products will have an insignificant effect in this work and in the work of Doescher and Wise.[4g,k]

The recent direct determinations of the electron affinity of fluorine[4n,r] when combined with other thermochemical data yield a $D_0(F_2)$ of 37 ± 2 kcal./mole. A third law interpretation[4s] of Doescher's and Wise's results yields a value of 36.7 ± 0.1 kcal./mole, and the value deduced from the continuous absorption spectra[4q] of F_2 plus a knowledge of certain ground state parameters is 37.8 ± 0.85 kcal./mole. In addition, Iczkowski and Margrave[4u] have reported a direct spectroscopic determination of $D_0(F_2)$, involving a vibrational analysis of transitions from the ground state to a stable upper state, which gives $D_0(F_2) = 37.5 \pm 2$, depending on the upper state dissociation products.

In view of this evidence there may be unknown systematic errors that tend to make the present results a few kilocalories too high. Nevertheless, these results leave no doubt that the dissociation energy of fluorine is low, in fact between that of Br_2 and I_2. The electron affinity of F is nearly that of Br.

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Some Studies in Molecular Orbital Theory. I

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A simple interaction theory based on the single configuration LCAO MO method is applied to the problem of the ionization potentials and the near ultraviolet absorption spectra of mono-substituted benzenes with special reference to the evaluation of the empirical parameters. Both conjugative and inductive effects are included. To estimate parameters, only interactions between the highest occupied and the lowest vacant molecular orbitals of benzene and the occupied π-orbital of the substituent are considered, but the theory predicts the perturbed orbital energies with reasonable accuracy. General principles for parameter determination are given and three separate methods are applied to halogen monosubstituted benzenes. Parameters obtained in the three ways are found to reproduce the observed spectroscopic data quite satisfactorily. Extensive further applications of the theory are shown to be possible.

1. Introduction

There are two main ways in which a substituent containing π-electrons may affect the electronic structure of an aromatic hydrocarbon. One of these is the conjugative effect or charge transfer effect, in which the π-electrons of the substituent enter into conjugation with the aromatic system. The other is involved when the substituent to some extent perturbs the potential acting on the π-electrons of the hydrocarbon; it is known as the inductive effect. In substituted benzenes it would be particularly desirable to have available a systematic treatment of the electronic structure which would allow one to estimate to what extent the two effects interact or coöperate.

Therefore the electronic structures of substituted benzenes have been treated by several authors by the semi-empirical LCAO MO approximation, with special reference to the question of how to estimate the integral values entering the molecular computations as parameters. Wheland[2a] has first introduced the method of calculation and estimated parameters using the directing properties in chemical reactivity, and Robertson and Matsen[2b] have evaluated parameters from the observed spectral shifts of the near ultraviolet absorption spectra of the substituted benzenes relative to benzene (and the corresponding intensities). Recently, Knipe[3] has employed a similar method in discussing the dipole moments of some halogen-substituted benzenes and compared his results with the other authors.

The most important problem is the difficulty of determining the energy parameters, which involve in most cases atomic integrals or coulomb integrals for heteroatoms, resonance integrals for heteropolar bonds, and coulomb integral contribution due to the inductive effect. The parameters determined up to date[4] often depend upon too arbitrary assumptions for them to be usable in computations including nearest neighbor overlap integrals. In this paper an interaction theory based on the molecular orbital method is presented to estimate parameters and three methods of parameter determination are given which involve the use of experimental data on ionization potentials and near ultraviolet absorption spectra. Several applications to halogen-substituted benzenes are made, and the results of applying the three methods of parameter evaluation are compared.

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[2] (a) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942); (b) F. A. Matsen, *ibid.*, **72**, 5243 (1950); W. W. Robertson and F. A. Matsen, *ibid.*, **72**, 5252 (1950).

[3] R. H. Knipe, *J. Chem. Phys.*, **23**, 2089 (1955).

[4] Other works not cited above are: C. Sandorfy, *Bull. soc. chim France*, **16**, 615 (1949); H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

2. Interaction Theory Based on Second-order Perturbation Method

In a recent paper,[5] the author presented a generalized second-order perturbation theory including overlap integrals between nearest neighbor atoms and discussed the correlation and difference between inductive and hyperconjugative effects. It would be expected that this method would be applicable with good accuracy for the single configuration LCAO MO approximation, but its precise application involves complexities because of the many terms which arise in the orbital energy expressions. In this section, second-order perturbation theory will be rescrutinized and a new simplified theory will be described which can function as a substitute for it. For simplicity only the case of mono-substituted benzene is treated.

We begin by using Dewar's[6] formulation of linear combination of molecular orbitals (LCMO), and expand the molecular orbitals in the form

$$\chi_j = \sum_{i=1}^{n} x_{ij}\psi_i \tag{1}$$

where ψ_1 to ψ_6 are the six orthonormal molecular orbitals of benzene formed by six carbon 2pπ atomic orbitals ϕ_i, given by

$$\begin{aligned}
\psi_1 &= (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/(6 + 12S)^{1/2} \\
\psi_2 &= (\phi_2 + \phi_3 - \phi_5 - \phi_6)/(4 + 4S)^{1/2} \\
\psi_3 &= (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/(12 + 12S)^{1/2} \\
\psi_4 &= (\phi_2 - \phi_3 + \phi_5 - \phi_6)/(4 + 4S)^{1/2} \\
\psi_5 &= (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/(12 - 12S)^{1/2} \qquad (2) \\
\psi_6 &= (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/(6 - 12S)^{1/2}
\end{aligned}$$

The forms of ψ_7 to ψ_n depend upon the substituent, and in general are not orthogonal to the above six wave functions for benzene. To construct the secular equation, we assume the six molecular orbitals of benzene are approximately orthogonal after the perturbation, although in the strict sense they are no longer mutually orthogonal due to the introduction of the substituent.

