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MOLECULAR ORBITAL TREATMENT OF SUBSTITUTED BENZENE SPECTRA

by

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PREFACE

Originally, it had been planned to undertake a short problem on the spectral intensities of polysubstituted benzenes. But it soon became evident that previous theoretical treatments were inadequate and that a deeper insight into monosubstituted benzene spectra would first be needed. This thesis is the result of these efforts to understand monosubstituted benzenes.

I. INTRODUCTION

Since the advent of the quantum theory in the late 1920's, chemists are turning more and more to the description of molecules through Quantum Mechanics. This movement received its impetus from the initial success in the description of the gross properties of simple molecules.

As Ross (1) has so eloquently put it, chemical quantum mechanics is essentially an art, for the Schrödinger equation does not admit analytic solutions for systems of more than two particles. While exact solutions may be obtained in certain particular cases, these are often not sufficiently general to afford insight into classes of molecules. The theoretical chemist then finds one of his tasks is to devise approximations which will permit solving the Schrödinger equation for sufficiently general cases, that useful chemical information may be obtained. This has resulted in a number of assumptions and methods void of any physical "proof". The well-known Heitler-London and empirical molecular orbital methods, for example, stand on tenuous physical ground. Even the much used π - electron description of conjugated molecules has little *a priori* theoretical basis. The real justification, then, has been agreement of theoretical descriptions with experiment.

Since many calculations of molecular properties, using one or another simplified framework, have appeared in the literature, a word of caution is in order. It is frequently very difficult to assess the effect of the most basic assumptions on calculated quantities. This has resulted in calculations in which no regard is paid to their influence. Indeed, the basic simplicity of the simplest form of the empirical molecular orbital method makes it too easy for the uncritical to compute important molecular quantities. Two examples will make this clear: Energy levels are not very sensitive to the wave functions, but charge densities are; hence charge densities obtained from calculations of energy levels, without critical consideration of inductive effects, uncertainties in bond and core integrals, etc., are likely to be poor. The neglect of electron repulsion integrals in resonance energy calculations is another example where simplifying assumptions may profoundly influence the result.

Therefore, the worth of molecular quantum mechanics is best brought out, not in the detailed quantitative description, but in the qualitative physical picture that oversimplified wave mechanical models afford. The notion of resonance, for instance, has radically influenced chemical thinking. Another example is the idea of lone-pair moment as opposed to the exact calculation of molecular dipole moments. One can only feel that until such diverse problems as core effects, validity of the π-electron approximation and of calculation of excited state energies from a ground state Hamiltonian are understood--to mention only three examples--the significant contributions of quantum mechanics to the chemist will be more conceptual than numerical.

In this thesis, a particular approximate method, the semi-empirical molecular orbital procedure, is modified and tested on three representative conjugated hydrocarbons. The method is then applied to substituted hydrocarbons. In addition, a treatment of transitions arising from localized non-bonding electrons to excited delocalized states is formulated, and some consideration is given to the effect of substitutions on transitions arising from a normal ground state to an excited σ-state, the so-called N-Q transition --all within the molecular orbital framework. Finally, the theory is applied to the specific case of substituted benzenes, and certain theoretical predictions are made regarding the spectra of this class of molecules.

The thesis is divided into six main chapters. Chapters II and III comprise an exposition of a general theory of substituted conjugated hydrocarbons. Chapter IV is devoted to the application of the theory to substituted benzenes; the mathematical form that the theory takes in this special case, the empirical parameters, and calculation of integrals are all discussed in this chapter, which also considers previous treatments of substituted benzenes. Chapter V lists the major conclusions, and VI gives a brief summary.

II. A MODIFICATION OF THE NAIVE SEMI-EMPIRICAL MO METHOD

A. Basic Approach

In this section we formulate a general approach to substitution of conjugated hydrocarbons. The framework is that of the familiar π-electron approximation, in which explicit account is taken only of those electrons occupying molecular orbitals (MO's) which are antisymmetric to the molecular plane, the σ-electrons being considered only by their influence upon the effective field in which the π-electrons move. In a later section, this framework is extended to the non-bonding (n) electrons which are σ in symmetry type but are rather sharply differentiated from the remaining bonding electrons.

B. Semi-Empirical Treatment of Monosubstitution

We consider first a conjugated hydrocarbon of N conjugated carbon atoms, each of which is regarded as being in a state of sp^2 hybridization and having an identical effect on its π-electron. In addition, we assume that the π MO's and orbital energies are known for the hydrocarbon. These may be obtained, say by detailed self-consistent-field (SCF) or semi-empirical treatment, although the final results will depend to some extent on this choice. In either case, the MO's are taken as a linear combination of atomic orbitals (LCAO) and are given by

$$\Phi_j = \sum_{u=1}^{N} C_{ju}\phi_u \quad (j=1 \ldots N), \qquad (2.1)$$

where the ϕ_u are $2p\pi$ carbon atomic orbitals (AO's). Φ_j must transform according to the irreducible representation of the molecular point group; the role of symmetry in the formulation will be discussed further on.

We begin by utilizing Dewar's (2) formulation of molecular orbital theory in terms of linear combinations of molecular orbitals (LCMO), but inquire somewhat more critically into several steps of this process. One uses the set of orbitals Φ_j of the reference hydrocarbon (eq. 1) as the basis for a perturbation treatment (Dewar) in which the perturbing function is that of the π orbital on the substituent, Φ_X. We should notice that in general, Φ_X is not orthogonal to Φ_j, $j = 1 \ldots N$, although the latter set is orthonormal.

In the simplified MO approach which we are using, it is assumed implicitly that the Hamiltonian can be divided into a linear combination of one-electron effective Hamiltonians, and furthermore, that a simple product wave function, not antisymmetrized, is a satisfactory representation of the correct wave function. With these assumptions, minimization of the total energy is equivalent to minimization of the energy of the individual MO's, with the restriction that they remain mutually orthogonal. From the energy minimization or from the perturbation treatment, one obtains a secular equation of degree (N + 1) which can be solved to obtain the orbital energies and the orbital wave functions, ψ_i. The latter is a linear combination of the Φ_j and Φ_X:

$$\psi_i = \sum_{j=1}^{N+1} a_{ij}\Phi_j \quad (i = 1 \ldots N+1), \qquad (2.2)$$

in which Φ_{N+1} is taken as Φ_X.

In the event that the substituted molecule has no symmetry (above that of a plane of reflection in the molecular plane) no reduction in size of the secular equation is possible. The form of the determinant is then identical with (2.3) below, but is (N+1)-dimensional. Should the monosubstituted hydrocarbon possess some other twofold symmetry element, either a twofold axis, a vertical plane of symmetry, or both, then reduction in size of the secular equation is possible. In particular, for the case of C_{2V} symmetry, which is the highest symmetry a monosubstituted hydrocarbon may possess, K of the N + 1 orbitals, including Φ_x, will belong to the B_2 irreducible representation (antisymmetric to C_2 and symmetric to σ_v), while L = N + 1 - K will belong to A_2 (symmetric to C_2 and antisymmetric to σ_v). As a result, the secular equation is factorable into two parts, one Kth order equation (eq. 2.3), and one Lth order equation (eq. 2.4).

$$\begin{vmatrix} H_{11}-E & \cdots\cdots & H_{1j} & \cdots\cdots & H_{1x}-S_{1x}E \\ \cdot & \cdots\cdots & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot & \cdots\cdots & \cdot \\ H_{j1} & \cdots\cdots & H_{jj}-E & \cdots & H_{jx}-S_{jx}E \\ \cdot & \cdots\cdots & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot & \cdots\cdots & \cdot \\ H_{x1}-S_{x1}E & \cdots & H_{xj}-S_{xj}E & & H_{xx}-E \end{vmatrix} = 0 \qquad (2.3)$$

$$\begin{vmatrix} H_{ii} - E & \cdots\cdots & H_{ik} \\ \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot \\ H_{ki} & \cdots\cdots & H_{kk} - E \end{vmatrix} = 0 \qquad (2.4)$$

Equations (2.3) and (2.4) take explicit account of the fact that Φ_x is orthogonal to the A_2 orbitals by symmetry, but not orthogonal to those of the set having B_2 symmetry. H_{ij} is here defined as $\int \Phi_i H \Phi_j dv$, in which H is the total Hamiltonian of the substituted hydrocarbon. S_{ij} is the corresponding overlap integral.

The total Hamiltonian is now divided into a linear combination of two parts: a term H^o, which has as eigenfunctions the Φ_j of equation (2.1), and a perturbation term H', due to the substituent. This of course glosses over the question of electron interaction, but the procedure will be partially justified later. The matrix elements may now be written:

$$H_{ij} = \int \Phi_i H \Phi_j dv = H^o_{ij} \delta_{ij} + H'_{ij} \qquad \text{for } i, j \neq x$$

$$H_{ix} = H_{xi} = H^o_{ix} + H'_{ix} \qquad (2.5)$$

We now expand the off-diagonal elements not involving Φ_x $(i \neq j \neq x)$ by using equation (2.1).

$$H'_{ij} = \sum_{u=1}^{N} \sum_{w=1}^{N} C_{ju}C_{iw}\int \phi_u H' \phi_w dv = \sum_{u=1}^{N} C_{ju}C_{iu}\int \phi_u H' \phi_u dv$$

$$+ \sum_{\substack{u=1 \\ u \neq w}}^{N} \sum_{w=1}^{N} C_{ju}C_{iw}\int \phi_u H' \phi_w dv. \qquad (2.6)$$

The integral $\int \phi_u H' \phi_u dv$ is the increment in the Coulomb integral of the uth carbon atom in the hydrocarbon arising from the presence of the substituent. Similarly, $\int \phi_u H' \phi_w dv$ is the increment in the exchange integral between carbon atoms u and w. It is clear that these are just the quantities that have been attributed to the inductive effect by Coulson and Longuet-Higgins in the LCAO method (3). Solution of an LCMO equation for this effect is considerably simpler than the equivalent LCAO formulation, but we will defer further details on this point to Section E.

We now turn to the matrix elements involving i or j = x. These are:

$$H_{jx} = \sum_{u=1}^{N} C_{ju}\left[\int \phi_u H^o \, \Phi_x dv + \int \phi_u H' \, \Phi_x dv\right]$$

$$H_{xx} = \int \Phi_x H^o \, \Phi_x dv + \int \Phi_x H' \, \Phi_x dv \qquad (2.7)$$

At this point especial caution is needed in the interpretation of H'_{xx}. The arbitrary separation of the Hamiltonian into two parts $H^o + H'$ was made on the basis of choosing H^o so that Φ_i of equation (2.1) were its eigenfunctions. As a result, H' must contain not only terms arising from the substituent alone, but also electron repulsion terms arising from the perturbation of the electron arrangement of the parent hydrocarbon resulting from the presence of the substituent. Examination of the magnitude to be expected from the latter terms shows them to be very significant, and in addition, very sensitive to the perturbed charge distribution. It is therefore quite incorrect to assume that Φ_x can be taken as an eigenfunction of H', i.e., $H' \, \Phi_x = E_x \, \Phi_x$ corresponding to an eigenvalue of the free substituent radical. Such an assumption does indeed permit a theoretical calculation of H_{jx} and H_{xx} as Sklar and Herzfeld have done (4,5) (with additional assumptions as well), but their procedure must be regarded as fundamentally in error as a result. Evaluation of the matrix elements H'_{ix} and H'_{xx} must be carried out through an empirical process, and the values thus obtained have, in general, no relation to those obtained by the Sklar-Herzfeld procedure. Alternatively, H could have been broken up in the following manner: $H = H^{o'} + H''$. Here, H'' represents the SCF Hamiltonian for the free substituent, so that $H'' \Phi_x = E_x \Phi_x$ rigorously. In this case, however, $H^{o'}$ contains electron interaction terms in addition to those in H^o, and determines by an empirical procedure a new set of coulomb and exchange integrals for the hydrocarbon atoms, not equal to those for the parent hydrocarbon.

We now turn to the consideration of the determinantal equations (2.3) and (2.4). The solution of (2.4) is straightforward. The roots are dependent only upon the inductive effect, and in general are not equal to the corresponding hydrocarbon orbital energies. The exact solutions of (2.3) yield an expression which can be solved for any energy level by an iterative procedure. In the advent of a small perturbation which leaves E near one H_{ii}, but not close to any other H_{ii}, one can reduce the secular equation (which is equivalent to generalized perturbation theory) to the equations of ordinary second order perturbation theory, by neglecting all the off-diagonal elements except those in the ith row or rth column. One obtains for any orbital energy:

$$E_j = H_{jj} + \sum_{i=1}^{N+1}{}' \frac{(H_{ji} - S_{ji}H_{ii})^2}{H_{jj} - H_{ii}}, \tag{2.8}$$

in which the prime indicates omission of the term $i = j$. This expression may be rewritten with application of equation (2.5) to give:

$$E_j = H_{jj} + \sum_{i=1}^{N}{}' \frac{(H'_{ji})^2}{H_{jj} - H_{ii}} - \frac{(H_{jx} - S_{jx}H_{jj})^2}{H_{xx} - H_{jj}}, \quad j \neq x \tag{2.9}$$

$$E_x = H_{xx} + \sum_{i=1}^{N} \frac{(H_{xi} - S_{xi}H_{xx})^2}{H_{xx} - H_{ii}}$$

Equation (2.9) admits simple physical interpretation: If the integrals in equation (2.6) defining the inductive effect are zero, then the first equation of (2.9) becomes:

$$E_j = H^o_{jj} + \frac{\left(H_{jx} - S_{jx}H^o_{jj}\right)^2}{H^o_{jj} - H_{xx}} \; . \qquad (2.10)$$

The second equation of (2.9) remains unchanged. The latter, together with (2.10), is the generalization of Matsen's formulas for the resonance effect in substituted benzenes (6). If there is no resonance interaction between the substituent and hydrocarbon,

$$E_j = H_{jj} + {\sum_{i=1}^{N}}' \frac{\left(H_{ji}\right)^2}{H_{jj} - H_{ii}}$$

$$E_x = H_{xx} \qquad (2.11)$$

Equations (2.11) are formally identical to the formulas of Coulson and Longuet-Higgins for the influence of the inductive effect on orbital energies (3).

The total energy (the sum over the energies of the occupied MO's) of the ground state assuming a closed shell configuration*, $\psi_1^2 \ldots\ldots \psi_{N/2}^2 \, \psi_x^2$, is

$$E_g = 2\sum_{j=1}^{N/2} H_{jj} + 2H_{xx} + 2\sum_{j=1}^{N/2} {\sum_{i=1}^{N}}' \frac{(H'_{ji})^2}{H_{jj} - H_{ii}}$$

$$- 2\sum_{j=1}^{N/2} \frac{(H_{jx} - S_{jx}H_{jj})^2}{H_{jj} - H_{xx}} - 2\sum_{i=1}^{N} \frac{(H_{xi} - S_{xi}H_{xx})^2}{H_{xx} - H_{ii}}. \quad (2.12)$$

A similar expression for the total energy of an excited state is obtained by transferring an electron from a filled orbital <u>a</u> to an orbital <u>b</u> vacant in the ground state. If one assumes that the excitation process leaves the remaining orbitals unchanged, one finds for the excitation energy:

$$E_e - E_g = H_{bb} - H_{aa} + \sum_{i=1}^{N} \left[\frac{(H'_{bi})^2}{H_{bb} - H_{aa}} - \frac{(H'_{ai})^2}{H_{aa} - H_{ii}} \right]$$

$$+ \frac{(H_{bx} - S_{bx}H_{bb})^2}{H_{bb} - H_{xx}} - \frac{(H_{ax} - S_{ax}H_{aa})^2}{H_{aa} - H_{xx}}. \quad (2.13)$$

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*This necessarily restricts the treatment to derivatives of parent hydrocarbons with even numbers of π-electrons.

This may be compared with the energy of the corresponding transition in the hydrocarbon itself:

$$E_e^o - E_g^o = H_{bb}^o - H_{aa}^o \qquad (2.14)$$

Since our approach is empirical, we shall try to have as many "errors" cancel out as is possible. Consequently, we shall in general consider the difference between the transition energy of the substituted compuond and that of the corresponding transition in the hydrocarbon itself. This has the disadvantage of requiring identification of "corresponding" transitions, but attendant therewith is the advantage of not infrequently being able to use the theory to identify the transition. The difference between equations (2.14) and (2.13) yields:

$$(E_e - E_g) - (E_e^o - E_g^o) = \Delta^2 E = (H_{bb} - H_{bb}^o) - (H_{aa} - H_{aa}^o)$$

$$+ \sum_{i=1}^{N} \left[\frac{(H'_{bi})^2}{H_{bb} - H_{ii}} - \frac{(H'_{ai})^2}{H_{aa} - H_{ii}} \right] + \frac{(H_{bx} - S_{bx}H_{bb})^2}{H_{bb} - H_{xx}}$$

$$- \frac{(H_{ax} - S_{ax}H_{aa})^2}{H_{aa} - H_{xx}} \qquad (2.15)$$

C. Self-Consistent-Field Foundation of Empirical Method

It is worthwhile at this point to consider the empirical MO method from the following viewpoint. One examines what the best MO treatment possible is, involving a single configuration for the ground state. For the LCAO procedure, this best method, the self-consistent-field (SCF) method, has been developed in detail by Roothaan (7), and indeed has been applied to several hydrocarbons (8,9,10). Now, it is possible to examine the types of integrals involved in this "best" treatment, and separate them into groups which can be associated with corresponding terms in the semi-empirical treatment. In the following, we assume with Roothaan that the "excited" orbitals arising from the minimization of the ground state energy are sufficiently good approximations to the orbitals which would have been obtained had the energy of the excited state configuration been minimized directly. For the hydrocarbon itself, SCF theory yields the result that the ionization potential from the highest filled orbital a, is just the negative of the SCF orbital energy, e_a:

$$\overset{\circ}{I}_a = - \overset{\circ}{e}_a = - \overset{\circ}{H}_a - \sum_j^{\circ} (2J_{aj} - K_{aj}) , \qquad (2.16)$$

in which j runs over the occupied ground state orbitals. H_a^o refers to the nuclear field energy of orbital a. An analogous equation can be written for the mono-substituted hydrocarbon, using primed quantities throughout. The primes indicate, first, that the Hamiltonian now has a perturbation added to it, and second, that the SCF orbital wave functions occurring in the electron repulsion integrals are, of course, somewhat changed from the corresponding unperturbed hydrocarbon wave functions.

