eqQ*, of halogen nuclei are observed in pure nuclear quadrupole resonance (PQR) spectroscopy. In conjugated chlorides these constants are connected to the σ electron density, $q^{\sigma}{}_{\text{Cl}}$, and to the π electron density, $q^{\pi}{}_{\text{Cl}}$, on the chlorine atom by the following equation:

$$eqQ=\left(\frac{q^{\pi}{}_{\text{Cl}}+2}{2}-q^{\sigma}{}_{\text{Cl}}\right)eqQ_{\text{atom}} \qquad (1)$$

where the eqQ_{atom} is the coupling constant of an atomic chlorine and is set at 109.7 Mc. In Eq. 1 the orbital of chlorine is assumed to be a pure p orbital. If the s character of the orbital is considered to be *s*%, *eqQ* is given by Eq. 2 instead of Eq. 1:

$$eqQ=\left[\frac{q^{\pi}{}_{\text{Cl}}+2}{2}-q^{\sigma}{}_{\text{Cl}} -\frac{s}{100}(2-q^{\sigma}{}_{\text{Cl}})\right]eqQ_{\text{atom}} \qquad (2)$$

By adopting the π and the σ electron densities calculated in previous paragraphs in Eq. 1, the values of *eqQ* shown in Tables X and XI are obtained; their parallelism with the experimental values seems to be sufficient.

The difference in the calculated coupling constants among chlorobenzenes is unexpectedly small. As the coupling constants of these compounds were experimentally determined from the resonance spectra in the solid state, a part of this discrepancy may be attributed to the effects of crystal fields, which in some other cases might change the constant by 0.8 Mc[6]. The difference is also probably due in

TABLE X. CHLORINE COUPLING CONSTANTS IN PQR OF CHLOROETHYLENES

Substituent	Calculated			Observed *eqQ*
	$q^{\pi}{}_{\text{Cl}}$	$q_{\text{Cl}}{}^{\sigma}$	*eqQ*	
Cl	1.955	1.298	75.1 Mc	67.2 Mc 70.2(gas)
1,2-di-Cl	1.955	1.289	75.6	70.0(cis) 71.2(trans)
1,1-di-Cl	1.956	1.251	79.8	78.7(gas)
tri-Cl	1.956 1.954	1.246 1.284	80.3 76.0	— —
tetra-Cl	1.955	1.237	81.3	77.2

TABLE XI. CHLORINE COUPLING CONSTANTS IN PQR OF CHLOROBENZENES

Substituent	Calculated			Observed[a] *eqQ*
	$q_{\text{Cl}}{}^{\pi}$	$q_{\text{Cl}}{}^{\sigma}$	*eqQ*	
Cl	1.96200	1.28022	76.9Mc	69.2Mc
p-di-Cl	1.96188	1.28000	76.9	69.6
o-di-Cl	1.96166	1.27540	77.4	71.5
hexa-Cl	1.96126	1.26793	78.2	76.8

a) P. J. Bray, R. G. Barnes and R. Bersohn, *J. Chem. Phys.*, **25**, 813 (1956).

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[5] K. Fukui and K. Morokuma, to be published.

[6] In the case of chloroalkanes: H. O. Hooper and P. J. Bray, *J. Chem. Phys.*, **33**, 334 (1960).

part, however, to the crudeness of our approximation in calculating molecular orbitals. On the approximation of this calculation, some discussions will be published in the future⁽⁵⁾.

Other Problems

Interesting relations between the electronic structures and the potential of polarographic reduction of conjugated halides have also been found and will be presented in a separate paper⁽⁷⁾.

The proton chemical shifts of these halides in NMR spectra will be discussed in connection with σ electron distributions in another paper⁽⁸⁾.

Summary

The simple LCAO MO method previously developed by the present authors has been adopted to the calculation of the σ electronic structures—σ molecular orbitals, their energies, separate and total σ electron densities, etc.—of conjugated halides. The general results of the computation—the so-called inductive effects along σ bonds, the unoccupied levels with the very low energy which is characteristic to halides, and so forth—have been described. Sigma dipole moments and the coupling constants in PQR have been calculated with the σ electron densities obtained and discussed in comparison with the experimental values.

The numerical calculations were carried out on the digital computer KDC-I of Kyoto University.

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7) K. Fukui, K. Morokuma and H. Kato, This Bulletin in press.

8) T. Tonegawa and K. Fukui, to be published.