If we restrict the treatment to mono-substituted benzenes such that the substituent possesses π-electrons which can enter into conjugation with the benzene ring, ψ_7 can be taken as the π-orbital of the substituent ψ_t. Application of generalized second-order perturbation theory[7] now leads to the orbital energies of benzene and of the substituent after the perturbation has been introduced

$$E_j = H_{jj} + \sum_{i=1}^{6} \frac{H_{ji}^2}{H_{jj} - H_{ii}} + \frac{(H_{jt} - \Delta_{jt}H_{jj})^2}{H_{jj} - H_{tt}} \tag{3}$$

$$E_t = H_{tt} + \sum_{i=1}^{6} \frac{(H_{ti} - \Delta_{ti}H_{tt})^2}{H_{tt} - H_{ii}} \tag{4}$$

Here

$$H_{ij} = \int \psi_i H \psi_j \, dv, \quad \Delta_{ij} = \int \psi_i \psi_j \, dv$$

and the total Hamiltonian H can be divided into a part H_0, to which eigenfunctions ψ_i of eq. 1 belong, and a perturbation term H', due to the substituent.

In eq. 3, the second term involves pure inductive effects but is negligibly small compared with the last term (see ref. 5 and Appendix). The most important case which appears to make contributions to the energy levels arises when the occupied energy level of the substituent is very close to one of the occupied π-electron levels of benzene, but in such a case the perturbation theory formula above is not valid.[8] As a matter of fact, the π-electron energy levels of substituents in mono-substituted benzenes are in most cases close to the occupied levels of benzene, and so it may be concluded that the second-order perturbation theory as given above is not suitable for the quantitative discussions of such a molecule. We therefore merely assume that the second term of eq. 3 is negligible compared with the last term. If then the correct energy E_j is substituted for H_{jj} in the last term, that equation becomes

$$E_j = H_{jj} + \frac{(H_{jt} - \Delta_{jt}E_j)^2}{E_j - H_{tt}} \tag{5}$$

Alternatively, we could consider the interaction only between the highest occupied and lowest vacant molecular orbitals of benzene ψ_3, ψ_5,[9] and the atomic orbitals of the substituent, ψ_t. Orbital energies produced as a result of interaction between ψ_3 and ψ_t and between ψ_5 and ψ_t then could be found by solving the determinantal equations

$$\begin{vmatrix} H_{jj} - E_j & H_{jt} - \Delta_{jt} E_j \\ H_{jt} - \Delta_{jt} E_j & H_{tt} - E_j \end{vmatrix} = 0, j = 3 \text{ and } 5 \tag{6}$$

where the notations for the matrix elements are the same as before. These are identically the same as eq. 5. Accordingly the solutions of these two equations are expected to give with considerable accuracy the perturbed highest occupied and lowest vacant orbital energies of benzene after the substituent has been introduced. In fact it will be shown in Sec. 4 that this interaction theory, based on eq. 5 or eq. 6, leads to the orbital energies which are very close to the ones computed from the complete secular equation.

3. Methods of Parameter Determination

Method I.—As has been mentioned, the wave function for the substituent is restricted to a π-type atomic orbital, next to a carbon atom of benzene. Three assumptions are made.

(1) A coulomb integral contribution $\delta_1\beta$ is manifest on the carbon atom adjacent to the substituent X due to the coulomb integral of the X atom $H_{tt} = \int \phi_t H \phi_t dv = \alpha + \delta_t\beta$, where α and β are the coulomb and bond integrals of unperturbed benzene, respectively. Accordingly, the coulomb integral of this carbon atom becomes $\alpha_1 = \int \phi_1 \cdot H\phi_1 dv = \alpha + \delta_1\beta$. This assumption is based on the fact that the electronegativity difference or polarity of the chemical bond between the substituent and the carbon atom will modify the potential acting on the π-electron systems and the main result of

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(5) Y. I'Haya, *J. Chem. Soc. Japan* (*Pure Chemistry Section*), **77**, 314 (1956).

(6) M. J. S. Dewar, *Proc. Cambridge Phil. Soc.*, **45**, 638 (1949). See also A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(7) See L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Co., New York, N. Y., 1935, p. 191ff.

(8) The reason for this is as follows: when eq. 3 and 4 are derived from the secular equation by the usual perturbation method, one assumes that the H_{jj} is the first approximation of the eigenvalue E_j and neglects off-diagonal matrix elements except H_{ji} and H_{ij}. If the perturbation is not small, this assumption is not justified. The errors arise mainly from the numerators of the third term of eq. 3 and of the second term of eq. 4.

(9) ψ_2 and ψ_4 states do not interact with the ψ_t state and remain unchanged.

TABLE I

Molecule	(O–O)[a] (cm.$^{-1}$)	Ionization[b] potential (e.v.)	Excitation energy	Z_0[c]	Z_v[c]
C_6H_6	38,089	9.24	-2.133333β	−0.800000	1.333333
C_6H_5F	37,818	9.19	-2.118155β	−0.767442	1.335535
C_6H_5Cl	37,052	9.07	-2.075251β	−0.666667	1.350502
C_6H_5Br	36,996	8.98	-2.072115β	−0.596899	1.413998
C_6H_5I	...	8.73	...	...	...

[a] H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941). [b] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [c] Z_o, Z_v = $(\alpha - E)/\beta$, where E's are the energies of the highest occupied and lowest vacant molecular orbitals, respectively.

this effect is a change of coulomb integral of the adjacent carbon atom.[10]

(2) The carbon atoms other than the one adjacent to X receive no such inductive effect.[11]

(3) The resonance integral γ_{ij} between atoms i and j is proportional to the overlap integral S_{ij} between the π-atomic orbitals of the two atoms.[12] With these three assumptions and carbon-carbon (1.39 Å.) overlap integral 0.25, eq. 6 becomes (see Appendix)

$$\begin{vmatrix} Z_0 + \frac{4}{5} + \frac{4}{15}\delta_1 & \frac{2}{\sqrt{15}} S_{cx}(Z_0 + 4) \\ \frac{2}{\sqrt{15}} S_{cx}(Z_0 + 4) & Z_0 + \delta_t \end{vmatrix} = 0 \quad (7)$$

and

$$\begin{vmatrix} Z_v - \frac{4}{3} + \frac{4}{9}\delta_1 & \frac{2}{3} S_{cx}(Z_v + 4) \\ \frac{2}{3} S_{cx}(Z_v + 4) & Z_v + \delta_t \end{vmatrix} = 0 \quad (8)$$

where S_{cx} is the π-overlap integral for the C–X bond and $Z = (\alpha - E)/\beta$; Z_o and Z_v correspond to the highest occupied and lowest vacant orbital energies for the substituted benzene.