Let us now consider the shift in ionization potential in going from the hydrocarbon to the substituted hydrocarbon. For this we take the difference between the substituent analogue of equation (2.17) and equation (2.17) itself. This yields:

$$\Delta I = I_a' - I_a^o = - H_a' - H_a^o - \sum_j^{o} (2J_{aj}' - 2J_{aj} - K_{aj}' - K_{aj}) - (2J_{ax}' - K_{ax}') \,. \qquad (2.17)$$

The additional terms involving x appear, of course, since there is one additional occupied ground state orbital, ψ_x , in the substituted hydrocarbon. Equation (2.18) may now be compared with the corresponding equation from the semi-empirical approach:

$$\Delta I = I_a' - I_a = (- H_{aa}' + H_{aa}^o) - \sum_{i=1}^{N}{}' \frac{(H_{ai}')^2}{H_{aa} - H_{ii}} - \frac{(H_{ax} - S_{ax}H_{aa})^2}{H_{aa} - H_{xx}} . \qquad (2.18)$$

It is clear that each equation involves like kinds of terms:* nuclear field energy terms involving the vacated orbital a, electron interaction integrals between the substituent orbitals, Φ_x and Φ_a, and interaction integrals between the various ground state orbitals. As long as one evaluates empirically the quantities involved in equation (2.18), the simple MO orbital energies take on the aspects of the theoretically better founded SCF orbital energies, especially with respect to inclusion of the electron repulsion integrals. This does not mean, of course, that one can interpret the empirically determined quantities of equation

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*The semi-empirical expression, equation (2.13), contains additional interactions between a, and the entire set of excited orbitals, representing a portion of the inductive effect. These particular interaction terms are nearly always quite small, and the empirical procedure outlined in Section E will compensate in part for these quantities which lack an SCF foundation.

(2.18) as yielding values of theoretically defined integrals in equation (2.17). It merely suggests that some of the success of the semi-empirical procedure lies in its introduction empirically of the right kinds of parameters as judged from the SCF procedure.

Although second order perturbation theory relations have been used here, these general conclusions apply to the exact solutions of the secular equation.

D. Modification of Semi-Empirical Method

We now turn to a comparison of the simple MO procedure, with the corresponding SCF LCAO treatment of transition energies. For the hydrocarbon itself, we obtain directly from Roothaan's equation 67 (7) for the excitation energy to the lowest excited singlet state (excitation of an electron from a filled non-degenerate orbital a to a vacant non-degenerate orbital b):

$$E_e^o - E_g^o = H_b^o - H_a^o + \sum_j^{o} (2J_{jb} - K_{jb}) - \sum_j^{o} (2J_{aj} - K_{aj}) - (J_{ab} - 2K_{ab}) \,. \tag{2.19}$$

If we now consider the shift in transition energy for a substituted hydrocarbon from that of the hydrocarbon itself,

$$\begin{aligned}\Delta^2 E &= (E'_e - E'_g) - (E^0_e - E^0_g) \\ &= (H'_b - H^0_b) - (H'_a - H^0_a) + \sum_j^{0}(2J'_{bj} - 2J_{bj} - K'_{bj} - K_{bj}) \\ &\quad - \sum_j^{0}(2J'_{aj} - 2J_{aj} - K'_{aj} - K_{aj}) + (2J'_{bx} - K'_{bx}) \\ &\quad - (2J'_{ax} - K'_{ax}) - (J'_{ab} - J_{ab}) + (2K'_{ab} - 2K_{ab}), \qquad (2.20)\end{aligned}$$

where $\sum_j^{0}$ indicates summation over the occupied orbitals of the ground state of the unsubstituted hydrocarbon. Now as long as the empirical parameters in the corresponding semi-empirical equation (2.15) have been determined from ionization potentials, equation (2.16) is equivalent to just the difference in SCF orbital energies:

$$(e'_b - e^0_b) - (e'_a - e^0_a).$$

But if the appropriate SCF orbital energies defined by equation (2.16) are sustituted in equation (2.20), one has:

$$\Delta^2 E = (e_b' - e_b^o) - (e_a' - e_a^o) - (J_{ab}' - J_{ab}) + 2(K_{ab}' - K_{ab}) , \qquad (2.21)$$

which of course is not equivalent to the corresponding empirical expression (2.15), with parameters determined from ionization potentials.

It would seem logical, however, to use equation (2.21) to relate ionization potential data with spectral absorption data. Thus, one can obtain empirical parameters from data on ionization potential shifts, compute from these the orbital energy differences, and correct the latter by the electron repulsion integrals of equation (2.21), in order to obtain a transition energy shift which may be compared with experiment. In addition, the process may be applied in exactly the opposite direction to predict orbital energies and thus ionization potential shifts, using empirical parameters determined from the much more easily experimentally observable transition frequency shifts. Insofar as the electron repulsion integrals do not cancel out, it is generally impossible to proceed directly from $\Delta^2 E$ to ΔI, or vice versa, without explicitly including these terms.

A corollary of this procedure is to use orbital energies determined from the frequency of some particular transition and the appropriate electron repulsion integrals, and then predict the frequencies of other transitions. In this manner, for example, singlet-triplet transition energies may be predicted from a knowledge of the corresponding singlet-singlet excitation energy. The advantage over the usual empirical MO theory, which makes no distinction between states of different multiplicity, is obvious.*

Recently, Parr and Pariser (11,12) published a semi-empirical theory of electronic levels of unsaturated molecules, which, for application to hydrocarbons, is similar to ours in philosophy and scope. The assumptions and mathematical details inherent in the two theories are different in a number of places, but both make use of empirical core integrals, though in different ways. Both

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*It should be remarked that this procedure avoids the difficulty of the too-large singlet-triplet separations found in purely theoretical calculations, inasmuch as one makes no attempt to use a theoretically computed singlet-triplet splitting. One uses the theoretically computed values of the electron repulsion integrals together with the parameters determined from the shift of the singlet-singlet spectrum to predict the shift in the singlet-triplet spectrum from the observed singlet-triplet energy in the parent hydrocarbon.

are formulated in the language of the purely theoretical methods of antisymmetrized molecular orbitals, theirs in terms of a Goeppert-Mayer-Sklar type procedure (13) plus configuration interaction, ours in terms of Hartree-Fock SCF theory. What combination of assumptions will be the most satisfactory in the long run remains an open question at this point.

In order to test the validity of our approach, we introduce here some computations of the energy levels of hydrocarbons, based on the modified theory. In order to do this, an "effective" carbon-carbon nearest neighbor exchange integral, β^*, is evaluated from the observed center of gravity, $\overline{\Delta E}$, of the energy of the lowest excitations, or from the lowest excited singlet energy, $\Delta^1 E$, using semi-empirical orbital energy differences plus SCF electron interaction terms:

$$\bar{\beta}^* = \frac{\overline{\Delta E} + J_{ab} - K_{ab}}{n_b - n_a} = \beta^s + \frac{J_{ab} - K_{ab}}{n_b - n_a}, \qquad (2.22)$$

and

$$^1\beta^* = \frac{\Delta^1 E + J_{ab} - 2K_{ab}}{n_b - n_a}. \qquad (2.23)$$

Here n_b and n_a are defined by $e_j = n_j\beta$,where e_j is the semi-empirical jth orbital energy referred to the carbon coulomb integral as zero. β is the conventional carbon-carbon exchange integral of semi-empirical theory, defined

Table 1. Exchange and coulomb integrals[a] for ethylene,[b] benzene,[c] and trans-butadiene[d] (ev)

Molecule	β	β^N	$\bar{\beta}^*$	$'\beta^*$	α^S	α^N	$'\alpha^*$
Ethylene	-3.0	-3.5	-6.7	-5.8	-8.25	-5.1	-5.86
Butadiene	-3.8	-6.8	-8.2	-6.75	-7.0	-5.7	-5.41
Benzene	-2.56	-5.0	-5.63	-5.54	-7.2	-6.6	-4.72

a. β^N and α^N are theoretical LCAO exchange and coulomb integrals defined in reference 19. They are taken from references 10 and 19. β^S and α^S are spectroscopic integrals, determined from the first ionization potential and the center of gravity of the lowest excitation, by the naive MO method. $\bar{\beta}^*$ and $'\beta^*$ are effective exchange integrals determined from the center of gravity and lowest singlet excitation, respectively, by our modified MO procedure.

b. For ethylene, the necessary electron repulsion integrals are from reference 8.

c. Since the lowest excitation in benzene takes place between degenerate orbitals, equations (2.22) and (2.23) do not apply; additional excited state - excited state interaction integrals are needed. For the exact form these take, see Chapter IV, section D.

d. The necessary electron interaction integrals for butadiene were calculated using wave functions obtained from the naive MO procedure. See reference 42 and footnote a, Table 3.

by $\beta = \int \phi_1 H^\circ \phi_2 \, dv$. From the effective exchange integral an effective coulomb integral may be obtained, using ionization potential data as in the naive MO procedure (43). The energy levels of the hydrocarbon may now be found from equation (2.20) using orbital energies calculated from β^*. Tables 1 through 4 give the results of such calculations applied to ethylene and butadiene, as well as the results from the purely theoretical method. The agreement is quite reasonable for the low lying transitions and for the singlet triplet splitting. It is less good for higher excitation processes, but these are just the ones which configuration interaction will affect most in either method. Further refinements could be made, such as adjusting the singlet-triplet splitting, empirically, or including configuration interaction as Parr and Pariser have done (11,12, 15). However, the spirit of the computations presented here is not to obtain the best possible energy levels, but to test the reasonableness of the procedure.

We now turn to a consideration of the electron repulsion integrals. The change in the wave function can be attributed to two essentially independent points. First is the contribution from the non-orthogonality of Φ_X to the parent hydrocarbon MO's, $\Phi_1 \ldots\ldots \Phi_N$, mentioned previously. The use of the SCF development (7), however, requires orthogonalized

Table 2. Electronic energy levels of ethylene and benzene

Molecule	State[a]	Theoretical LCAO Energy[b]	Modified Empirical Energy[c]		Observed Energy[d]
Ethylene	$^{1}A_{1g}$	0.0	0.0	0.0	0.0
	$^{3}B_{1u}$	1.8	0.9	-0.8	3.1--5.6
	$^{1}B_{1u}$	10.2	9.3	7.6	7.6
Benzene	$^{1}A_{1g}$	0.0	0.0	0.0	0.0
	$^{1}B_{2u}$	5.7	5.2	4.9	4.9
	$^{1}B_{1u}$	6.9	6.4	6.1	6.2
	$^{1}E_{1u}$	9.5	9.0	8.7	7.0
	$^{3}B_{2u}$	5.4	4.9	4.6	...
	$^{3}B_{1u}$	2.8	2.3	2.0	3.8
	$^{3}E_{1u}$	4.1	3.6	3.3	...

a. For notation, see references 8,9 and 10, and Part III A of this thesis.

b. From references 8,9 and 10, with configuration interaction neglected.

c. Values in the first column are calculated by the modified theory outlined in this thesis, using $\bar{\beta}^*$; the second column uses $'\beta^*$.

d. The assignments of all these bands are not certain. See references 11,12 and 14, and Part IV of this thesis for discussions.

wave functions. We can classify this minimum necessary orthogonalization, following Mulliken (16), as "forced hybridization." It was found instructive to form the Lowdin many-center orbital wave functions (17) from the hydrocarbon MO's and the substituent AO for two cases: aniline and aminobuta-

Table 3. Electron repulsion integrals in trans-butadiene (ev)

Integral[a]	Exact SCF Method	Modified Empirical Method
J_{12}	9.31	8.66
J_{13}	9.22	8.39
J_{24}	9.43	9.32
J_{14}	9.96	10.81
K_{12}	2.55	3.02
K_{13}	2.09	1.68
K_{24}	2.17	1.91
K_{14}	1.83	2.13

a. These values are for Slater $2p\pi$ AO's with effective charge $Z=3.18$. The SCF values are taken from reference 10. The empirical method integrals are computed from LCAO wave functions obtained by conventional semi-empirical MO theory, overlap included, and all carbons considered identical (42). The necessary AO integrals are from reference 10.

Table 4. Electronic energy levels in trans-butadiene

State[a]	Theoretical LCAO Energy[b]	Modified Empirical Energy[c]	Naive MO Energy[d]	Observed Energy[e]
^1Ag	0.0	0.0	0.0	0.0
^1Bu	8.2	6.0	4.9	6.0
^1Ag	10.3	7.7	7.2	7.2
^1Ag	11.0	16.5	12.6	...
^1Bu	12.6	19.6	14.8	...
^3Bu	3.2	- 0.1	4.9	...
^3Ag	6.1	4.3	7.2	...
^3Ag	6.6	12.6	12.6	...
^3Bu	8.9	15.3	14.8	...

a. For notation, see reference 10.

b. Taken from reference 10.

c. Computed with β^* = -6.75 ev, and electron repulsion integrals given in Table 3.

d. Computed with β^s = 3.8 ev, and inclusion of nearest neighbor overlaps, all carbons considered identical. See reference 42.

e. Assignment of the 7.2 band is not certain. See reference 12.

Table 5. Singlet-triplet splitting of energy levels in ethylene, benzene and butadiene (ev)

Molecule	State[a]	E singlet - E triplet Modified Empirical Method[b]	E singlet - E triplet Theoretical LCAO Method
Ethylene		identical for all states	
Butadiene	Bu	6.0	5.1
	Ag	3.4	4.2
	Ag	3.8	4.3
	Bu	4.2	3.7
Benzene		identical for all states	

a. For butadiene, the order is that given in Table 4.

b. For molecules in which the orbitals are determined by symmetry, the singlet-triplet splitting must be identical by both the completely theoretical and the modified empirical theories, as then K_{ij} is identical for both procedures. Hence, both methods give identical singlet-triplet splitting ting for ethylene and benzene.

diene. These are listed in detail in Appendix A. The interesting point concerning these orbitals orthogonalized by Lowdin's recipe is the small amount of mixing introduced by the orthogonalization condition. It can be concluded safely that forced hybridization does not, of itself, cause a very large change in the orbital wave functions. The second factor influencing the form of the wave function is the actual perturbation of the wave functions by the presence of the substituent. It is apparent that, depending upon the amount of interaction between the substituent and the parent hydrocarbon, the hydrocarbon wave functions may be changed only to a very slight extent or in considerable degree. The following section considers in detail this aspect of the problem. Suffice it to point out here that in practice, substituents exist which influence the unperturbed wave functions to a moderate extent only, and for which it is reasonable to assume that the corresponding electron repulsion integrals in the hydrocarbon and the substituted hydrocarbon, respectively, are equal. Substituents falling into this category will be labeled here "weak" substituents, whereas those for which considerable changes in the wave functions occur will be designated as "strong" substituents. Mathematically speaking, weak substituents are those for which $|H_{jj} - H_{xx}|$ or H'_{ij} are large. The opposite statement holds for strong substituents.

For weak substituents, the shifts in transition energy and ionization potential may be obtained from equations (2.20) and (2.17), by canceling out the corresponding electron interaction integrals:

$$\Delta^2 E = (H'_b - H^0_b) - (H'_a - H^0_a) + (2J'_{xb} - K'_{xb}) - (2J'_{ax} - K'_{ax}) \tag{2.24}$$

and

$$\Delta I = - (H_a - H^0_a) - (2J_{ax} - K_{ax}) \; . \tag{2.25}$$

The terms involving $j = x$ remain, of course, because of the additional occupied ground state orbital in the substituted hydrocarbon. Equation (2.25), for the shift in ionization potential, now involves exactly those terms concerning orbital a which appear in equation (2.24) for $\Delta^2 E$. It can be concluded therefore, that for sufficiently weak substituents, the same empirical parameters which are determined to account for shifts in transition energies can be used to predict ionization potential shifts, and, if one desires, the procedure can also be applied in reverse. A little reflection shows that the difference between the shifts in singlet and triplet energies of the excited states in the SCF procedure involves only electron repulsion integrals which, for weak substituents, cancel out. This cancelation holds, whether any particular configuration or the center of gravity of all the excited configurations is under consideration, irrespective of any possible degeneracy of orbitals <u>a</u> or <u>b</u>. This is tantamount to the statement that, for weak substituents, the energy shift of the center of gravity is the same as that of any one of the individual configurations. Since equation (2.15) applies to the center of gravity of the transitions, it is apparent that one is justified, for sufficiently weak substituents, in comparing observed energy shifts of any of the transitions with the semi-empirically calculated shifts of the center of gravity involving the same orbitals.*

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*The semi-empirical center of gravity is of course not quite the same as the SCF center of gravity. However, as they differ by just $(J_{ab} - K_{ab})$, the shifts in both centers of gravity are identical for sufficiently weak substituents.