In order to determine the empirical parameters δ_t and δ_1, one must use experimental data for Z_o and Z_v; we use (a) the shifts of the near ultraviolet absorption spectra relative to benzene and (b) the ionization potentials. Table I presents the energies of highest occupied Z_o and lowest vacant orbitals Z_v and the excitation energies of halogen-substituted benzenes computed from the observed values of ionization potentials[13] and O–O band frequencies.

In doing the actual computations of excitation energies and determinations of Z_o and Z_v values, the following additional assumptions are made:

(4) In mono-substituted benzenes, the original orbital degeneracy is removed by the perturbation of the attached substituent; we consider that the observed ionization potential corresponds to an average of the perturbed and unperturbed occupied orbital energies.

(5) An excitation energy computed without electron repulsion is supposed to give an average value of the actual excited levels.[14] Thus

$$\Delta E_{av} = (^1/_2)(E_5 + E_4 - E_3 - E_2) \qquad (9)$$

Table II gives the overlap integrals between halogen and carbon atoms computed by the formula of Mulliken, *et al.*,[15] together with the resonance integrals of the corresponding atom pairs. The table shows that the resonance integrals are not so different in four halogen substituted benzenes if assumption (3) above is accepted. (Further discussion of this problem is contained in Sec. 5.)

TABLE II

OVERLAP INTEGRALS AND EXCHANGE INTEGRALS

	Bond	Distance (Å.)	S_{cx}	γ_{cx} (e.v.)[b]
Benzene	C–C	1.39	0.25	−4.38[c]
Fluorobenzene	C–F	1.29	.148	−2.59
Chlorobenzene	C–Cl	1.69	.158	−2.77
Bromobenzene	C–Br	1.88	.153[a]	−2.68
Iodobenzene	C–I	2.00	.147	−2.57

[a] The 2pπ-4pπ overlap integral is assumed to be an average value of the C–Cl and C–I for the same atomic distances. [b] The γ's are assumed to be proportional to overlap integrals, with the benzene value taken as standard. [c] Computed as $\alpha = -7.18$ e.v. and $\beta = -2.58$ e.v. See ref. 14.

Using the values of Z_o and Z_v in Table I and S_{cx} in Table II, the empirical parameters δ_t and δ_1 are determined by solving the simultaneous equations 7 and 8, and are listed in Table III. It will be shown in the following section that the empirical parameters so derived are excellently

TABLE III

EMPIRICAL PARAMETERS COMPUTED FROM INTERACTION THEORY

Molecule	Method	δ_t	δ_1	α_t[a] (e.v.)	$\Delta\alpha_1$[b] (e.v.)
Fluorobenzene	I	1.437	0.220	−10.89	−0.57
	II	1.750	.280	−11.70	− .72
Chlorobenzene	I	1.031	.262	− 9.84	− .68
	II	1.169	.330	−10.20	− .85
Bromobenzene	I	0.906	.114	− 9.52	− .29
	II	0.997	.167	− 9.75	− .43

[a] Coulomb integral of halogen atom computed as $\alpha = -7.18$ e.v. and $\beta = -2.58$ e.v. [b] This column gives the coulomb integral depression for the carbon atom, number 1, attached to the substituent.

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(10) W. Moffitt, *Proc. Roy. Soc.* (*London*), **A202**, 548 (1950).

(11) Jaffé proposed from the view of chemical reactivity that one should take the coulomb integral increments in the *n*th carbon atom counted from the substituent atom X as $\epsilon^n\delta\alpha$ ($\epsilon = {}^1/_3$). This fact indicates that the inductive effect on carbon atoms not adjacent to the heteroatom is negligibly small. H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

(12) See reference 2a.

(13) Here the ionization potentials determined by a photoionization method have been adopted, because these data presumably yield values corresponding to vertical ionization. Ionization potentials measured from an electron impact experiment also seem to correspond to vertical ionization but, at present, the available data have not been found sufficiently accurate for use for this purpose. The former values are very close to the ones obtained from spectroscopic observations on Rydberg series.

(14) C. C. J. Roothaan and R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

(15) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *ibid.*, **17**, 1248 (1949).

suitable for the calculation of the complete secular equation and for the interpretation of several molecular properties.

Method II.—Although, as will be seen in the following section, the computational results of the electronic structures of fluoro- and chlorobenzenes made assuming the resonance integral γ to be proportional to the overlap integral can reproduce fairly well both excitation energies and spectral intensities, theoretical ground for this assumption remains unjustified. Mulliken[16] defines the bond integral β_{ij} between atoms i and j as

$$\beta_{ij} = \gamma_{ij} - \frac{1}{2} S_{ij} (\alpha_i + \alpha_j) \tag{10}$$

where

$$\gamma_{ij} = \int \phi_i H \phi_j \, dv, \; \alpha_i = \int \phi_i H \phi_i \, dv, \; S_{ij} = \int \phi_i \phi_j \, dv$$

and shows that theoretically computed β varies very nearly as S for two-center homopolar σ and π bonds in the range of 1.20–1.60 Å. Of course the relation $\beta/S \approx$ constant should be proved to be valid for heteropolar σ and π bonds in general as internuclear distance varies, but it seems that in view of the theoretical evidence an assumption of β proportional to S is more adequate than the one γ proportional to S.[17] In this paragraph, therefore, we derive the empirical parameters for halogen-substituted benzenes adopting this assumption. Making the substitutions

$$\gamma_{cx} = \beta_{cx} + \frac{1}{2} S_{cx} (\alpha_1 + \alpha_t) = \left[\frac{1}{2} (\delta_1 + \delta_t) + \frac{1}{S}\right] S_{cx}\beta + S_{cx}\alpha \tag{11}$$

and

$$Z = (\alpha - E)/\beta$$

we obtain simultaneous equations which determine the parameters δ_t and δ_1

$$\begin{vmatrix} Z_o + \frac{4}{5} + \frac{4}{15}\delta_1 & \frac{2}{\sqrt{15}}\left[Z_o + \frac{1}{2}(\delta_t + \delta_1) + \frac{1}{S}\right] S_{cx} \\ \frac{2}{\sqrt{15}}\left[Z_o + \frac{1}{2}(\delta_t + \delta_1) + \frac{1}{S}\right] S_{cx} & Z_o + \delta_t \end{vmatrix} = 0 \tag{12}$$

and

$$\begin{vmatrix} Z_v - \frac{4}{3} + \frac{4}{9}\delta_1 & \frac{2}{3}\left[Z_v + \frac{1}{2}(\delta_t + \delta_1) + \frac{1}{S}\right] S_{cx} \\ \frac{2}{3}\left[Z_v + \frac{1}{2}(\delta_t + \delta_1) + \frac{1}{S}\right] S_{cx} & Z_v + \delta_t \end{vmatrix} = 0 \tag{13}$$

In these equations, α and β are coulomb and bond integrals for benzene.

Using the experimentally determined values of Z_o and Z_v listed in Table I, we can estimate two parameters δ_t and δ_1 as before. The results are shown in Table III together with the results of the Method I. It is interesting to note that these values are not greatly different from corresponding ones obtained by Method I.

Method III.—In previous paragraphs the resonance integral γ_{cx} or the bond integral β_{cx} has been assumed to be proportional to the overlap integral S_{cx}. As has been mentioned previously, Mulliken demonstrated that the theoretically computed β varies very nearly as for the limited case,[18] but no computations have been made for any heteropolar bond. Even though we could precisely reproduce observed ionization potentials, the positions of the O–O bands, and spectral intensities, we have at present no theoretical evidence for this assumption. Accordingly, we here make an attempt to derive the appropriate γ_{cx} values treating them as the unknown parameters.

Using the same notations as before, the determinantal equations of Sec. 2 take the forms

$$\begin{vmatrix} H_{33} + \frac{4}{15}\delta_1\beta - E_o & \frac{2}{\sqrt{15}}(\gamma_{cx} - S_{cx}E_o) \\ \frac{2}{\sqrt{15}}(\gamma_{cx} - S_{cx}E_o) & H_{tt} - E_o \end{vmatrix} = 0 \tag{14}$$

and

$$\begin{vmatrix} H_{55} + \frac{4}{9}\delta_1\beta - E_v & \frac{2}{3}(\gamma_{ox} - S_{cx}E_v) \\ \frac{2}{3}(\gamma_{cx} - S_{cx}E_v) & H_{tt} - E_v \end{vmatrix} = 0 \tag{15}$$

Here H_{33} and H_{55} are the highest occupied and lowest vacant molecular orbital energies of benzene and are fixed as -9.24 and -3.74 e.v., respectively, by the ionization potential and ultraviolet absorption spectrum.[14] The values of E_o and E_v to be substituted in above equations are $\alpha - Z_o\beta$ and $\alpha - Z_v\beta$, respectively, and are computed as $\alpha = -7.18$ e.v. and $\beta = -2.58$ e.v.

From these two equations, we can see how the parameters γ_{cx} and δ_1 vary independently as a function of H_{tt}, the coulomb integral of the substituent atom. Figures 1 and 2 show that the values of γ_{cx} and δ_1 in halogen-monosubstituted benzenes vary linearly as H_{tt} for the range -9.5 to -14 e.v. A further interesting point to be noted is that the rate of increase of γ_{cx} and δ_1 with H_{tt} in fluorobenzene is different from those of chloro- and bromobenzene, while in the latter two cases the proportionality factors are similar. This situation will be discussed in Sec. 5. Now Figures 1 and 2 certainly throw light upon how the parameters γ_{cx} and δ_1 vary as a function of H_{tt}, but unfortunately we have at present no available data to determine the H_{tt} values precisely.[19,20] However, it may be expected that the values of H_{tt} lie approximately in the neighborhood of $-I_{CH_3X}$, the negative of the ionization potential of the substituted methane, because the ionization process in this case may probably be thought as the one corresponding to ionization of the lone pair elec-

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(16) R. S. Mulliken, *J. chim. phys.*, **46**, 497, 675 (1949).

(17) In computations neglecting overlap integrals, the difficulties mentioned in this paragraph do not arise, since β becomes identical with γ.

(18) Mulliken shows in ref. 16 that approximate proportionality of theoretical β values to S holds for two-center homopolar σ and π bonds except unusually short ones. For example, in the H_2 1s—1s bond this relation breaks down at the shorter distance than 1.20Å.

(19) An escape from this dilemma is the use of the data from experimental measurements of the asymmetry of the halogen nuclear electric quadrupole interaction. As the π-election loss of the halogen atom can be obtained approximately from such experiments, we can relate this to molecular orbital theory.

(20) R. Bersohn, *J. Chem. Phys.*, **22**, 2078 (1954); Y. I'Haya, read at the Symposium on π-electrons, Tokyo, 1955.

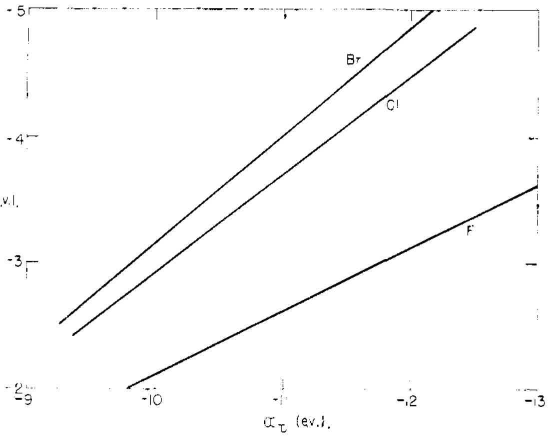

Fig. 1.—The relation of the resonance integral of the carbon-halogen bond in halogen-substituted benzene to the coulomb integral of the substituent halogen atom.