E. Evaluation of Empirical Parameters

It is assumed at the outset that the matrix elements H^o_{ii}, $i \neq x$, of equation (2.5) have been determined empirically from spectral data on the parent conjugated hydrocarbon, yielding a coulomb integral, α , and a carbon-carbon exchange integral, β . In order to evaluate empirically the unknown matrix element H_{xx} in equation (2.3), we follow Pauling (18) and Matsen (6) in establishing H_{xx} as $\alpha + \delta\beta$. Here, α and β are the integrals determined from the parent hydrocarbon, whereas δ now assumes the position of an empirical parameter which is a function of the substituent. As Mulliken (19) has pointed out, α and β will vary from hydrocarbon to hydrocarbon, since they depend on non-nearest neighbor effects. Such variation will shift the δ values for a substituent as a function of the parent hydrocarbon under consideration, but this need not concern us, as the effect is merely a shift in origin, and relative δ values for different substituents will remain significant.

The matrix elements remaining to be evaluated empirically are those related to the inductive effect: H'_{ij}

$(i,j \neq x)$. In equation (2.7), these were expressed in terms of the AO integrals: $\int \phi_u H' \phi_u dv$ and $\int \phi_u H' \phi_w dv$. The first of these is denoted empirically by $\delta_u \beta$, after Pauling (18). It is clear that the largest of these integrals is the one involving AO's on the carbon atom to which the substituent is attached. In succeeding notation, we will designate this carbon atom by the subscript s, and refer to it as "the substituted carbon." Various arbitrary relationships between this integral and those involving carbon atoms adjacent to the substituted carbon have been used (20,21), ranging from $\delta_{(s \pm 1)} = \delta_{s/10}$ to $\delta_{s/3}$. These recipes may be regarded as too arbitrary to be satisfactory. It is possible to determine uniquely all the δ_u's if one uses the spectra and ionization potentials of the disubstituted hydrocarbons (see Section K). For the present, it will be assumed for simplicity that $\delta_{u \neq s} = 0$, and in addition, that the exchange integral perturbations, $\int \phi_u H' \phi_w dv$, are negligible.

The exchange integral H_{jx} is approximated by $C_{js} \int \phi_s H \Phi_x dv$. While this may be poor for substituents whose π-electrons have principal quantum numbers much higher than two, it is not inconsistent with the neglect of higher order inductive effects. Our state of knowledge about this integral is such that about all we can do is regard it equal to the carbon-carbon value , or adopt Wheland's assumption, and assume it to be proportional to the overlap integral $\int \Phi_x \phi_s dv$ (22). If the C - X bond is strongly polar, neither of these assumptions appears *a priori* valid, and one must view them with caution. Since the empirical parameters must compensate, at least in part, for the inadequacy of these assumptions, they can be expected to differ in numerical magnitude but not in qualitative order for different parent hydrocarbons. With these assumptions, the secular equation (2.3) and (2.4), if symmetry is present takes on a form particularly amenable to simple solution. In the case of symmetry splitting the secular equation, equation (2.4) reduces to diagonal form such that its roots are just the orbital energies of the parent hydrocarbon. Inasmuch as there is evidence (23) that these orbital energies may be considerably perturbed from the values for the parent hydrocarbon, the need for an adequate method of determining higher order δ_u's is pointed up.

The orbital energies may now be obtained from equation (2.3) as a function of the known parameters α , β , and the overlap integrals, $\int \phi_u \Phi_x dv$, and of the unknown parameters, δ and δ_s. The latter may be determined from any two independent experimental data which can be expressed in terms of them. The most convenient data are the shifts in the vertical ionization potentials (given theoretically by the shift in energy of the highest occupied orbital) and the shifts in the vertical transition energies (given by the shift of the difference between appropriate orbital energies supplemented by electron interaction integrals as in equation 2.21).* One could use as well data on two different electronic transitions. In special cases, additional simplifying assumptions can be made. Thus, for example, the case of the anilinium ion should be an example of a virtually pure inductive effect, in which case H_{jx} and S_{jx} may be regarded as zero. The other extreme of a substituent introducing purely a resonance effect,

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*Ionization potentials determined from electron impact data presumably yield values corresponding to vertical ionization, but, unfortunately, the data available have not been found sufficiently accurate for use for this purpose. Hence, adiabatic ionization potentials determined from spectroscopic observations on Rydberg series have been used. For a closely related series of molecules, the shifts in the adiabatic ionization potentials are not expected to deviate too greatly from the shifts of vertical ionization potentials. Vertical transition energies correspondingly require the use of the frequency of the smoothed maximum of the absorption band. For lack of sufficient accuracy in this experimental datum, we have used the 0 - 0 band frequencies for determining shifts. These are primary reasons (in addition to theoretical reasons mentioned earlier) why we consider shifts in experimental data rather than the absolute data.

strictly speaking does not exist, since H' is never zero. For certain substituents, however, δ_s is small and may in practice be found negligible.

It is obvious that empirical values of the parameters δ and δ_s will depend strongly on the degree of approximation in which the secular equation is solved. With respect to overlap integrals, for example, this includes solution of the secular equations (2.3) and (2.4) including or omitting overlap integrals between the AO's in the parent hydrocarbon, and likewise including or omitting the off-diagonal S_{jx} terms. Neglect of the first of these affects the unperturbed energies (but not the unperturbed wave functions). The S_{jx} terms may, on the other hand, be largely compensated for by the semi-empirical procedure as far as the energy levels are concerned (24), but can be expected to influence considerably the wave functions. This influence is felt particularly strongly through the electron repulsion integrals of equation (2.21). In Appendix B we develop a computationally simple approach by which it is possible to take into account the inclusion of overlap, given the solutions obtained omitting overlap.

Longuet-Higgins and Coulson have in many papers presented the important properties of the special class of molecules termed by them "alternant hydrocarbons." We digress to show how these molecules can be treated by the scheme we are following in this thesis. We begin conceptually with an alternant hydrocarbon substituted with a hypothetical radical which exerts only a resonance effect. We wish to enquire as to the nature of the inductive effect, i.e., how the orbital energies depend upon the coulomb integral of the carbon to which the substituent is attached. We follow the Taylor series expansion used by Coulson and Longuet-Higgins (3) when they were examining the inductive effect alone:

$$\Delta E = \Delta E' + \left(\frac{\partial \Delta E'}{\partial \alpha_\Delta}\right)_{\Delta=0} \delta\alpha_\Delta + \cdots\cdots + \qquad (2.26)$$

where $\Delta E'$ is the transition energy for the substituted hydrocarbon with the coulomb integral of carbon 1 equal to α. The coefficient of $\delta\alpha_\Delta$ is found using (2.10):

$$\left(\frac{\partial \Delta E'}{\partial \alpha_\Delta}\right)_{\Delta=0} = \left[1 - \frac{(H_{bx} - S_{bx}H^{o}_{bb})^2}{(H^{o}_{bb} - H_{xx})^2} - 2S_{bx}\frac{(H_{bx} - S_{bx}H^{o}_{bb})}{H^{o}_{bb} - H_{xx}}\right]\left(\frac{\partial H^{o}_{bb}}{\partial \alpha_\Delta}\right)_{\Delta=0}$$

$$- \left[1 - \frac{(H_{ax} - S_{ax}H^{o}_{aa})^2}{(H^{o}_{aa} - H_{xx})^2} - 2S_{ax}\frac{(H_{ax} - S_{ax}H^{o}_{aa})}{(H^{o}_{aa} - H_{xx})}\right]\left(\frac{\partial H^{o}_{aa}}{\partial \alpha_\Delta}\right)_{\Delta=0} \qquad (2.27)$$

One needs the well-known relation

$$\left(\frac{\partial H^o_{jj}}{\partial \alpha_\Delta}\right)_{\Delta=0} = C^2_{j1} , \qquad (2.28)$$

noticing also that $|C_{b1}| = |C_{a1}|$, if one is interested in a transition between corresponding alternant levels and if carbon-carbon overlap integrals are neglected.* These relationships result in the dropping out of all but two terms, which may be combined to yield:

$$\left(\frac{\partial \Delta E}{\partial \alpha_\Delta}\right)_{\Delta=0} = C^4_{b1} \frac{(H^o_{bb}-H_{xx})^2(h_{1x}-SH^o_{aa})^2 - (H^o_{aa}-H_{xx})^2(h_{1x}-SH^o_{bb})^2}{(H^o_{bb}-H_{xx})^2(H^o_{aa}-H_{xx})^2} \qquad (2.29)$$

In this equation, H_{1x} refers to $\int \phi_1 H \, I_x dv$, and S to the corresponding overlap integral. For the case of little or no resonance interaction, every $|H_{jj}-H_{xx}|$ is large, and

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*If these overlaps are included, $C_{b1} = C_{a1} (1 - n_b S_c)/(1 - n_a S_c)$, which makes $|C_{b1}|$ approximately, rather than exactly, equal to $|C_{a1}|$.

$\left(\frac{\partial \Delta E'}{\partial \alpha_\Delta}\right)_{\Delta=0}$ is small or zero, as found by Coulson (25), who considered just this case. On the other hand, if there is a strong resonance interaction between the substituent and the ring, then at least one $|H^0_{jj} - H_{xx}|$ will be small, and in nearly all cases $|H^0_{aa} - H_{xx}|$ will be smaller than $|H^0_{bb} - H_{xx}|$. The greater the resonance interaction, the more pronounced this inequality will be. For this case, equation (2.29) reduces to:

$$\left(\frac{\partial \Delta E'}{\partial \alpha_\Delta}\right)_{\Delta=0} = c_{b1}^4 \frac{(h_{1x} - SH^0_{aa})^2}{(H^0_{aa} - H_{xx})^2} . \qquad (2.30)$$

If one substitutes this in equation (2.26) and adds in the shift in transition energy produced by the resonance effect alone, $(\Delta^2 E')$, one obtains for the total shift in transition energy:[*]

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[*] Longuet-Higgins and Snowden (26) have derived a similar relation for methylated alternant hydrocarbons. Their derivation, however, starts with the parent hydrocarbon orbitals and assume that the resonance and inductive effects upon the transition energy shift are independent and additive. Our derivation concludes that interaction terms are far from negligible.

$$\Delta^2 E = C_{b1}^4 \frac{(h_{1x} - SH^o_{aa})^2}{(H^o_{aa} - H_{xx})^2} \delta_a \beta + \Delta^2 E' \qquad (2.31)$$

For a sufficiently large inductive effect, equation (2.31) may become a considerable portion of the total transition energy shift.*

The important conclusion to be drawn here is that for strong resonance interaction between substituent and hydrocarbon, one is not justified in neglecting the influence of the inductive effect upon the frequencies, as some authors have done (e.g., Sklar (4), Herzfeld (5), and Matsen(27)). If one goes to the other extreme of a weak resonance effect, one can show rather easily that the inductive first term of equation (2.31) goes to zero faster than the resonance shift.**

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*This is true even within the validity of equation (2.31), which was developed with the assumption of a small inductive effect. It can be shown that more nearly exact treatments including higher derivatives or direct solution of the secular equation reinforce this general viewpoint. The results are changed only slightly by inclusion of carbon-carbon overlap. for no resonance interaction, $\left(\frac{\partial \Delta^2 E}{\partial \alpha_a^2}\right)_{\Delta=0}$ does not quite go to zero, as Coulson has shown. For large resonance interaction, the qualitative results of this section are still valid.

**From equation (2.10), for the resonance shift, $\Delta^2 E'$ depends only on the square of the coefficient of carbon s, and inversely on the first power of $(H^o_{aa} - H_{xx})$. C_{ba} is always less than unity. As $(H^o_{aa} - H_{xx})$ becomes large (resonance effect becoming smaller) the resonance term, $\Delta^2 E'$, rapidly becomes dominating.

As a result, the transition shifts are essentially independent of the inductive parameter δ_Δ for small resonance interaction.* In this special case, a one-parameter theory (resonance parameter) may provide a good approximation for calculation of excitation energies. Conversely, where little or no resonance interaction exists (e.g., if the substituent is $-NH_3^-$) excitation energy data are unsatisfactory for the evaluation of inductive parameters.

An analysis similar to that on the transition energies may be carried out on the ionization energy, leading to

$$\left(\frac{\partial I}{\partial \alpha_\Delta}\right)_{\Delta=0} = \left[1 - \frac{(h_{1x} - SH^o_{aa})^2}{(H^o_{aa} - H_{xx})^2} - 2S\,\frac{(H_{ax} - SH^o_{aa})}{(H^o_{aa} - H_{xx})}\right] c^4_{a1} \tag{2.32}$$

For little or no resonance interaction, a large inductive

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*This is not precisely true, since the inductive effect does have a strong influence on the orbital energies themselves in this limiting case, whereas the differences between orbital energies cancel. As a result, there is a change in the orbital wavw functions, which is felt through the electron repulsion integrals of equation (2.21). For the cases we have considered (benzene, butadiene, ethylene), the effect is not large, but not negligible either. For very large parent hydrocarbons where the orbital levels are close together, the effect may become considerable.

effect provides large shifts in the orbital energies, and under these conditions, the ionization energy shift may be considered a function of δ_Δ alone. Thus the inductive parameter may be determined from this information directly. If the resonance interaction is large, however, this simplification is not valid. Equation (2.32) shows that $(\partial I/\partial\alpha_\Delta)_{\Delta=0}$ has a maximum value of $-C^4_{a1}$ when there is no resonance interaction. For large resonance interaction this term may become quite small,* and the ionization energy shift will not depend very strongly on the inductive parameter. The conclusions on ionization potentials are of course independent of whether the hydrocarbon is alternant or not. Another important result is that the empirical parameter in heterocyclics derived from alternant hydrocarbons should not be determined from transitions between the alternant levels, but from the ionization potential or other transitions.

F. Calculation of Integrals

The electron repulsion integrals entering the modified semi-empirical theory can be expanded by equation (2.2) to

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*The general result is true even though equation (2.32) breaks down when $|H^o_{aa} - H_{xx}|$ is small.

$$M'_{ijkl} = \sum_{t}\sum_{t'=1}^{N+1}\sum_{s}\sum_{s'} a_{it}a_{jt'}a_{ks}a_{ls'}M_{ss'tt'} , \qquad (2.33)$$

where $M_{ss'tt'} = \int \Phi_s(u)\ \Phi_{s'}(u)\frac{1}{r}uv\ \Phi_t(v)\ \Phi_{t'}(v)dv_u dv_v$

and $M'_{ijkl} = \int \psi_i(u)\ \psi_j(u)\frac{1}{r^{uv}}\ \psi_k(v)\psi_l(v)dv_u dv_v$.

From equation (2.33), it would seem that a great number of integrals of the type $M_{ss'tt'}$ would be needed to calculate a single coulomb or exchange integral for the substituted hydrocarbon. Since the integrals are obtained over all possible charge distributions, the number that needs independent evaluation is reduced to a specially great extent through use of symmetry properties of these MO's, by the methods of group theory. It is plain that the degree of simplification is more highly dependent upon the symmetry of the parent hydrocarbon than upon that of the substitution product. In addition, two other practicable simplifications have been found very helpful. It is shown in Appendix C that:

$$|M_{ijkl}| \leq \frac{1}{2}(M_{ijij} + M_{klkl}) = \frac{1}{2}(K_{ij} + K_{kl})$$

$$\leq \frac{1}{2}(M_{iijj} + M_{kkll}) = \frac{1}{2}(J_{ij} + J_{kl}) \ . \qquad (2.34)$$

In practice, a number of cases are found in which the exchange integrals are so small as to be negligible, or almost so. For each such case, a number of the integrals M_{ijkl} may be discarded as well.

Secondly, we are considering a perturbation of the hydrocarbon by the substituent orbital. If the substituent orbital energy is far from the energy of any particular parent hydrocarbon orbital, then that orbital will be essentially unperturbed (in which case, only the a_{ii} term of equation (2.2) need be retained), or at the very worst, mixing will be important only with orbitals of nearly the same energy, and the remainder may be eliminated. It has been found by actual computation that orbitals with energies more than 2β removed from Σ_i of equation (2.2) need not be considered in the expansion.

For the special case of a substituted hydrocarbon possessing C_{2v} symmetry, the combination of symmetry with small coefficients and with equation (2.34) make it unnecessary to calculate any integrals over the substituent orbital, Φ_X, for many interesting transitions. In these cases, the electron interaction integrals are determined solely by the change in electron repulsion due to the perturbed charge distribution in the hydrocarbon part of the molecule. Molecules which fall under this situation and whose parent hydrocarbons have been subjected to an SCF procedure may need no calculation of new integrals, and even if the SCF procedure has not been carried out, all necessary integrals can be determined from published tables, e.g., (28). As an indication of the simplification possible, one might mention that in the case of monosubstituted benzenes, of approximately 2400 integrals potentially required, only about 20 need specific evaluation, and for two sets of transitions, no integrals over substituent AO's need be calculated.