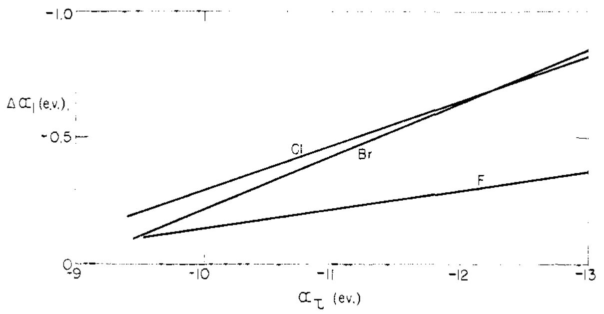

Fig. 2.—Coulomb integral depression caused by the inductive effect in halogen-substituted benzenes.

trons of the atom X. Using the H_{tt} values thus estimated, parameters γ_{cx} and δ_1 of halogen-substituted benzenes may be determined; they are given in Table IV.

TABLE IV

EMPIRICAL PARAMETERS COMPUTED FROM INTERACTION THEORY (METHOD III)

	$H_{tt}(= -I_{CH_3X})$[a] α_t (e.v.)	γ_{cx} (e.v.)	δ_1	$\Delta\alpha_1$[c] (e.v.)
Fluorobenzene	(-21.5)[b]	-3.37	0.334	-0.86
Chlorobenzene	-11.28	-3.91	.527	-1.36
Bromobenzene	-10.53	-3.57	.330	-0.85

[a] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [b] Assumed values. In Price's table (*Chem. Revs.*, 41, 257 (1947)) 15.0 e.v. was reported, but such a large value cannot be accepted as $-H_{tt}$ in this case. [c] See footnote *b* in Table III.

4. The Electronic Structures of Fluorobenzene and Chlorobenzene

We can solve the complete determinantal equations of mono-substituted benzenes using the empirical parameters derived by the three methods of Sec. 3. Under the assumptions adopted in the opening paragraph of that section, the secular equation including nearest neighbor overlap integrals has the form

$$\begin{vmatrix} \xi_t(Z+\delta_t) & S_{cx}/S & 0 & 0 & 0 \\ S_{cx}/S & \xi_1(Z+\delta_1) & 1 & 0 & 0 \\ 0 & 2 & Z & 1 & 0 \\ 0 & 0 & 1 & Z & 2 \\ 0 & 0 & 0 & 1 & Z \end{vmatrix} = 0 \quad (16)$$

Here $\xi_i = 1 - \delta_i S$ and $Z = (\alpha - E)/(\gamma - SE)$. The orbital energies computed for fluorobenzene and chlorobenzene are listed in Table V together with the ones which were calculated from approximate eq. 7 and 8. The last column shows that the interaction theory proposed in Sec. 2 predicts the perturbed orbital energies to a good approximation; *i.e.*, estimating the empirical parameters from this theory is justified.

TABLE V

COMPUTED ORBITAL ENERGIES OF FLUOROBENZENE AND CHLOROBENZENE: (METHOD I)[a]

	$Z(1)$[b,d]	$Z(2)$[c,d]	$\lvert Z(1) - Z(2)\rvert$
	Fluorobenzene		
$4b_1$	$+1.335514$	$+1.335513$	0.000001
$3b_1$	-0.767812	-0.767504	0.000308
$2b_1$	-1.278686	...	...
$1b_1$	-1.594053	...	...
	Chlorobenzene		
$4b_1$	$+1.350231$	$+1.350265$	0.000034
$3b_1$	-0.666272	-0.666793	0.000521
$2b_1$	-1.138648	...	...
$1b_1$	-1.453171	...	...

[a] The energies of the upper orbitals are omitted, and also the energies of unperturbed ψ_2 and ψ_4 orbitals ($\alpha + 4/5\,\beta$ and $\alpha - 4/3\,\beta$, respectively) are not listed. [b] Computed from eq. 16. [c] Computed from eq. 7 and 8. [d] See footnote *c* of Table I.

Excitation energies computed from the assumption (11), ionization potentials, and wave length shifts (relative to benzene) are given in Table VI. The oscillator strength is given by[21]

$$f = 1.085 \times 10^{11} \nu Q^2 \quad (17)$$

where ν is the frequency of absorption in cm.$^{-1}$. Q, the dipole strength for the transition, has the following form for excitation of the benzene ring[22]

$$Q = 2^{1/2}[\chi_2 r \chi_5\, dv + \int \chi_3 r \chi_4\, dv] \quad (18)$$

Here the χ_i are the molecular orbitals of the mono-substituted benzene and r is the coördinate of electrons perpendicular to figure axis. Calculated f-values are shown in the last column of Table VI. The agreement between the computed and observed values is fairly satisfactory.

Following the formulation of Chirgwin and Coulson,[23] the total π-electron density q_μ on atom

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(21) R. S. Mulliken and C. A. Rieke, *Repts. Prog. Phys.*, **8**, 231 (1941).

(22) For mono-substituted benzenes, we assume a set of hypothetical states with the electron configuration

$$\begin{aligned} &\Psi(Y){:}\quad (\chi_0)^2(\chi_1)^2(\chi_2)(\chi_3)^2(\chi_5) \\ &\Psi(Y'){:}\quad (\chi_0)^2(\chi_1)^2(\chi_2)^2(\chi_3)(\chi_4) \\ &\Psi(Z){:}\quad (\chi_0)^2(\chi_1)^2(\chi_2)(\chi_3)^2(\chi_4) \\ &\Psi(Z'){:}\quad (\chi_0)^2(\chi_1)^2(\chi_2)^2(\chi_3)(\chi_5) \end{aligned}$$

The wave function of the lowest lying singlet state is written as follows by analogy with the corresponding $^1B_{2u}$ state of benzene

$$\Psi(V) = [\Psi(Y) - \Psi(Y')]/2^{1/2}$$

although $\Psi(Y)$ and $\Psi(Y')$ for benzene are degenerate so that the coefficients should be equal in magnitude, for mono-substituted benzenes, they are no longer degenerate and the coefficients should be slightly altered. Matsen discussed the errors resulting from neglecting overlap integrals: THIS JOURNAL, **72**, 5243 (1950). See also, R. S. Mulliken, *J. Chem. Phys.*, **7**, 353 (1939). However, the results of the author or of many others show that the errors are probably not too serious. See Y. I'Haya, *Bull. Chem. Soc. Japan*, **28**, 369 (1955).