The calculation of energy shifts provides a futher reduction in the number of integrals that need be computed, which would not be possible if absolute energy values were calculated. This hinges upon the assumption of neglect of all δ_u, $u \neq s$. For then, orbitals which do not mix with Φ_X on symmetry grounds remain unchanged with respect to those in the parent hydrocarbon, and the difference $(M'_{ijkl} - M_{ijkl})$

vanishes, provided i, j, k, and l refer to such orbitals.

III. MODIFIED-MO TREATMENT OF SUBSTITUTION

A. Introduction

The previous chapter (which will be referred to as "II") presented an analogy between the naive semi-empirical molecular orbital approach and the more rigorously founded self-consistent-field theory. It was shown that physically reasonable results could be obtained for three representative hydrocarbons by complementing the results of the naive approach with theoretically computed integrals in a manner suggested by SCF theory. In this chapter we examine the implications of this approach, insofar as they can be ascertained from a generalized study of substituted conjugated hydrocarbons, with respect to the physically observable properties of these molecules. We pay particular attention to the transition energy shifts, transition probabilities, various properties of the ground state itself, the effect of polysubstitution, and finally, to two special classes of transitions that may arise in practice: $n-\pi$ and N-Q transitions. In succeeding chapters we apply the methods and results of these first two chapters for quantitative calculation, comparison with experiment, and discussion of individual cases.

B. Prediction of Transition Energy Shifts

For the present we assume it has been possible by the general methods outlined in the previous chapter to obtain a series of δ and $\delta_\perp$ values for various substituents of interest. From the naive semi-empirical molecular orbital theory one can ascertain that a given transition will shift in a well-defined manner upon substitution by a radical with known δ and $\delta_\perp$ value. In Table 1 we bring together for convenience information that has been derived concerning such information. The last three entries of Table 1 result directly from II, particularly equation (2.15), while the remainder have been discussed by Coulson (25) and Longuet-Higgins and Sowden (26). We now wish to consider what influence the introduction of theoretical integrals into the naive theory, as suggested in II, has upon predictions listed in Table 6.

In the case that the transition in the parent hydrocarbon is the excitation of an electron from an orbital Φ_a to an orbital Φ_b, at least one of Φ_a or of Φ_b being non-

Table 6. Transition energy shifts predicted from naive semi-empirical MO theory upon monosubstitution

Type of Substituent-Hydrocarbon Interaction[a]	Type of Transition in Parent Hydrocarbon[b]	Predicted Energy Shift ($\Delta^2 E$)
R only	general	red
I only: $\left\{\begin{matrix}\delta_a > 0 \\ \delta_a < 0\end{matrix}\right\}^c$	general	blue or red red blue
R + I: $\left\{\begin{matrix}\delta_a < 0 \\ \delta_a > 0\end{matrix}\right\}$	general	red or blue blue red
R only	alternant	red
I only	alternant	~ 0
R + I: $\delta_a > 0$	alternant	red (S)[d]
weak R and weak I: $\delta_a < 0$	alternant	red
strong R and strong I: $\delta_a < 0$	alternant	blue

a. R = Resonance interaction; I = Inductive interaction.

b. alternant refers to a transition between levels symmetrically situated about $E = \alpha$.

c. δ_a is the inductive parameter defined in II as $\int \phi_s H' \phi_s dv$ of equation (2.6), for example.

d. S refers to strengthening of the shift due to combined R and I.

degenerate,* one can write for the transition energy shift

$$ {}^{1,3}\Delta^2 E = \Delta^2 e - (J'_{ab} - J_{ab}) + (K'_{ab} - K_{ab}) \pm (K'_{ab} - K_{ab}), \tag{3.1} $$

in which the plus sign holds for transition from a closed shell ground state to an excited state, and the minus sign holds for the corresponding singlet-triplet transition. We define $\Delta^2 e$ as $(e_b - e_b^o) - (e_a - e_a^o)$. See equation (2.15). There seem to be available no general inequalities from which in given circumstances the sign of the sum of the electron interaction integrals of equation (3.1) can be determined. Hence, in this general case, we are unable to extend the useful generalized predictions of Table 6 to our modified semi-empirical theory. One can make the general observation that the predictions of Table 6 are borne out in practice, and consequently the electron repulsion integral sum of equation (3.1) is either of the same sign as $\Delta^2 e$ or smal-

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*We also assume that the corresponding levels in the resulting substituted hydrocarbon are non-degenerate. It is possible to conceive of peculiar situations in which substitution creates degeneracies, but we will not consider these.

ler in absolute magnitude than $\Delta^2 e$,

In the special case in which Φ_a and Φ_b are each doubly degenerate, a more complex situation prevails. In the following analysis of this situation we have been guided by the particular situation that prevails in benzene, but the general principles involved in the argument have rather more general application, even though possibly some of the specific equations may need to be modified in other specific examples. In the form in which the equations are given here, they will apply to any case of monosubstitution of a general conjugated hydrocarbon which has a threefold axis of symmetry.

Let the parent conjugated hydrocarbon belong to the point group G_1, and let the monosubstitution product belong to the point group G_2, necessarily a subgroup of G_1. Now choose the members of the degenerate orbital pair occupied in the ground state, Φ_a and Φ_{-a}, so that each of them belongs to an irreducible representation of the subgroup G_2. Similar orbitals are selected for the degenerate orbital pair vacant in the ground state, Φ_b and Φ_{-b}.* Now we wish to consider the excitation of an electron from the oc-

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*In the case of benzene, for example, this means we choose to use the real forms of the MO's. Cf. Matsen, reference 6.

cupied pair to a vacant orbital. One can write four possible excitation processes to yield the zeroth order excited states $\Phi_a^2 \ \Phi_{-a} \ \Phi_b$, $\Phi_a^2 \ \Phi_{-a} \ \Phi_{-b}$, $\Phi_a \ \Phi_{-a}^2 \ \Phi_b$, and $\Phi_a \ \Phi_{-a}^2 \ \Phi_{-b}$, which, for convenience, will be denoted respectively by χ_{-ab}, χ_{-a-b}, χ_{ab}, χ_{a-b}. Now in general the various χ's will not belong to irreducible representations of G_1, and, in fact, appropriate linear combinations must be taken to form the correct first-order wave functions for these excited states. Upon substitution, it can be expected in general that the amount of mixing of the zeroth order wave functions necessary, will change. Since we are interested in shifts in transition energies which are much smaller than the transition energies themselves, the contribution of this excited state mixing, as we choose to call this process,* may in some cases be a dominating factor in the calculated shifts.

It can be shown that χ_{ab} and χ_{-a-b} belong to the same irreducible representation of G_2, and likewise, χ_{a-b} and χ_{-ab} belong to a single representation different from that of the first pair. In the parent hydrocarbon one can find the correct first-order wave functions by the usual

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*We have avoided the term "configuration interaction" be cause the latter term is usually understood to involve a higher-order theory than is considered here.

treatment of configuration interaction of the zeroth-order functions. In this case, however, it is unnecessary to carry out the procedure explicitly as the functions are determined from symmetry considerations. One must determine them so as to belong to irreducible representations of G_1, and one thus obtains:

$$\chi_1^{\pm} = (\chi_{ab} \pm \chi_{-a-b})/\sqrt{2}$$

$$\chi_2^{\pm} = (\chi_{-ab} \pm \chi_{a-b})/\sqrt{2} \qquad (3.2)$$

in which the respective superscripts refer to the signs chosen in each equation. In the parent hydrocarbon (for the case of trigonal symmetry which we are considering) one pair of the four functions of equation (3.2) is degenerate. This pair will consist of one member from each of $\chi_1^{\pm}$ and $\chi_2^{\pm}$. The other member of each pair of functions will be non-degenerate. Of course, which particular ones these are will depend upon the signs chosen for the individual Φ functions. Each function of equation (3.2) has a corresponding energy using the ground state SCF excited state Hamiltonian (an approximation we use throughout this thesis). The energy differences between these and that of the ground-state energy may be written, for the singlet transition:

$$
\begin{aligned}
{}'\Delta E_1^{\pm} &= e_b^0 - e_a^0 - \tfrac{1}{2}(J_{ab} - K_{ab}) - \tfrac{1}{2}(J_{-a-b} - K_{-a-b}) \\
&\quad + (K_{ab} + K_{-a-b}) \pm H_{ab,-a-b} \\
{}'\Delta E_2^{\pm} &= e_b^0 - e_a^0 - \tfrac{1}{2}(J_{-ab} - K_{-ab}) - \tfrac{1}{2}(J_{a-b} - K_{a-b}) \\
&\quad + (K_{-ab} + K_{a-b}) \pm H_{-ab,a-b}
\end{aligned}
\qquad (3.3)
$$

in which e_b^0 and e_a^0 are the SCF orbital energies of the respective degenerate orbitals, and

$$
\begin{aligned}
H_{ab,-a-b} &= 2M_{-a-b,ab} - M_{-aa,-bb} \\
H_{-ab,a-b} &= 2M_{a-b,-ab} - M_{-aa,-bb}
\end{aligned}
\qquad (3.4)
$$

in the notation defined in II.

Now consider the effect of substitution. First of all the degeneracy is removed and the amount of excited state mixing is no longer determined by symmetry. Then, in general, the best wave functions that can be formed from the zeroth-order functions will involve unequal mixing determinable by the usual minimization procedure. The singlet state wave functions for the monosubstitution product will then be:

$$\begin{aligned} \chi_1'^{\pm} &= (C^{\pm}_{ab}\,\chi'_{ab} \pm C^{\pm}_{-a-b}\,\chi'_{-a-b}) \\ \chi_2'^{\pm} &= (C^{\pm}_{-ab}\,\chi'_{-ab} \pm C^{\pm}_{a-b}\,\chi'_{a-b}) \end{aligned} \qquad (3.5)$$

with, of course, three relations connecting the C's in χ_1 and three in χ_2 from orthogonality. The shift in transition energy from that of the parent hydrocarbon to that of the substituted compound is then given for the singlet states:*

---

*Similar formulas apply to the triplet state with a minus sign before the terms $(K_{ab} + K_{-ab})$ and $(K_{-ab} + K_{a-b})$ in equation (3.3) and corresponding changes in sign in equation (3.6). Of course, one will find different values of the C's, depending on whether the energy of the singlet states or of the triplet states was minimized. One could alternatively, but less rigorously, minimize the energy of the center of gravity of all the singlet and triplet states.

$$
{}^{1}\Delta^{2}E_{1}^{-} = \Delta^{2}e - C_{ab}^{\pm 2}(J'_{ab} - K'_{ab}) - C_{-a-b}^{\pm 2}(J'_{-a-b} - K'_{-a-b})
+ \frac{1}{2}(J_{ab} - K_{ab} + J_{-a-b} - K_{-a-b}) \pm (C_{ab}^{\pm 2}K'_{ab}
+ C_{-a-b}^{\pm 2}K'_{-a-b} - \frac{1}{2} K_{ab} - \frac{1}{2} K_{-a-b}) \pm 2 (C_{ab}^{\pm}C_{-a-b}^{\pm}H'_{ab-a-b}
- \frac{1}{2} H_{ab-a-b}) \tag{3.6}
$$

Here, $\Delta^{2}e = (e_b - e_b^0) - (e_a - e_a^0)$ and primed integrals indicate that orbital wave functions of the substituted molecule must be used in evaluating the respective integrals. A similar equation holds for ${}^{1}\Delta^{2}E_{2}^{\pm}$.

For the case in which the substituted compound still has a twofold element of symmetry in addition to the horizontal plane of reflection to which the π AO's are antisymmetric, then the functions $\chi_1'^{\pm}$, $\chi_2'^{\pm}$ will belong to two different irreducible representations of G_2 and the substituent will interact directly with only that one of these which has the same symmetry. Necessarily, the pair of states which was degenerate in the parent hydrocarbon becomes separated,* and, in general, the larger the substituent-parent hydrocarbon interaction, the larger the splitting. In the limit of very strong interaction, the levels can be separated so far that $\chi_1^{\prime +} = \chi'_{-a-b}$ and $\chi_1^{\prime -} = \chi'_{ab}$ if this is the originally degenerate pair. Thus we have the picture of a "weak" substituent case involving essentially complete and symmetrical excited state mixing as in the parent hydrocarbon adiabatically going over into the "strong" substituent case, as the interaction increases adiabatically, in which the excited states are completely uncoupled. The process is shown diagrammatically in Figure 1.

Finally, let us consider the interaction integrals $H'_{ab,-a-b}$ and $H_{ab,-a-b}$ appearing in equation (3.6), and their counterparts, $H'_{a-b,-ab}$ and $H_{a-b,-ab}$, which appear in the energy equation for the other pair of wave functions. In general, $|H'_{ab,-a-b}| \leqslant |H_{ab,-a-b}|$ where the equal sign

---

*Since it can be shown that the degenerate pair of G_1 in this case must resolve into two different irreducible representations of G_2.

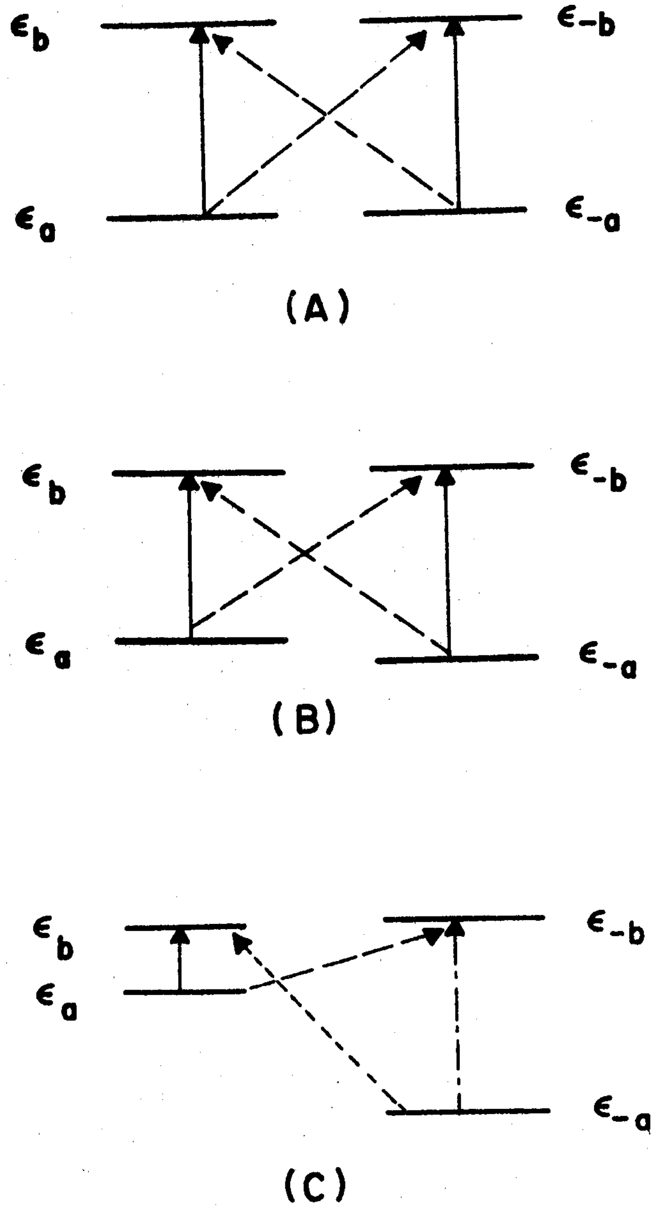

Fig. 1. Excited state mixing for doubly degenerate orbitals. Transitions denoted by the same symbol are coupled. (A) represents the hydrocarbon itself and the limiting case of a "weak" substituent, (B) intermediate coupling represented by equation (3.5), and (C) the limiting "strong" substituent case.

holds for the case of zero interaction.* If one considers the case of a strong substituent, $|E'_{ab} - E'_{-a-b}|$ may become so large, and $|H'_{ab,-ab}|$ so small, that the excited states may be considered as completely uncoupled (Fig. 1). $H_{ab,-a-b}$ may be either positive or negative and can be quite large, perhaps several ev in given cases, The possibility exists, therefore, that Δ^2E may be negative for some transition arising from a degenerate configuration in the parent hydrocarbon, corresponding to a blue shift upon substitution by a radical interaction solely through the resonance parameter. This possible behavior is not predicted at all from the naive treatment alone. The inclusion of inductive interaction does not alter the sense of the argument. It is important to note, however, that the inductive effect may result in a reversal of the energy order of the zeroth-order configurations χ'_{ab} and χ'_{-a-b} .

C. Oscillator Strengths

For the case in which neither Φ_a nor Φ_b of the pa-

---

*This results from the change of the nature of the orbital wave functions perturbation. The admixing of substituent orbital reduces the parent hydrocarbon contribution to the orbital, thus reducing this repulsive term without adding any compensatory term from the substituent orbital. A similar statement applies to $|H'_{a-b,-ab}|$ as compared to $|H_{a-b,-ab}|$.

rent hydrocarbon is degenerate, one can write for the f-number of the transition a → b (44):

$$f^{o}_{ab} = 2.170 \times 10^{11}\, \nu\left(\int \Psi_a \vec{r}\, \Psi_b \, dv\right)^2, \qquad (3.7)$$

in which ν is in cm.$^{-1}$ and $\Psi_{a,b}$ are the functions of equation (2.2). Using this equation to expand equation (2.7), one obtains:

$$f_{ab} = 2.170 \times 10^{11}\, \nu\left(a_{aa}a_{bb}\vec{M}_{ab} + \sum_{i\neq a}^{N+1}\sum_{k\neq b} a_{ai}a_{bk}M_{ik}\right)^2, \qquad (3.8)$$

in which the transition moment $\vec{M}_{ik}$ is defined as $\int \Phi_i \vec{r}\, \Phi_k dv$. In the case that the transition a → b in the parent hydrocarbon is allowed (and there is no accidental cancellation to make its spectroscopic moment unduly small) the quantity $a_{aa}a_{bb}\vec{M}_{ab}$ will be the leading term in the summation of equation (3.8). This leads to an interesting approximate formula for the ratio of the oscillator strengths of substituted and parent hydrocarbon:

$$\frac{f_{ab}}{f^o_{ab}} \approx (a_{aa}a_{bb})^2 \frac{\nu}{\nu^\circ} \approx (a_{aa}a_{bb})^2 . \qquad (3.9)$$

The advantage of calculating ratios of oscillator strengths should be especially noted. Mulliken and Rieke (44) have indicated the success of the use of a simple multiplicative corrective factor on the f's. It is obvious that such a factor, assumed unchanged upon substitution, cancels out of such a ratio and need not be explicitly determined.

If the transition a̲ - b̲ in the parent hydrocarbon has a small transition moment, even though formally allowed, equation (3.9) breaks down, as the off-diagonal spectroscopic moments must be taken into account. Another somewhat less rigorous procedure, however, may be used to obtain good results. If $\vec{M}_{ik}$ $(i,k \neq x)$ is expanded, then:

$$\vec{M}_{ik} = \sum_u^N \sum_w^N c_{iu}c_{kw} \int \phi_u \vec{r} \, \phi_w \, dv . \qquad (3.10)$$

The quantity $\int \phi_u \vec{r}\, \phi_u$ may be considered as a vector $\vec{R}_u$, directed from the origin to the location of ϕ_u (for a limited number of cases, including the π-orbital situation we are considering). Then $\int \phi_u r\, \phi$ is equal to $S_{u\omega}\vec{R}_{u\omega}$, where $\vec{R}_{u\omega}$ is a vector to the midpoint of the carbon-carbon bond u-ω, and $S_{u\omega}$ is the corresponding overlap integral. From the geometry of the hydrocarbon the vectors $\vec{R}_u$ and $\vec{R}_{u\omega}$ may be written in terms of the distance between nearest carbon neighbors R_{12} and the geometric vector quantities $\vec{U}_u$ and $\vec{U}_{u\omega}$, so that equation (3.10) becomes:

$$\vec{M}_{ik} = \Big(\sum_{u=1}^{N} C_{iu}C_{ku}\vec{U}_u + \sum_{u\neq\omega}^{N} C_{iu}C_{k\omega}\vec{U}_{u\omega}S_{u\omega}\Big)R_{12} \qquad (3.11)$$

For the substituted hydrocarbon, by an analogous argument, one can write:

$$
\begin{aligned}
f_{ab} = 2.170 \text{ x } 10^{11}\nu \Bigg[\sum_{i=1}^{N} \sum_{k=1}^{N} a_{ai}a_{bk} \Bigg\{ \sum_{u=1}^{N} C_{iu}C_{ku}\vec{U}_{u} \\
+ \sum_{\substack{u \neq \omega \\ = 1}}^{N} C_{iu}C_{ku}S_{u\omega}\vec{U}_{u\omega} \Bigg\} R_{12} + a_{ax} \sum_{k=1}^{N} a_{bk} \int \Phi_{x}\vec{r}\, \Phi_{k}dv \\
+ a_{bx} \sum_{i=1}^{N} a_{ai} \int \Phi_{x}\vec{r}\, \Phi_{i}dv + a_{ax}a_{bx} \int \Phi_{x}\vec{r}\, \Phi_{x}dv \Bigg]^{2}
\end{aligned}
$$

(3.12)

The three integrals involving the substituent AO, Φ_x, may be broken down in the following manner:

$$\int \Phi_{x}\vec{r}\, \Phi_{x}dv = \vec{R}_{x} \qquad (3.13a)$$

$$
\begin{aligned}
\int \Phi_{x}\vec{r}\, \Phi_{k}dv &= \sum_{u=1}^{N} C_{ku} \int \Phi_{x}\vec{r}\phi_{u}dv \\
&= \sum_{u=1}^{N} C_{ku} \left(\vec{R}_{ux}S_{ux} + \int \Phi_{x}\vec{r}\,'\phi_{u}dv\right) \qquad (3.13b)
\end{aligned}
$$

where $\vec{R}_{ux}$ is defined in the same way as $\vec{R}_{u\omega}$, a vector to the midpoint of the u-x bond and $\vec{r}'$ is a vector from this point to the center of change of the u-x bond. Now, if the transition is polarized perpendicular to the s-x bond, $\vec{R}_x$ and $\vec{R}_{sx}$ are zero. Hence the integral defined by equation (3.13a) is zero, and that defined by (3.13b) small. Writing $\vec{R}_x$ and $\vec{R}_{ux}$ as $\vec{U}_x R_{12}$ and $\vec{U}_{ux} R_{12}$, respectively, and assuming $\int \Phi_x \vec{r}' \phi_u dv$ is only a small part of equation (3.12), as is usually the case, we may approximate equation (3.12) by an expression homogeneous in R_{12}^2 :

$$f_{ab} \approx 2.170 \times 10^{11} \nu \Big[\overset{N+1}{\sum_{i=1} \sum_{k=1}} a_{ai} a_{bi} \sum_{u=1}^{N-1} C_{iu} C_{ku} \vec{U}_u + \overset{N+1}{\sum_{\substack{u \neq \omega \\ =1}} \sum} C_{iu} C_{ku} S_u \vec{U}_u \Big]^2 R_{12}^2 \qquad (3.14)$$

This equation provides a convenient formula for the oscillator strength of the substituted hydrocarbon.

If the transition in the parent hydrocarbon is a forbidden one (either because of symmetry or accidentally), $M_{ab} = 0$ and the off-diagonal terms, $\overset{n+1}{\sum_{i\neq a}\sum_{k\neq b}} a_{ai}a_{bk}\vec{M}_{ik}$, determine the oscillator strength. It should perhaps be emphasized that wave functions obtained by perturbation theory methods seldom are adequate for this purpose, because the forbidden case involves a large number of small terms of the same order of absolute magnitude, but with varying signs. Inaccuracies in the wave functions in such a case can lead to large percentage errors in f. For the case where M_{ab} is the dominating term, perturbation wave functions may be expected to do much better.

If the transition in the hydrocarbon was forbidden by accidental cancellation, substitution will in general remove the cancellation and increase the oscillator strength of the transition. On the other hand, if f^{o}_{ab} is large, the effect of substitution will be in general to decrease the intensity. In intermediate cases, the effect of substitution may be in either direction.

If one has the situation, considered in detail in the previous section, in which orbital degeneracy exists in the parent hydrocarbon but is removed by substitution, then the f-numbers of the substituted compounds will be direct functions of the excited state mixing coefficients.[*] It is essential to take this into account in such a computation. The qualitative behavior is most easily ascertained by computing the oscillator strengths for the limiting cases of no excited state mixing and complete excited state mixing (as in the parent hydrocarbon) as a function of the resonance parameter of the substituent. The correct curve will approximate the no excited state mixing curve for strong substituents, and the complete excited state mixing curve for weak substituents. In the particular situation in which the transition is weak in the parent hydrocarbon because of cancellation of the transition moments due to complete and symmetrical excited state mixing, the change in the amount of this mixing upon substitution may be the dominant factor in determining the magnitude of the oscillator strenghh of the substituted compound. The importance of this term will be demonstrated in a quantitative calculation on benzene in a forthcoming chapter.

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[*] For the degenerate case, the transition moments corresponding to the zeroth-order excited states belonging to the same irreducible representation of G_2, must be exactly equal in magnitude. This requires that there exist one forbidden and one allowed (if the transition moments are non-zero) transition for each of the two irreducible representations of G_2 given in equation (3.2). Since the forbidden transition arises from the cancellation of equal but opposite transition moments, any change in excited state mixing removes the forbiddance, even if the transition moments remain unchanged.

The inductive effect, in general, influences the coefficients a_{ij} , where i or j , or both, refer to levels high in energy compared to e_x, more than the resonance effect. This tends to affect the off-diagonal elements in the oscillator strength expression, so that inductive interaction is more effective in removing forbiddenness of a transition than resonance interaction. It is possible for a combination of resonance and inductive effects to produce an accidentally forbidden transition. This may happen when $\delta_a > 0$. On the other hand, if $\delta_a < 0$, the inductive and resonance effects will act on the intensities in the same direction. Finally, one should mention that the present treatment cannot of itself give a convincing interpretation of the intensities of electronic spectra (in common with previous treatment) inasmuch as it does not treat the effects of vibrational perturbations upon the intensities. This is a particularly troublesome factor in comparing calculated with experimental intensities, and, unfortunately, no treatment of this factor seems adequate at the present time.

D. Assignment of Transitions Through Substitution

One of the most interesting and valuable uses that a theory of substitution can be put to, is assignment of transitions in the parent hydrocarbon. Both the energy shifts and oscillator strengths may be used for this purpose, with the advantage that sharp and plentiful band systems are not absolutely necessary, as in vibrational analyses, although care must be taken in assessing vibrational perturbations.

In the calculation of transition energies in hydrocarbons, configuration interaction (CI) has shown itself to be an important factor in obtaining close agreement of theoretically computed with observed levels.(39) It is reasonable to assume that on substitution, the CI does not change radically, and hence, as long as energy shifts are calculated, is a factor of much less importance.* A semi-quantitative treatment may however be instructive. Consider two levels of the same symmetry: E_{ab} and E_{cd}. We assume now that the CI is known for the parent hydrocarbon. The shift in excited state energies including CI, ΔE^*, is approximately:

---

*Here we mean interactions between non-degenerate levels in the parent hydrocarbon. These are higher-order effects which are not as radically affected by substitution as the excited state mixing of section B.

$$E^{\#}_{ab} = E^{*}_{ab} - E_{ab} = E_{ab} + \frac{\left(\int \chi'_{ab} \frac{1}{r^{uw}} \chi'_{cd} dv \right)^{2}}{E'_{ab} - E'_{cd}}$$

$$- \frac{\left(\int \chi_{ab} \frac{L}{r^{uw}} \chi_{cd} dv \right)^{2}}{E^{o}_{ab} - E^{o}_{cd}}$$

(3.15)

with a similar expression for E^{*}_{cd}. The integral $\int \chi'_{ab} \frac{1}{r^{uw}} \chi'_{cd} \, dv$ may be expanded out straightforwardly in terms of integrals of the form M'_{ijkl}, and its trend for a series of substituents ascertained by the remarks made in II F. In this way, at least the direction of the change in CI on going to the substituted hydrocarbon can be ascertained without detailed calculation. Such knowledge is frequently sufficient to make a positive statement about the transition assignment. A similar line of reasoning can be applied to the oscillator srengths.

It is also clear that substituents which are primarily inductive or primarily resonance-active cause a transition to behave in different ways, and different orientations of substituents , as well as polysubstitution, provide additional important information intimately tied up with the symmetry properties of transitions. (See reference (25) for an example.)

E. Properties of the Ground State

The properties of the ground state which are usually of interest to the chemist are: delocalization energies, charge densities, band orders and dipole moments. The computation of these quantities by the empirical method have been considered in many of its subtle facets in a comprehensive series of papers by Mulliken, Coulson and Longuet-Higgins. We therefore confine ourselves here to remarks on the calculation of excess delocalization energies through the use of orbital energies determined by the modified semi-empirical method, and on the calculation of π-electron dipole moments.

The concept of delocalization energy in the LCAO method involves the difference in energy of the electrons assigned to localized (two-center) and the best delocalized (many-center) MO's. In the LCMO method, one selects as the zeroth-order set of orbitals the best n-center LCAO MO's obtainable, for the groups under interaction. It then seems reasonable to think of the difference in energy of the electrons assigned to the zeroth-order MO's and the best LCMO MO's, as the excess delocalization energy of the π-electron system. Since we are associating our orbital energies with SCF quantities, the discussion in Mulliken and Parr (45) applies, and an orthonormalized set of orbitals must be used as the reference state. The excess delocalization energy is then:

$$\Delta^2 E_g = (E_g' - E_o') - (E_g^o - E_o^o)$$

$$= 2\left[\sum_{i=1}^{N/2} (e_i - e_i^o) + e_x\right] - 2\left[\sum_{i=1}^{N/2} (e_{i_o} - e_{i_o}^o) + e_{x_o}\right] \tag{3.16}$$

where E_g' is the ground state energy of the substituted hydrocarbon, E_o' the energy of the reference state, and E_g^o and E_o^o are the corresponding hydrocarbon quantities. The first term on the right is just the difference in orbital energies between the two compounds, and the second term is the difference in orthogonalization energies. This latter term is not necessarily zero; hence, to calculate the excess delocalization energy, the difference in orbital energies must be supplemented by this quantity.*

A few remarks about π-electron moments will now be appended. In the LCMO method, the dipole moment integral may be broken down as follows:

$$\vec{R} = \int \chi_g \vec{r}\, \chi_g dv = 2\sum_{j=1}^{N/2}\Big[\sum_{k=1}^{N}\sum_{i=1}^{N} a_{jk}a_{ji}\int \Phi_i^u \vec{r}_u\, \Phi_k^u dv_u$$

$$+ a_{jx}^2 \int \Phi_x \vec{r}\, \Phi_x dv + 2\sum_{i=1}^{N} a_{ji}a_{jx}\int \Phi_i \vec{r}\, \Phi_x dv\Big] \qquad (3.17)$$

---

*The important point is that both E_g' and E_o' are determined in terms of β^*. Hence, from a spectroscopic parameter, "true" resonance energies can be determined, provided the orthogonalization energies are taken into account. Contrast this with the conventional semi-empirical method in which resonance energies determined from spectroscopic β's are not equal to those determined from ground state β's, and do not represent a "true" resonance energy (45). Though we developed this from the excess delocalization energy of a substituted hydrocarbon, exactly similar reasoning holds for

In the special case that the hydrocarbon possesses a center of symmetry, $\int \Phi_i \vec{r}\, \Phi_i dv = 0$ for each i, and

$$\sum_{j=1}^{N/2} \sum_{i=1}^{N} a_{ji}^2 \int \Phi_i \vec{r}\, \Phi_i dv = 0\ . \qquad (3.18)$$

In equation (3.17), the first set of terms over hydrocarbon orbitals corresponds to a π-electron moment in the hydrocarbon part of the molecule, produced by the perturbed charge distribution. The second term is just a vector to the substituent R_x. It is just these terms that Matsen and Jaffe (6,21) have essentially attributed to the "resonance moment" in substituted benzenes. Plainly, however, terms involving $\int \Phi_i \vec{r}\, \Phi_x dv$ are left over. These reduce in a first approximation to $2 \sum_i a_{ji} a_{jx} C_{is} \left[\vec{R}_s S_{xs} + \int \phi_s \vec{r} \phi_x \right]$.

The same kind of remarks that applied to oscillator strengths apply here -- i.e., if the hydrocarbon moment $\vec{R}_o$ is large, the off-diagonal terms may safely be neglected; if $\vec{R}_o$ is zero, they generally cannot be neglected. In any case, it is clear that the procedure of taking the

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(Continued from page 71) the delocalization energy of the hydrocarbon.

difference between dipole moments of a substituted hydrocarbon and the corresponding alkyl compound will not cancel out the substituent hydrocarbon interaction terms, and hence, this difference does not directly determine the resonance moment.

F. Conjugated Substituents

In the preceding sections, we have tacitly assumed that the substituent interacts with the π-electron system of the hydrocarbon through a single orbital. This is tantamount to regarding the substituent as possessing a lone pair, e.g., a halogen. If, now, formally conjugated substituents are considered, Dewar's approach (2) may again be utilized at the outset. If the substituent possesses M conjugated atoms, the resulting secular equation will be of (N+M)th order. All the preceding considerations can be readily extended to this more general case (in effect, closed shell lone pair substituents represent the case $M = 1$); however, two considerations outside of additional complexity may make theoretical considerations less reliable: (a) The possibility of transitions between hydrocarbon and substituent orbitals may lead to a number of degeneracies or near degeneracies between the various configuration energies. (b) The greater number of transitions possible may lead to a cluttered spectrum, making interpretation less certain. The first consideration means that for reliable results, CI in the substituted hydrocarbon may be a necessity. And since some of the transitions do not exist in the parent hydrocarbon, absolute energies rather than shifts, and the absolute amount of CI rather than the shift in CI, must be calculated. Similar remarks apply to the oscillator strengths where absolute values rather than relative ones may be required. The second consideration may mean that the spectrum is diffuse and hence unreliable, both with regard to assignment and as a source of transition energies.