(23) B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc. (London)*, **A201**, 196 (1950).

TABLE VI

EXCITATION ENERGIES, IONIZATION POTENTIALS, POSITIONS OF THE O–O BAND, AND OSCILLATOR STRENGTHS OF FLUOROBENZENE AND CHLOROBENZENE

	Method	Excitation energy (in β) Calcd.	Excitation energy (in β) Obsd.	I_P (e.v.) Calcd.[a]	I_P (e.v.) Obsd.	λ(O–O), (Å.) Calcd.	λ(O–O), (Å.) Obsd.[d]	$f \times 10^3$ Calcd.	$f \times 10^3$ Obsd.
	I	−2.118329		9.200		2644		8.02	
C_6H_5F	II	−2.118598	−2.118155	9.200	9.19[b] 9.197[c]	2643	2644	5.22	9[e]
	III	−2.118532		9.200		2644		6.31	
	I	−2.074918		9.070		2699		2.12	
C_6H_5Cl	II	−2.075035	−2.075251	9.069	9.07[b]	2699	2699	1.13	1[f] 3[e]
	III	−2.075126		9.070		2699		1.02	

[a] Computed as $\alpha = -7.18$ e.v. and $\beta = -2.58$ e.v. [b] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [c] Spectroscopic data, V. G. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Disc. Faraday Soc.*, **9**, 53 (1950). [d] H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941). [e] Sponer and Lowe, *J. Opt. Soc. Am.*, **39**, 840 (1941). [f] R. S. Mulliken and C. A. Rieke, "Reports on Progress in Physics," **VIII**, 231 (1941).

μ and the mobile bond order $p_{\mu\nu}$ between adjacent atoms μ, ν can be calculated from the formulas

$$q_\mu = \sum_{j=1}^{n} n_j x_{j\mu} y_{j\mu} \tag{19}$$

and

$$p_{\mu\nu} = 1/2 \sum_{j=1}^{n} n_j (x_{j\mu} y_{j\nu} + x_{j\nu} y_{j\mu}) \tag{20}$$

where the y_1 are the "covariant" coefficients associated with x_j and are defined by

$$y_{j\mu} = \sum_{\nu=1}^{n} S_{\mu\nu} x_{j\nu} \tag{21}$$

and

$$\sum_{\nu=1}^{n} x_{j\nu} y_{j\nu} = 1 \quad (j = 1, 2, \ldots, n) \tag{22}$$

In eq. 19–22, the summation is over all the occupied MO's j and n_j is the number of electrons occupied in the jth MO. Migrations of the π-electron charge and the mobile bond orders thus obtained are shown in Table VII. The results seem to be in satisfactory accord with what one expects from the directing properties according to the simple theory of chemical reactivity.

For the purpose of examining how the parameters determined by Methods II and III reproduce several molecular properties, similar molecular orbital calculation of electronic structures of fluoro- and chlorobenzenes were carried out. Also in these cases it turns out that the interaction theory can predict the highest occupied and lowest vacant orbital energies with considerable accuracy, although the results are not listed here. Excitation energies, ionization potentials, wave length and oscillator strengths of absorption computed from the complete secular equations are given in Table VI and the π-electron charge displacement and mobile bond orders in Table VII. It is seen that the agreement with the corresponding observed values is quite satisfactory.

5. Comparison of the Three Methods

Although it may be stated that the interaction theory appears very promising for the computation of the orbital energies after the perturbation is introduced, the problem of estimating empirical parameters such as γ_{cx}, α_t and δ_1 still remains unsettled. We now turn to the comparison of the three methods and of the parameters obtained by making use of the individual methods. Of the assumptions used in Methods I and II separately, it already has been emphasized in the first paragraph of Sec. 3 that the latter should be more acceptable than the former in view of purely theoretical evidence.

The parameters which have been obtained from the three methods are gathered and compared with one another in Table VIII. Referring to this table, it is of interest to note that both the resonance integral γ_{cx} and the bond integral β_{cx} tend to be proportional to overlap integral S_{cx} except for γ_{cx} in fluorobenzene and bromobenzene from Method II, in spite of the particular assumptions in the different methods. This trend already has been illustrated in Fig. 2, and it may be stated that the resonance integral or bond integral of the C–X bond should become smaller in the sequence: chloro-, bromo- and fluorobenzene, unless extremely unreasonable value are assigned to the coulomb integral of the halogen atom. The conjugative effect therefore should become smaller in this order.

So far as the inductive parameter δ_1 is concerned, the three methods all present the increasing trend: chlorine, fluorine and bromine. The statement that the Cl atom exerts a greater inductive effect on the benzene ring than the F atom seems to be incompatible with the empirical evidence conventionally quoted, but some support of this result has been reported in connection with the discussion of the dipole moments.[24]

All of the computations reproduce quite satisfactorily the observed ionization potentials, excitation energies and spectral intensities, so we cannot conclude definitely which is the best method. However, as has been mentioned in ref. 20, there are other available data from nuclear quadrupole interaction. Experimental measurements of the asymmetricity of the halogen nuclear quadrupole

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(24) I. Watanabe, *Rep. Inst. Phys. Chem. Res. Tokyo*, **21**, 468 (1942), and see also, K. Higasi, "Fundamental Theory of Molecular Structure" (in Japanese), Kawade Publishing Co., Tokyo, 1952, p. 20. The author is indebted to Prof. Higasi for his kindness in giving suggestions on this matter.