G. Polysubstitution

This section presents a brief summary of aspects (needed in the following sections) of a comprehensive treatment of polysubstitution which will be published elsewhere (46). We consider a series of substituents, X_1, X_2, ... , X_n, not necessarily identical, attached to the hydrocarbon at carbon atoms s_1, s_2, ..., s_n; then:

$$\Psi_i = \sum_{j=1}^{N+n} a_{ij} \Phi_j , \tag{3.19}$$

where Φ_j $(j = 1 \ldots\ldots N)$ are hydrocarbon MO's and Φ_{N+1} to Φ_{N+n} are substituent AO's. The total Hamiltonian for a polysubstituted hydrocarbon may be written as follows:

$$H = \sum_{\ell=1}^{n} H_{s_\ell}^{\ell} - (n-1)H^{o} + H^{*}_{\ell,s_\ell} \tag{3.20}$$

where $H_{s_\ell}^{\ell} = H^{o} + H_{s_\ell}^{\prime\ell}$ is the total Hamiltonian for the monosubstituted hydrocarbon $R - X_\ell$; $H_{s_\ell}^{\prime\ell}$ is the perturbation due to the substituent X_ℓ . H^{*}_{ℓ,s_ℓ} represents additional electron interaction terms which arise from the additional perturbation of the charge distribution in the hydrocarbon part of the molecule. It depends of course on the nature and orientation of the substituents.

The exact form and solutions of the secular equation and the role of symmetry are discussed in (46). Here, we utilize second-order perturbation theory solutions, which are equivalent to the first-order ones, using the Ψ_i

(monosubstituted hydrocarbon wave functions) as zeroth-order functions. The matrix elements are:

$$\int \Psi_j H \Psi_j dv = e''_j = H^o_{jj} + \sum_{\ell=1}^{n} \Delta e^{\ell}_j + \int \Psi_j H^*_{\ell, s_\ell} \Psi_j dv, \qquad j \neq x$$

$$\int \Psi_{x_k} H \Psi_{x_k} dv = e_{x_k} = H^o_{x_k x_k} + \sum_{\ell=1}^{n} \Delta e^{\ell}_{x_k} + \int \Psi_{x_k} H^*_{\ell, s_\ell} \Psi_{x_k} dv, \tag{3.21}$$

where $\Delta e^{\ell}_j = e^j_{\ell} - H^o_{jj}$, and $\Delta e^{\ell}_{x_k} = e^{\ell}_x - H_{x_\ell x_\ell}$; e_j^{ℓ} and e^{ℓ}_x are just the orbital energies of the monosubstituted hydrocarbon, R - X_ℓ, give by equation (2.9). Terms involving interactions between different substituents disappear in this approximation, but they are immaterial for the discussion which follows. Equation (3.21) shows that the orbital energies of the polysubstituted hydrocarbon would be just the sum of the perturbations due to each substituent, except for the term involving H*. The magnitude of this last term depends upon the rearrangement of the electron distribution in the hydrocarbon, and hence on the degree of substituent-hydrocarbon interaction. We can state this conclusion in the following way: In an empirical molecular orbital theory, the orbital energies and wave functions of a polysubstituted molecule having a delocalized electron system, cannot be obtained as a sum of perturbations derived from empirical data on monosubstituted molecules. This statement is not dependent upon the use of perturbation theory, but applies to exact solutions of the secular equation. (Henceforth, the term "perturbation treatment" will imply the exact solutions of the secular equation with the perturbation type Hamiltonian of 3.20.) This very procedure has been used frequently, and its success hinges upon the substituents having little effect on the electron distribution in the parent part of the molecule.

The same sort of result may be obtained for the SCF orbital energies in the polysubstituted hydrocarbon. They may be written:

$$e_i'' = H_i'' + \sum_j {}^{o}(2J_{aj}'' - K_{aj}'') + \sum_{\ell=1}^{n} (2J_{ix_\ell}'' - K_{ix_\ell}'') \, , \tag{3.22}$$

where the doubly primed integrals are over polysubstituted hydrocarbon wave functions. Since the values of the integrals in equation (3.22) have no direct relation to the corresponding integrals of the corresponding expression for monosubstituted hydrocarbons, polysubstituted SCF energies may not be determined by perturbation theory from monosubstituted SCF energies. It is clear that any excitation process will involve electron interaction terms determined by the polysubstituted wave functions, so that even if the orbital energies can be considered additive, the excitation energies are not (except for the limiting case of "weak" substituents, for which, both orbital energies and excitation energies are additive).

One asks, at this point, how these difficulties can be circumvented so that the empirical parameters obtained from monosubstituted hydrocarbons can be used to predict the polysubstituted levels. It is clear that the fundamental problem is to determine the orbital energies, as these will determine the wave functions from which the electron interaction integrals are calculated. A detailed account of this procedure is given in reference (46), and we will outline only briefly three approaches discussed there.

1. Validity of perturbation treatment is, to a good approximation (for orbital energies), equivalent to:

$$(2J''_{aj} - K''_{aj}) - \sum_{\ell=1}^{n} (2J'^{\ell}_{aj} - K'^{\ell}_{aj}) << \sum_{\ell=1}^{n} (2J''_{ix_\ell} - K''_{ix_\ell}) \tag{3.23}$$

where the superscript ℓ indicates that integration is performed using wave functions of the monosubstituted hydrocarbon $R - X_\ell$. As noted above, even if this is satisfied, the transition energies are in general still not additive.

2. The ionization potential and one excitation energy of polysubstituted hydrocarbons are predicted by a perturbation treatment of the orbital energies, using parameters obtained from monosubstituted hydrocarbons. Any discrepancies between the predicted and observed values are absorbed in new hydrocarbon α and β values, a different set being required in general for each orientation of the substituents. This procedure automatically includes the H^* part of the Hamiltonian, and the electronic properties of the polysubstituted hydrocarbon may now be predicted. Such a prediction, however, may not be very useful.

3. This method is a compromise procedure which, theoretically and practically, seems the most promising. We start out in a similar manner as above, but predict only the spectra of identically disubstituted hydrocarbons for each possible orientation. The discrepancy between prediction and experiment is now removed by a set of δ_u^{l}'s which is assigned for all the hydrocarbon atoms , for each substituent X . In this way, a set of δ_u^{1}'s may be associated with each substituent. Introduction of two or more substituents requires addition of the δ_u^{l}'s, at each atom position. In order to justify this procedure, consider the core Hamiltonian for the hydrocarbon:

$$H^{core} = T + U_u^{+} + \sum_{w=u} U_w^{+} + \sum_{h} U_h , \qquad (3.24)$$

where U_h refers to the potential of the neutral hydrogen atoms, and U_w^{+} to the potential of a carbon-plus-ion given by the Goeppert-Mayer-Sklar assumption (13), as:

$$U_w^{+} = U_w - \int \phi_w \phi_w \frac{1}{r^{12}} dv_1 . \qquad (3.25)$$

These yield the well-known expression for the core energy of a π-electron on atom u:

$$\alpha_u^o = \int \phi_u H^{core} \phi_u = W_u - \sum_{\substack{w \neq u \\ =1}}^{N} \left[(uu:ww) - (U_w:uu) \right]$$

$$+ \sum_r (U_r:uu) \ . \qquad (3.26)$$

In a monosubstituted hydrocarbon, the charge density on carbon atom u may be taken as Q_u, where $Q \gtrless 1$. Then Q times the interaction energy of one electron must be subtracted from the nuclear field energy to yield the potential of a C^{+Q} ion:

$$U_w^{+Q_w} = U_w - Q_w \int \phi_w \phi_w \frac{1}{r^{12}} dv_1 \qquad (3.27)$$

that is to say, if the charge density on w is less than or more than unity, we remove less than or more than one electron, respectively, in order to leave a neutral carbon core.

The core energy of a π-electron on atom u then becomes:

$$\alpha'_u = W_u - \sum_{w=u} (U_w:uu) - \sum_r (U_r:uu) - \sum_{\substack{w\neq u\\=1}}^{N} Q_w(uu:ww)$$

$$+ (1 - Q_w)(uu:uu) \qquad (3.28)$$

If we define $\Delta_w = 1 - Q_w$, then:

$$\alpha'_u = \alpha^o_u - \sum_{w=1}^{N} \Delta_w(uu:ww). \qquad (3.29)$$

This last sum is the theoretical counterpart of $\delta_u \beta$; and as a first approximation, Δ_w may be considered additive for each substitution, which is tantamount to adding the δ_u's. This also suggests that the ratios of the various δ_u's may be determined as the ratios of the Δ_u's. A refinement may also be made in the carbon-carbon exchange integrals, using rather similar reasoning. This is discussed in detail in reference (46).

H. $n \rightarrow \pi$ Transitions

We have restricted ourselves to transitions between the delocalized π orbitals of the conjugated system. However, another set of transitions is possible in a substituted hydrocarbon, provided the substituent possesses an occupied non-bonding orbital. Such a possibility exists for substituents having localized σ orbitals. Heretofore we have considered electrons falling in this category as part of the "core" of the substituent, but now we explicitly include them in the ground state configuration. n_x and n_y are the non-bonding σ orbitals (including spin) parallel and perpendicular to the C-X bond respectively. There are then two types of $n \rightarrow \pi$ transitions possible: $n_x \rightarrow b$ and $n_y \rightarrow b$, the energies of which are given by:

$$^{1,3}\Delta E = e_b - e_n - (J'_{nb} - K'_{nb}) \pm K'_{nb} \qquad (3.30)$$

From this point on, the symbol n will represent either n_x or n_y, except where it is necessary to distinguish between them. The orbital energy e_n is given by:

$$e_n = \sum_{i=1}^{N/2,x} (2J'_{ni} - K'_{ni}) - J_{nn} - H_n \qquad (3.31)$$

The core energy, H_n, may simply be obtained from:

$$H_n = W_n - 2\sum_{u=1}^{N+1} \rho_u J_{nu}, \qquad (3.32)$$

where W_n is a valence state ionization potential, and ρ_u the π charge density of atom u. Because of the very simple form of the expressions involved, ΔW and e_n may be readily calculated from equations (3.31) and (3.32), the only ambiguous term being W_n (which is known at least approximately in most cases). e_b, ρ_u and a_{ji} are obtained from the modified empirical procedure. It is convenient, however, to interpret these relations in terms of the semi-empirical quantities of section E of Chapter II. The semi-empirical e_n is given by $H_{nn} = H^o_{nn} + H'_{nn} + H^*_{nn}$, where H^* is due to the redistribution of charge in the hydrocarbon part of the molecule. The empirical quantity δ is defined by $\alpha + \delta\beta = H_{xx}$, assuming H'_{xx} and H^o_{xx} may be taken approximately equal to H_{nn} and H^{o}_{nn}, respectively, it follows that $H_{nn} = \alpha + \delta\beta + H^{*}_{nn} - H^{*}_{xx}$. In order to draw qualitative conclusions easily, we make important simplifications which were not possible for $\pi - \pi$ transitions. An approximate form of equation (3.31) is obtained through replacement of e_n by the semi-empirical expression $\alpha + \delta\beta$, assuming $(H^{*}_{nn} - H^{*}_{xx})$ is negligible;[*] and utilizing $J_{ni} >> K_{ni}$ and $J_{nu} < J_{nx}$ $(u \neq x)$, the $n \rightarrow \pi$ transition energy becomes, to a first approximation,

$$^{13}E = e_b - (\alpha + \delta\beta) - a^{2}_{bx}(J_{nx} - K_{nx} \mp K_{nx}). \qquad (3.33)$$

Three interesting conclusions can be drawn. These are:

1. For any series of substituents, for which the resonance effect varies widely, e_b varies much less than e_n, and hence, is roughly proportional to δ for not too small values of δ. As the resonance interaction of substituent and hydrocarbon increases, δ becomes smaller in magnitude and the $n \rightarrow \pi$ transition energy decreases. This red shift in

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[*] This is valid when interaction between substituent and hydrocarbon is small, as then δ is large and $(H_{nn} - H_{xx})$ is small.

the $n \rightarrow \pi$ transition energies in any series of substituents of increasing resonance effect, will be very much greater than the corresponding red shift of the $n \rightarrow \pi$ transitions. Indeed, this greater dependence upon δ makes $n \rightarrow \pi$ transitions a better source of this empirical parameter than $\pi - \pi$ ones. These effects have been discussed for the case of substituted benzenes (47).

2. The singlet-triplet splitting of $n \rightarrow \pi$ states will vary widely, depending upon the degree of interaction of the substituent with the hydrocarbon. In the limiting case of no interaction with the hydrocarbon, the singlet and triplet levels will very nearly be degenerate. As this splitting is proportional to a_{bx}^2, for all but very large interactions, the singlet-triplet splitting will be smaller than for $\pi - \pi$ states.* This is the observed situation (48).

3. In case there exists excited π states of the same symmetry as the n states, the interaction integrals between these states can be expected to be smaller than

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*Kasha, in reference (48), has suggested that there may be greater spin-orbit coupling for non-bonding electrons than for π-electrons, which would also predict less S-T separation for $n - \pi$ states than for $\pi - \pi$ states. However, we note that $|K_{nx}|$ is frequently $< |K_{ab}|$. See equation (3.35).

interaction integrals.

One of the most interesting properties of n → π transitions is its behavior upon further substitution. As it is quite different from that of π–π transitions, it should be of value in separating and identifying the two types of transitions. In the following we assume that the substituents are not ortho to each other. Under this condition, we can write as the analogue of equation (3.33) for the shift in energy of the n → π transition upon substitution:

$$^{1,3}\Delta^2 E = e_b' - e_b - [(a_{bx}')^2 - (a_{bx})^2](J_{nx} - K_{nx} \mp K_{nx}) \tag{3.34}$$

where the primed quantities are for the polysubstituted hydrocarbon. The changes that e_b and a_{bx} undergo for different types of substituents are summerized below:

1. For additional resonance interaction e_b' moves to higher energies than e_b, and $|a_{bx}'| < |a_{bx}|$.

2. For an inductive effect which removes charge from the hydrocarbon ($\delta_2 > 0$), e_b' is lowered relative to e_b, and $|a_{bx}'| > |a_{bx}|$.

3. For the opposite inductive effect ($\delta_2 < 0$), e_b' is raised and $|a_{bx}'| < |a_{bx}|$.

Since $J_{nx} >> K_{nx}$, $(J_{nx} - K_{nx} \mp K_{nx}) > 0$ and the following table may be constructed:

Table 7. Comparison of $n \rightarrow \pi$ and $\pi - \pi$ transition energy shifts upon polysubstitution

Type of Substituent-Hydrocarbon Interaction[a]	Predicted Energy Shift ($\Delta^2 E$)		Predicted Shift in $n \rightarrow \pi$ S-T Splitting ($\Delta^2 E^S - \Delta^2 E^T$)[c]
	$n \rightarrow \pi$	$\pi - \pi$[b]	
R only	blue	red	red
I only	red blue	red or blue blue or red	blue red
R+I[d]	I(D)	I(D) or R(D)	I(D)

a. Symbols are the same as in Table 6.

b. These are for a general hydrocarbon. If alternant, and if the substituents are "weak," the shifts in the transition energy is small; the $n \rightarrow \pi$ shifts, though, Since the shift in the energy of a $\pi-\pi$ transition depends upon the difference in shifts of two levels which are affected by substitution in much the same way, in general, $n-\pi$ shifts upon substitution will be greater than $\pi-\pi$ shifts. This is not necessarily true, however, since the case of $\delta_a > 0$ opposes the resonance effect in $n-\pi$'s but can aid the resonance effect in $\pi-\pi$'s. It is interesting to consider the splitting between the singlet and triplet levels upon substitution. For qualitative purposes, this is:

$$ {}^1E - {}^3E = (a^1_{bx})^2 K_{nx} \; . \qquad (3.35) $$

The entries in the fourth column of Table 7 were constructed from this relation. It is clear from Table 7 that the different behaviors of the two types of transitions, upon substitution and with the use of the solvent effects formulated by Kasha (32) should allow assignment between them.

(Continued from page 88)
are independent of the type of hydrocarbon.

c. ($\Delta^2 E^S$ - $\Delta^2 E^T$) refers to the shift in the separation of the singlet and triplet excited states.

d. (D) indicates that whatever effect precedes it is the dominating one.

In the special case where there is a substituent ortho to the substituent from which the n arises, the effect on e_n will be expressed through an extra substituent-substituent interaction term:

$$\frac{(H'_{nx} - S'_{nx}H_{nn})^2}{\delta - \delta'} ,$$

the sign of $(\delta - \delta')$ determining whether e_n is lowered or raised. In any given case, this can be immediately ascertained.

We now turn to the oscillator strengths. It is clear that since the π state is antisymmetric to reflection in the plane of the molecule, all $n \rightarrow \pi$ transitions must be polarized perpendicularly to the molecular plane. The oscillator strength of the transition $n \rightarrow b$ is:

$$f_{n \quad b} = 2(1.085 \times 10^{11})\nu \left(\int nZ \psi_b dv \right)^2 \qquad (3.36)$$

Expansion of ψ_b to $\sum_{i=1}^{N} a_{bi} \Phi_i + b_x \Phi_\chi$ reduces the oscillator strength integral to integration over hydrocarbon orbitals since $\int nZ\phi_x dv = 0$ on symmetry grounds. To a good approximation, the integral $\int nZ\phi_s dv$ is the dominating term, hence

$$f_{n-b} = 2.170 \times 10^{11} \nu \left[\sum_{i=1}^{N} a_{bi} C_{is} \int nZ\phi_s dv \right]^2 . \qquad (3.37)$$

Both n_x and n_y transitions are formally allowed, but there is a great difference in the intensities. For the integral $\int n_y Z\phi_s dv$ is forbidden, while $\int n_x Z\phi_s dv$ is not. This means that the leading terms in transitions of the type n_y-b, comes from the integrals $\int n_y Z\phi_{s\pm 1} dv$ which are much smaller than the ones involving n_x and ϕ_s. Hence the oscillator strength of transitions arising from n_y are much smaller than those arising from n_x (47). The $n-\pi$ (unlike the $\pi-\pi$) oscillator strength is quite insensitive to the degree of substituent-hydrocarbon interaction. However, f will be a marked function of the electronegativity of X as well as the nature of the non-bonding orbital (47).

It will be recalled that the effect of polysubstitution on $\pi-\pi$ oscillator strengths is extremely orientation-dependent, and produces appreciable change in f. If we add a second substituent, the usual effect is to lower a_{bb} slightly. This gives $f_{poly}/f_{mono} \approx \left(\frac{a'_{bb}}{a_{bb}}\right)^2$, and since a_{bb} is usually not much lowered, the substituent effect on $n-\pi$ oscillator strengths will be only a slight change in intensity. Now consider n substituents identical to the original $n-\pi$ "emitter." It is easily shown that the oscillator strength ratio is now $f_{poly}/f_{mono} = n\left(\frac{a'_{bb}}{a_{bb}}\right)^2$. Hence the intensity is increased by a factor nearly equal to n. This kind of result, of course, is completely different from $\pi-\pi$ intensity effects, and suggests that a weak $n-\pi$ band may be found by "loading up" the molecule with identical substituents. Just as in the case of $\pi-\pi$ spectra, steric hinrance will affect the intensities and transition energies of an $n-\pi$ band, but in radically different ways (48), suggesting that these transitions may be useful for calculating twist angles.

Kasha (32) and McConnell (49) have elegantly shown that $n-\pi$ transitions undergo a blue shift in an acidic solvent. This is equivalent to saying that if solvent B is more acidic than solvent A, it will tie up the n electrons more than A; hence $W_n(B) > W_n(A)$, or $\delta_B > \delta_A$. Now, if the n orbitals of a substituent are solvent-stabilized, in effect, we pull charge off X and raise Z_{eff}

that the π orbital on X "sees." This change of Z_{eff} may be expected to cause (W_π) of the substituent to change. Writing $W_{\pi x}$ in terms of $W_{\pi c}$, as follows:

$$W_{\pi x} = \frac{1}{S_{xs}}\left[(U_x{:}xs) - (xx{:}xs) - (ss{:}xs) - (U_s{:}xs) - W_{2pc}\right] \tag{3.38}$$

the effect of raising Z_{eff} is to increase $(U_x{:}xs)$ and $(U_s{:}xs)$, and decrease S_{sx} , but $(xx{:}xs)$ may either increase or decrease, since there are two opposing factors: an increase in the repulsion of X for X, and a decrease in the repulsion of X for S. $(ss{:}xs)$ will be affected only slightly; hence the direction of change of $W_{\pi x}$ with an increase in Z cannot be ascertained in general. But this raises the possibility of blue shifts of π-π transitions upon acidification, although these should be of much smaller magnitude than the corresponding n$-\pi$ shifts, since the effect must be transmitted by a change (in the same direction) in both the excited and the ground state orbital energies, and the change of Z_{eff} is itself a second-order effect. The effect on intensities would follow that predicted by changing the mixing of the substituent orbital with hydrocarbon π orbitals. This kind of mechanism would predict little or no $\pi - \pi$ solvent effects for such substituents as $-N(CH_3)_2$ (with no n electrons) but appreciable effects with, say, the halogens.

I. N-Q Transitions

There is still another transition which can take place in substituted hydrocarbons, but not in the parent hydrocarbon. This is the perpendicular type (to molecular plane) transition characterized by Mulliken as N-Q (57). In actuality, there are two transitions possible which fall under this classification. (The $n - \pi$ transitions of the preceding section are also a special N-Q type.) We can imagine two N-Q processes taking place: $\sigma \rightarrow b$ and $n \rightarrow \sigma^*$, where σ refers to a bonding orbital in the C-X bond, and σ^* arises from excitation of the C-X bond. This second type of transition has been treated by Mulliken in alkyl halides and mixed halogens (55,56,57). As a rule, process (a) will represent a rather high energy excitation; hence, the transitions observed in practice are type (b). It is clear that this transition involves only localized or semilocalized σ type orbitals, and hence, to a first approximation, may be taken independent of the π-electron system of the molecule. Then, if for some substituent there exists an N-Q transition of type (b), further non-ortho substitution of the hydrocarbon should shift the $\pi - \pi$ (and $n - \pi$) spectra but leave the N-Q transition unchanged. In this way, the transitions may be identified, and if they overlap they can be made to separate by polysubstitution. And it can be shown that the N-Q transition may shift either to the red or to the blue, depending upon the electronegativity of the substituents.

IV. MONOSUBSTITUTED BENZENES: EMPIRICAL PARAMETERS

A. Introduction

The purpose of this chapter is to consider rather critically the evaluation of the empirical parameters defined in Chapter II, for substituted benzenes. This is carried out in a number of approximations, so that an understanding of their significance may be obtained. In addition, prior calculations on substituted benzenes are critically considered.

In a way, benzene is the most difficult hydrocarbon on which to apply a theory of substitution, because of the multiple degeneracies, which leads to a large number of interaction integrals. On the other hand, it has several desirable features: all carbons are equivalent, a large amount of experimental data has been gathered on benzene and its derivatives, and the very property that introduces the complexity leads to a number of interesting features not found in hydrocarbons of lower symmetry.

B. Wave Functions

For the benzene MO's we utilize the functions listed in Table 8. It proves more convenient, in considering substituted benzenes, to utilize the real forms of these MO's than the alternative imaginary functions. The functions are identical to those used by Sklar (4) and Matsen (6), except for the normalizing constants. For convenience we also include in Table 8 an orbital, ϕ_7, on a substituent adjacent to the ring. The ϕ_i are taken as π AO's. It should be noted that Table 8 corrects a number of the irreducible representations listed by Matsen (6).

We shall find it necessary in the following sections to utilize the configurational wave functions of substituted benzenes and understand their correspondence to those in benzene itself. The complex form of the benzene functions are given in (13), and their real counterparts may be obtained by substituting in the properly antisymmetrized configurational wave functions, the real orbitals in terms of the complex ones. The real forms are tabulated with their symmetry properties in Table 5.

Table 8. Forms and irreducible representations of benzene MO's

MO's	Symmetry[a]		
	D6h	C2V[b]	D2h[c]
$I_1 = (\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6)/(6\quad {}_{o})^{1/2}$	A2u	B2	B2u
$I_2 = (\quad \phi_2+\phi_3 \quad -\phi_5-\phi_6)/(4\quad {}_{2})^{1/2}$	E1g	A2	B1g
$I_3 = (2\phi_1+\phi_2-\phi_3-2\phi_4-\phi_5+\phi_6)/(12\quad {}_{3})^{1/2}$	E1g	B2	B3g
$I_4 = (\quad \phi_2-\phi_3 \quad +\phi_5-\phi_6)/(4\quad {}_{4})^{1/2}$	E2u	A2	Au
$I_5 = (2\phi_1-\phi_2-\phi_3+2\phi_4-\phi_5-\phi_6)/(12\quad {}_{5})^{1/2}$	E2u	B2	B2u
$I_6 = (\phi_1-\phi_2+\phi_3-\phi_4+\phi_5-\phi_6)/(6\quad {}_{6})^{1/2}$	B2g	B2	B3g
$I_7 = \phi_7$	...	B2	...

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a. We take the Z axis through atoms 1 and 4, and the Y axis perpendicular to the ring. The substituent is regarded as being attached to atom 1.

b. Irreducible representation for the subgroup C2V of D6h.

c. Irreducible representation for the subgroup D2h of D6h.

Table 9. Configurational wave functions for monosubstituted benzenes

Wave Function[a]	Symmetry	
	D6h[b]	C2V[c]
X_g	A1g	A1
$(1/2)^{1/2}(X_{25}+X_{34})$	B2u	B1
$(1/2)^{1/2}(X_{24}-X_{35})$	B1u	A1
$(1/2)^{1/2}(X_{25}+X_{34})$	E1u	B1
$(1/2)^{1/2}(X_{24}-X_{35})$	E1u	A1

---

a. X_g refers to the antisymmetrized wave function, $N_g\psi_1(1)\psi_1(2)\psi_2(3)\psi_2(4)\psi_3(5)\psi_3(6)\psi_7(7)\psi_7(8)$; X_{ij}, to the properly antisymmetrized wave function corresponding to the state arising from the one-electron excitation, $i \rightarrow j$.

b. These are listed in order of increasing theoretical energy. See reference (13) for complex forms of these functions.

c. These belong to the irreducible representations listed for the orientation of axes given in footnote a to Table 8.

C. Solutions of the Secular Equation

The secular equation for a substituted benzene is factorable into one fifth and one second degree equation. The roots of the latter are $e_2 = \alpha + \beta$ and $e_4 = \alpha - \beta$. The solutions of the former, overlap neglected, and $h_{ix} = \beta$, are found from the function F_j (See Appendix B).

$$F_j = \frac{(A_j^2 - 3)\ A_j}{(A_j^2 - 4)\ (A_j^2 - 1) + \delta_1 A_j (A_j^2 - 3)} \ . \tag{4.1}$$

The wave functions are determined from equation (B.6), which gives (overlap neglected):

$$\frac{a_{j1}}{a_{j7}} = \frac{1}{6^{1/2}} \ \frac{(A_j - 2)(A_j^2 - 1)\ F_j}{A_j(A_j^2 - 3)} \ , \tag{4.2}$$

with similar relationships for the other ratios. The function F_j, A_j, and wave function coefficients a_{ji} were calculated for a wide range of δ and δ_1 values, with overlaps both neglected and included. An extensive tabulation of these is forthcoming, and will not be reproduced here. However, the variation of the wave function coefficients a_{ji} of equation (2.2), as a function of δ for $\delta_1 = 0$, with all overlaps neglected, is presented graphically in Figures 2 through 5, for four of the five MO's affected by this empirical parameter. It should be noted that inclusion of the overlap integrals rather strongly affect these coefficients for low δ values, but only slightly at high values. It is at once obvious that considerable mixing of the benzene MO's Φ_i occurs, even for rather high δ values. Consequently, one must be cautious about applying second-order perturbation theory (which neglects a_{ji}, $j \neq 7$) in the computation of these wave functions.

D. Calculation of Integrals

The D2h symmetry of benzene provides the following irreducible representations of the possible charge distributions:

<u>Ag</u>: (11), (22), (33), (44), (55), (66), (15), (36)
<u>B1u</u>: (13), (16), (24), (35), (56)
<u>B2u</u>: (12), (25), (34), (46)

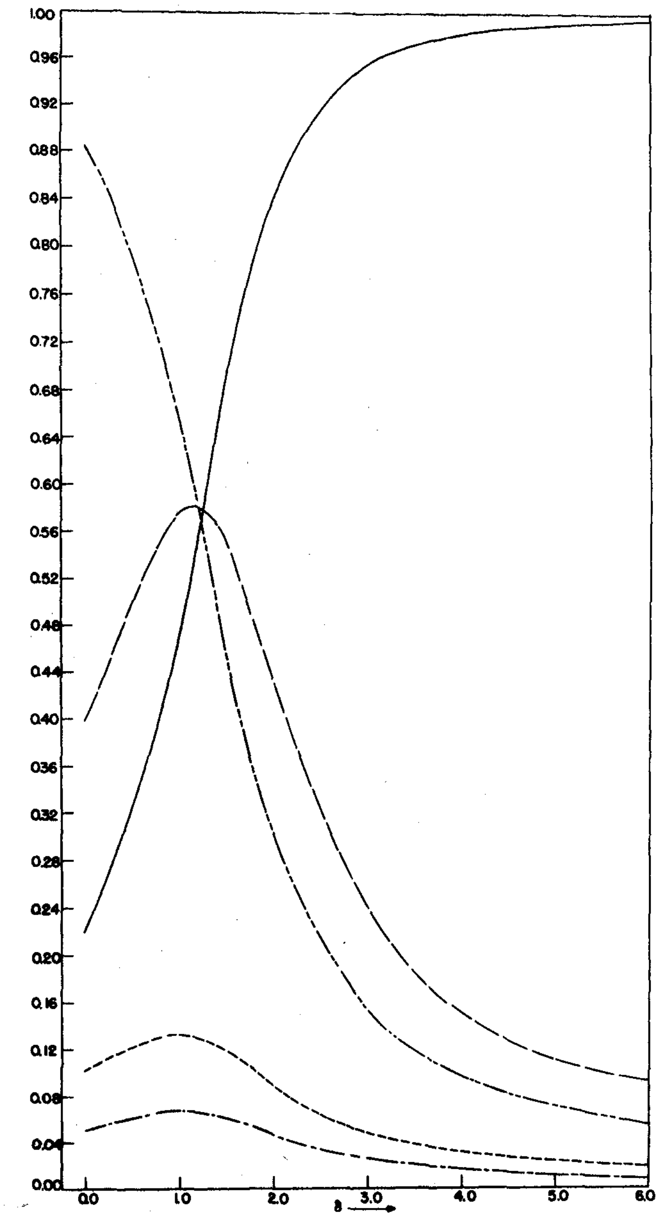

Fig. 2. ψ_7 : — a_{77}, ---- a_{71}, — — a_{73}, ---- a_{75}, —·—· a_{76}.

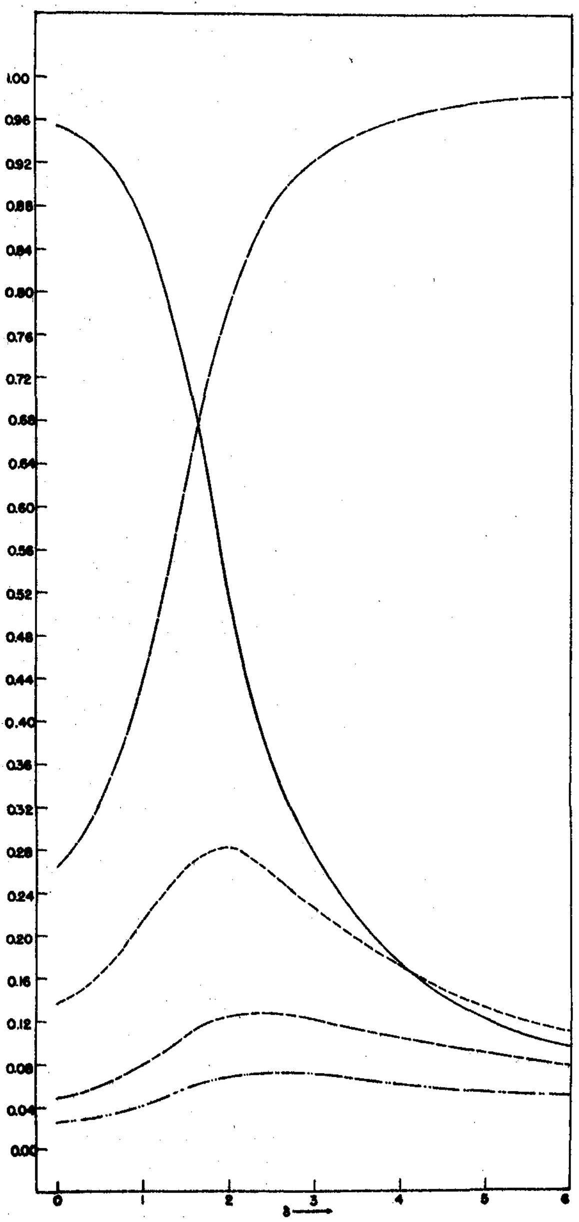

Fig. 3. ψ_1: — — a_{11}, — a_{17}, --- a_{13}, — - — a_{15}, — ·· — a_{16}.

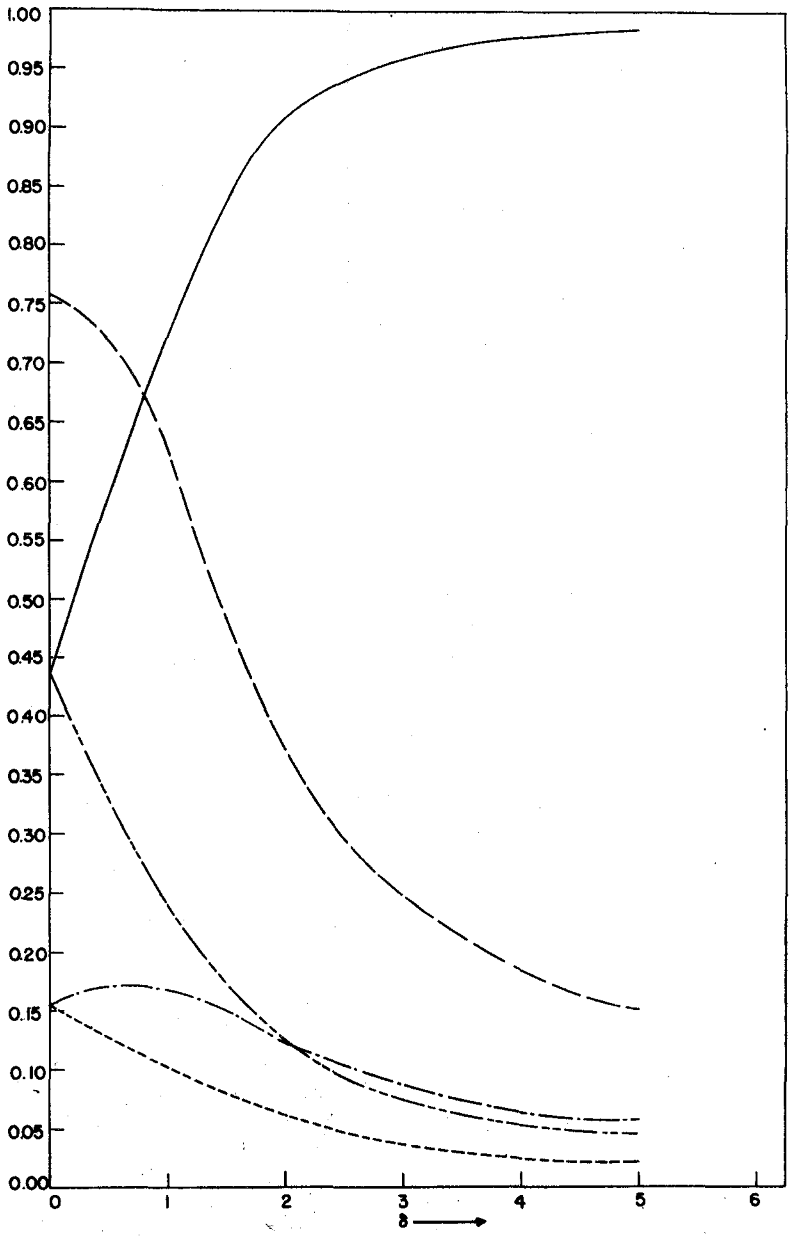

Fig. 4. Ψ_3 : — a_{33}, — — a_{37} — -- — a_{35}, -.-. a_{31},
--- a_{36}.