TABLE VII

THE π-ELECTRON CHARGE DISPLACEMENTS AND MOBILE BOND ORDERS IN FLUOROBENZENE AND CHLOROBENZENE[a]

	Method	π-Electron charge displacements 1	2	3	4	7
	I	−0.0449	−0.0006	+0.0002	−0.0010	+0.0468
C_6H_5F	II	− .0524	− .0006	.0000	− .0020	+ .0556
	III	− .0762	− .0008	.0000	− .0025	+ .0803
	I	− .0357	− .0081	+ .0003	− .0145	+ .0658
C_6H_5Cl	II	− .0724	− .0064	+ .0002	− .0101	+ .0950
	III	− .1029	− .0098	.0000	− .0147	+ .1371

	Method	Mobile bond orders 1–2	2–3	3–4	1–7
	I	0.6528	0.6673	0.6661	0.2096
C_6H_5F	II	.6492	.6678	.6658	.2305
	III	.6417	.6682	.6641	.2614
	I	.6365	.6676	.6671	.2837
C_6H_5Cl	II	.6370	.6703	.6641	.2957
	III	.6230	.6727	.6628	.3480

[a] The atoms are numbered from the carbon atom, number 1, to which the substituent atom, number 7, is attached.

TABLE VIII

COMPARISON OF EMPIRICAL PARAMETERS DERIVED FROM THREE METHODS[a,b,c]

	C_6H_5F				C_6H_5Cl				C_6H_6Br			
Method	β_{cx}	γ_{cx}	α_t	$\Delta\alpha_1$	β_{cx}	γ_{cx}	α_t	$\Delta\alpha_1$	β_{cx}	γ_{cx}	α_t	$\Delta\alpha_1$
I	−1.21	−2.59	−10.89	−0.57	−1.40	−2.77	− 9.84	−0.68	−1.38	−2.68	− 9.52	−0.29
II	−1.53	−2.98	−11.70	−0.72	−1.63	−3.07	−10.20	−0.85	−1.58	−2.91	− 9.75	−0.43
III	−1.85	−3.37	−12.5	−0.86	−2.34	−3.91	−11.28	−1.36	−2.15	−3.57	−10.53	−0.85

[a] All in electron volt units. [b] See footnotes *a* and *b* in Table III. [c] For overlap integrals of the carbon–halogen π-bonds, see Table II.

coupling[25,26] show that the π-electron losses of the halogen atom in *p*-dichlorobenzene and *p*-dibromobenzene are approximately 0.03e and 0.06e, respectively. Although these experiments involve considerable uncertainties both in measurements of the asymmetricity and in estimation of the π-electron loss, if this is so, the π-electron migrations in Table VII are too big. As this π-electron migration tends to decrease with the increase of α_t (note that the value of α_t is the negative), we should expect that the α_t values of fluoro-, chloro- and bromobenzenes should be a little larger than −10.89, −9.84 and −9.52 e.v., respectively. Of course we cannot say definitely what should be done in this connection because of the obscurities in the interpretation of the data from nuclear quadrupole coupling measurements.

In conclusion, while the three methods have about equal reliability for the reproduction of data, Method III is preferable from the standpoint of the assumptions required. Of course for this method, α_t should be given values in the neighborhood of the ones listed in the first line of Table VIII rather than the values of the last line.

6. Discussion

This paper has studied the validity and general application of a simple interaction theory with special reference to the method of parameter determination. Although illustrations were taken from halogen-monosubstituted benzenes, extensive other applications should be possible. For example, applications to aniline, nitrobenzene, acetophenone, etc., will be of much interest, particularly because strong charge transfer or electron migration effects should occur in these molecules. Nagakura and Tanaka[27] have pointed out that the interaction between the highest occupied and lowest vacant molecular orbitals of benzene and the substituent should play an important role in the electron migration effect of *meta*-directing molecules. Contrary to their treatment of the interaction as involving only two orbitals, it has been demonstrated in this paper that a treatment including three orbitals, one from the substituent and two others from benzene, is more successful for the computations of molecular energy levels.

In order to obtain a clearer understanding of molecular energy levels and empirical parameters, the conjugative and inductive effects are once again discussed in the following Part II in terms of a mixing of the locally excited states of benzene and charge transfer states.

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Appendix

Matrix Elements of the Secular Equation for Mono-substituted Benzenes.—Under the assumptions (1) and (2) of Sec. 3, the matrix elements of the secular equation not zero are as

$$H_{11} = \alpha + (4/3)\beta + (1/9)\delta_1\beta \qquad H_{13} = 2/(3\sqrt{5})\delta_1\beta$$
$$H_{22} = \alpha + (4/5)\beta \qquad H_{15} = (2/9)\delta_1\beta$$
$$H_{33} = \alpha + (4/5)\beta + (4/15)\delta_1\beta \qquad H_{16} = 1/(3\sqrt{3})\delta_1\beta$$
$$H_{44} = \alpha - (4/3)\beta \qquad H_{35} = 4/(3\sqrt{15})\delta_1\beta$$
$$H_{55} = \alpha - (4/3)\beta + (4/9)\delta_1\beta \qquad H_{36} = 2/(3\sqrt{5})\delta_1\beta$$
$$H_{66} = \alpha - 4\beta + (1/3)\delta_1\beta \qquad H_{56} = 2/(3\sqrt{3})\delta_1\beta$$
$$H_{77} = \alpha + \delta_t\beta$$

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(25) S. Kojima, K. Tsukada and Y. Hinaga, *J. Phys. Soc. Japan*, **10**, 498 (1955).

(26) H. C. Meal, THIS JOURNAL, **74**, 6121 (1952).

(27) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

$$H_{17} = (1/3)S_{\mathrm{cx}}\gamma_{\mathrm{cx}} \qquad \Delta_{17} = (1/3)S_{\mathrm{cx}}$$

$$H_{37} = (2/\sqrt{15})S_{\mathrm{cx}}\gamma_{\mathrm{cx}} \qquad \Delta_{37} = (2/\sqrt{15})S_{\mathrm{cx}}$$

$$H_{57} = (2/3)S_{\mathrm{cx}}\gamma_{\mathrm{cx}} \qquad \Delta_{57} = (2/3)S_{\mathrm{cx}}$$

$$H_{67} - (1/\sqrt{3})S_{\mathrm{cx}}\gamma_{\mathrm{cx}} \qquad \Delta_{67} = (1/\sqrt{3})S_{\mathrm{cx}}$$

where

$$\gamma_{\mathrm{cx}} = \int \phi_{\mathrm{l}} H \phi_{\mathrm{t}}\, \mathrm{d}v,\ S_{\mathrm{cx}} = \int \phi_{\mathrm{l}}\phi_{\mathrm{t}}\, \mathrm{d}v$$

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Some Studies in Molecular Orbital Theory. II

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Conjugative and inductive effects in substituted benzenes are scrutinized by means of a second-order perturbation method based on molecular orbital theory including electron interaction but neglecting overlap. It is found that a mixing of the one- and two-electron excited states of benzene and the so-called electron transfer states which arise from the transfer of an electron from the substituent to benzene play an important role in determining the energies of the lower electronic states of substituted benzene. The conjugative and inductive parameters are determined for chlorobenzene, bromobenzene and phenol using the observed ionization potentials and the spectral shifts of the lowest L_b bands in these molecules. The agreement between the computed and observed energies of the lower electronic states in these molecules is satisfactory for the L_a band, not so good for the B_b band.

1. Introduction

In the previous paper,[2] a general interpretation of the conjugative and inductive effects was given with special reference to the first ionization potentials and the spectral shifts of the O–O bands in substituted aromatic hydrocarbons, particularly halogen-monosubstituted benzenes. Essentially the method was based on an effective one-electron Hamiltonian including overlap integrals but neglecting electron interactions. Although this method should be promising for the semi-quantitative interpretation of electronic spectra in substituted aromatic hydrocarbons, it is desirable to get a more detailed picture of the spectra by taking account of electron interaction.

Recently, Pariser and Parr,[3a] and Pople[3b] have put forth a useful idea for evaluation of the effect of electron interaction without rigorous computation of complicated integrals, and showed how their treatment including electron interaction accounts for many detailed features of the electronic spectra of an aromatic hydrocarbon. An important feature of the method consists of expressing the lowest excited states of an aromatic hydrocarbon as combinations of various configurations in which one or more electrons in the ground state have been excited to higher vacant orbitals. The method seems to be useful for discussing the effect of perturbations which are caused by introduction of the substituent, because it appears reasonable to expand the lower electronic states of a substituted hydrocarbon in terms of the corresponding lower states of the unperturbed hydrocarbon neglecting the various higher electronic states. Recently Murrell, *et al.*,[4] have in fact investigated in just such a manner the effects of conjugation and induction in some substituted benzenes, and they determined the empirical parameters from the shifts of the lowest $A_{1g} \rightarrow {}^1B_{2u}$ transitions.

Mixing of the one- and two-electron excited states of the hydrocarbon and the so-called "electron transfer" states plays an important role in both the electron migration and induction effects. In this paper, discussion will be given of the four main singlet–singlet transitions of substituted benzenes which Platt called L_b, L_a, B_b, and B_a, making use of second-order perturbation theory and configuration interaction; the conjugative and inductive parameters will be determined using the observed ionization potentials and the spectral shifts of the lowest L_b bands.

2. General Consideration of Configurations

The ground state configuration of an alternant hydrocarbon Ψ_0 can be written as an antisymmetrized product (Slater determinant) built up from orthogonal molecular orbitals ψ_1, ψ_2, ----, ψ_n which are linear combinations of carbon $2p_\pi$ atomic orbitals ϕ_1, ϕ_2, ----, ϕ_{2n}

$$\Psi_0 = \left(\frac{1}{(2n)!}\right)^{1/2} \sum_p (-1)^P \{(\psi_1\alpha)(\psi_1\beta)(\psi_2\alpha) \cdots\cdots (\psi_n\beta)\} \quad (1)$$

$$\psi_{\mathrm{i}} = \sum_{\mu=1}^{2n} \chi_{\mathrm{i}\mu}\phi_\mu \qquad (i = 1, 2, \cdots\cdots, n) \quad (2)$$

We shall be interested only in the two highest occupied orbitals ψ_{i}, ψ_{j}, and the two lowest vacant ones ψ_{k}, ψ_{l}, and so we abbreviate the notation for the ground state configuration ψ_0 as

$$\Psi_0 = |(\psi_{\mathrm{i}}\alpha)(\psi_{\mathrm{i}}\beta)(\psi_{\mathrm{j}}\alpha)(\psi_{\mathrm{j}}\beta)| \quad (3)$$

We write $\Psi_{\mathrm{i}}^{\mathrm{k}}$ for the singlet configurational wave function in which one electron is raised from an occupied orbital ψ_{i} to a vacant one ψ_{k}. This singly excited configuration $\Psi_{\mathrm{i}}^{\mathrm{k}}$ will be a sum of two Slater determinants[5] and is written as

$$\Psi_{\mathrm{i}}^{\mathrm{k}} = 2^{-1/2}\{|(\psi_{\mathrm{i}}\alpha)(\psi_{\mathrm{k}}\beta)(\psi_{\mathrm{j}}\alpha)(\psi_{\mathrm{j}}\beta)| + |(\psi_{\mathrm{i}}\beta)(\psi_{\mathrm{k}}\alpha)(\psi_{\mathrm{j}}\alpha)(\psi_{\mathrm{j}}\beta)|\} \quad (4)$$

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(2) Part I of this series, THIS JOURNAL, **81**, 6120 (1959).

(3) (a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953). (b) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

(4) (a) J. N. Murrell and H. C. Longuet-Higgins, *ibid.*, **A68**, 329 (1955); (b) J. N. Murrell, *ibid.*, **A69**, 969 (1956); (c) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).

(5) The corresponding triplet wave function is

$${}^3\Psi_{\mathrm{i}}^{\mathrm{k}} = \sqrt{\tfrac{1}{2}}\{|(\psi_{\mathrm{i}}\ \alpha)(\psi_{\mathrm{k}}\ \beta)(\psi_{\mathrm{j}}\ \alpha)(\psi_{\mathrm{j}}\ \beta)| - |(\psi_{\mathrm{i}}\ \beta)(\psi_{\mathrm{k}}\ \alpha)(\psi_{\mathrm{j}}\ \alpha)(\psi_{\mathrm{j}}\ \beta)|\}$$

but is not considered in this paper.