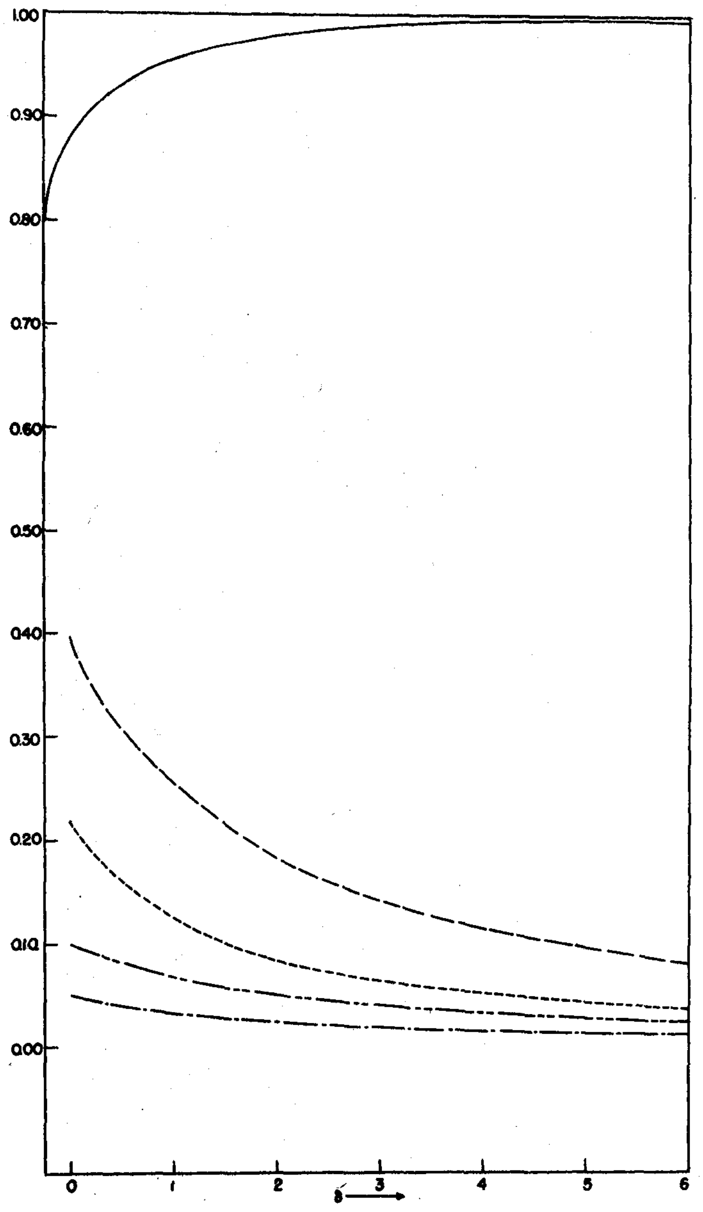

Fig. 5. ψ_5 : — a_{55}, —— a_{57}, --- a_{53}, – - – a_{56},
— · — · a_{51}.

B3g: (14), (23), (26), (45),

where (ij) refers to (I_i I_j). In order to obtain the empirical parameters and describe the excited states listed in Table 9, it is necessary to know J'_{25}, K'_{25}, J'_{34}, K'_{34}, $H'_{25,35}$, J'_{24}, K'_{24}, J'_{35}, K'_{35}, and $H'_{24,35}$. These were calculated by expansion in terms of benzene integrals. Except for J'_{35} and K'_{35}, integrals involving the substituent orbital may be neglected; thus the B1 levels, to a good approximation, are independent of the substituent-ring electron repulsion integrals. On the other hand, the A1 levels do require a knowledge of these integrals. The expansions used for the calculation of the various electron interaction integrals are discussed in Chapter II, section F. There now remains the problem of evaluating integrals over the molecular orbitals and resulting from the expansion of these, the integrals over atomic orbitals. Table 10 lists the electron repulsion integrals necessary in this calculation, including both those over AO's and those over MO's. The coulomb integrals (xx:oo) of Table 11 (see footnote to the table for notation) for OH and F were calculated by the following approximation:

$$(aa{:}bb) = 1/2\left[(aa{:}bb)_a - (aa{:}bb)_b\right], \qquad (4.3)$$

in which the heteronuclear integral (aa:bb) is approximated by averaging the values of corresponding homonuclear integrals at the same internuclear distance, but first with the effective nuclear charge of a, and then with that of b. For integrals (xx:oo) we have for NH_2, $(xx{:}oo)_x$ = 5.807 ev. Fischer (29) found by the method of Barnett and Coulson (exact expansion) the value 5.90 ev.* For OH, the approximating terms of equation (1.21) are 5.821 and 5.658 ev, respectively; and for F, 6.052 and 5.834. The close agreement of these limiting values make one expect the approximation to be an excellent one for these integrals. By way of contrast, the use of Sklar's approximation yields results quite inconsistent with these values. The Sklar result for NH_2 is 7.2 ev; for OH, 13.1 ev; and for F, 16.0 ev. This is a result of the more rapid fall off at high ρ values of the overlap as compared

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*It should be remarked in passing that Fischer (3) has clearly used an incorrect value for the integral (xx:mm) her (nn:mm) . It can easily be shown that her value is in error by a factor of 2, since at high ρ values the classical result is correct within 2 per cent. This error has been incorporated in those integrals over MO's which involve this particular AO integral, and care must be taken in utilizing values of integrals obtained from her paper.

Table 10. Electron interaction integrals (ev)

Benzene MO Integrals

(11/22)[a]	(J_{21})[b]	16.58	(26/26)	(K_{26})[b]	0.883
(22/33)	(J_{23})[b]	11.26	(14/14)	(K_{14})[b]	1.53
(22/55)	(J_{25})[b]	6.78	(34/34)	(K_{34})[b]	1.22
(22/66)	(J_{26})[b]	5.56	(45/45)	(K_{45})[b]	0.358
(33/55)	(J_{35})	7.91	(46/46)	(K_{46})[b]	1.13
(11/44)	(J_{14})[b]	9.84			
(33/44)	(J_{34})[b]	6.78	(25/43)		-1.115
(44/55)	(J_{54})[b]	4.23	(23/45)		-0.567
(44/66)	(J_{64})[b]	3.41	(26/45)		0.749
			(25/46)		1.289
(12/12)	(K_{12})[b]	5.02	(21/43)		2.051
(23/23)	(K_{23})[b]	1.05	(23/41)		1.268
(24/24)	(K_{24})	2.06	(35/24)		0.277
(25/25)	(K_{25})	1.22			

[a] $(ij/kl) \equiv M_{ijkl}$ of Chapter II.

[b] These were computed from reference (51), by multiplying by appropriate normalization constants to correspond to neglect of overlap integral, or directly from AO integrals given there.

Table 10. (Continued)

		MO Integrals Over ϕ_7			
		CH_2[c]	NH_2[d]	OH[e]	F[f]
(22/77)	(J_{27})	5.585	5.917	5.804	5.883
(44/77)	(J_{47})	3.339	3.537	3.470	3.517
(27/27)	(K_{27})	0.0013	0.0041	0.0001	0.0003
(47/47)	(K_{47})	0.0013	0.0041	0.0001	0.0003
(22/37)		0.655	0.652	0.452	0.432
(23/27)		0.0175	0.0167	0.0138	0.0117
(21/27)		0.0199	0.0197	0.0174	0.0147
(22/17)		0.505	0.499	0.343	0.325

c. $u = 1.625$; $Rc - x = 2.834$ a.u.

d. $u = 1.96$; $Rc - x = 2.570$ a.u.

e. $u = 2.35$; $Rc - x = 2.646$ a.u.

f. $u = 2.65$; $Rc - x = 2.493$ a.u.

Table 10. (Continued)

	AO Integrals Over $\phi_7(x)$			
	CH_2	NH_2	OH	F
$(xx/oo)^{h}$	5.481^{l}	5.904^{j}	5.739^{g}	5.943^{g}
(xx/mm)	3.803^{j}	3.931^{j}	3.909^{j}	3.836^{j}
(xx/om')	0.084^{k}	0.089^{k}	0.087^{k}	0.088^{k}
(xx/om)	1.207^{k}	1.279^{k}	1.254^{k}	1.271^{k}
(xx/oo')	0.213^{k}	0.229^{k}	0.223^{k}	0.231^{k}
(xx/mm')	0.148^{k}	0.153^{k}	0.152^{k}	0.149^{k}
(xx/cc)	0.433^{l}	9.278^{i}	11.152^{m}	13.614^{m}
(ox/ox)	0.010^{k}	0.0084^{i}	0.002^{k}	0.002^{k}
(mx/mx)	0.0003^{k}	0.0003^{i}	0.0000^{k}	0.0000^{k}

g. Approximated by method described in text: equation (1.20).

h. The latter notation is similar to that given in footnote a of this table, but the integral is over $2P\pi$ AO's. X refers to the substituent AO, c to the adjacent carbon AO; o, m, p, m', o', respectively, to the ring AO's listed consecutively from atom c.

i. From Fischer, reference (29).

j. Approximated by classical point-charge interactions.

k. Approximated by the Mulliken approximation.

l. By interpolation from reference (28).

m. Approximated by the Sklar approximation.

Table 10. (Continued)

	CH_2	NH_2	OH	F
(ox/mx)	0.0003[k]	0.0003[l]	0.00009[k]	0.00009[k]
(ox/m'x)	0.0002[k]	0.0003[l]	0.0001[k]	0.0001[k]
(ox/o'x)	0.0077[k]	0.0055[l]	0.0018[k]	0.0014[k]
(cx/oo)	1.514[k]	1.522[l]	1.070[k]	1.031[k]
(cx/om)	0.326[k]	0.331[k]	0.228[k]	0.220[k]
(cx/om')	0.0225[k]	0.0223[k]	0.0158[k]	0.0152[k]
(cx/oo')	0.0587[k]	0.0639[l]	0.0412[k]	0.0400[k]

to the slower fall-off of the coulomb integral, which at these values has reached essentially its classical point-charge counterpart.

Table 11 gives the overlap integrals between the substituent P_Z orbital and carbons 1 and 2. These have been either interpolated from Mulliken, Rieke, Orloff and Orloff's tables or calculated from formulas given here.

E. Computation of Empirical Parameters

In this section, we consider in some detail the effect of various approximations on the empirical parameters. At first we confine ourselves to neglect of overlap integrals. For the purpose of evaluating the empirical parameters, we consider only the shift in the long wavelength band corresponding to the 'Alg - 'B2u transition in benzene itself.

Since benzene is an alternant hydrocarbon, the analysis given in II E applies. In order to test this, the influence on the orbital energy part of the transition energy shift, of a large inductive effect, is shown for a wide

Table 11. Overlap integrals (au)[f]

X	U_x	R_{c7}	R_{o7}	s_{c7}	s_{o7}
CH_3	1.625	2.834[a]	4.730	0.206	0.030
C ≡ N	1.61	2.797[b]	4.700	0.216	0.031
F	2.65	2.493[a]	4.434	0.136	0.011
Cl	2.033	3.193[c]	5.048	0.155	0.021
Br	2.054	3.515[a]	5.337	0.151	0.021
I	1.95	3.874[a]	5.664	0.120	0.020
OH	2.35	2.646[b]	4.566	0.142	0.013
NH_2	1.96	2.570[d]	4.5005	0.205	0.02516
SH	1.82	3.382[b]	5.217	0.159	0.024

a. See reference (52).

b. Estimated from aliphatic distance, minus 0.025Å as aromatic correction. See reference (53).

c. See reference (54).

d. See reference (29).

e. This value assumes a virtual $2P_z$ orbital on carbon.

f. The numbering is the same as in Table 10.

range of resonance interaction, in Figure 6. For large δ values, the inductive effect has little influence on the transition energy shift, but becomes important when δ is small. It is interesting to note that for very weak resonance interaction, a strong inductive effect can produce a blue orbital energy shift.

Description of the lowest excited state by: $X = C_{25}X_{25} + C_{34}X_{34}$ yields:

$$
\begin{aligned}
{}'\Delta^2E = \Delta^2e &- C_{25}^2(-J'_{25} + 2K'_{25}) - C_{34}^2(-J'_{34} + 2K'_{34}) \\
&+ 2C_{25}C_{34}H'_{25,34} - \frac{1}{2}(-J_{25} + 2K_{34} - J_{34} + 2K_{34}) \\
&- H_{25,34} \qquad (4.4)
\end{aligned}
$$

Hence, it is necessary to calculate six electron interaction terms and the orbital energy shift, all as a function of the empirical parameters δ and δ_1 to describe this transition. The relative magnitudes of the orbital energy and electron interaction part of this expression is shown in Figure 7 as a function of resonance interaction: for

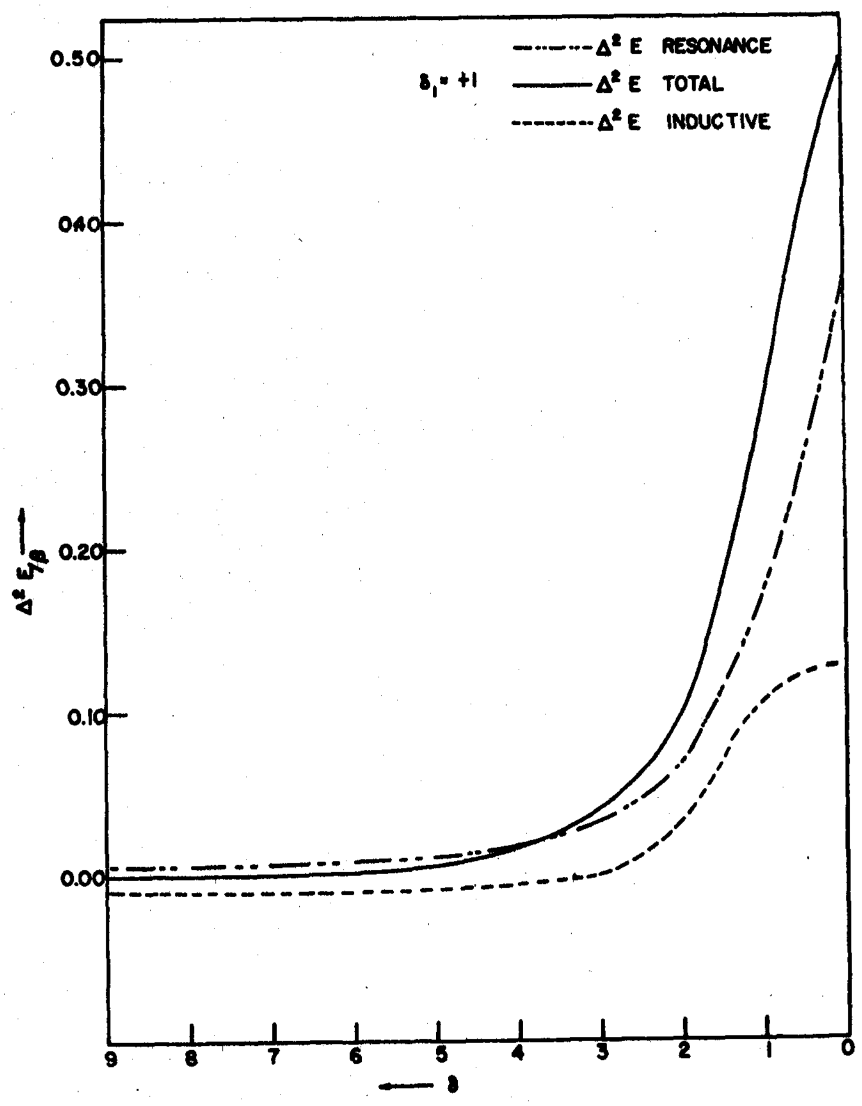

Fig. 6. Effect of inductive and resonance interaction on transition energy shift (orbital energy part) in substituted benzenes.

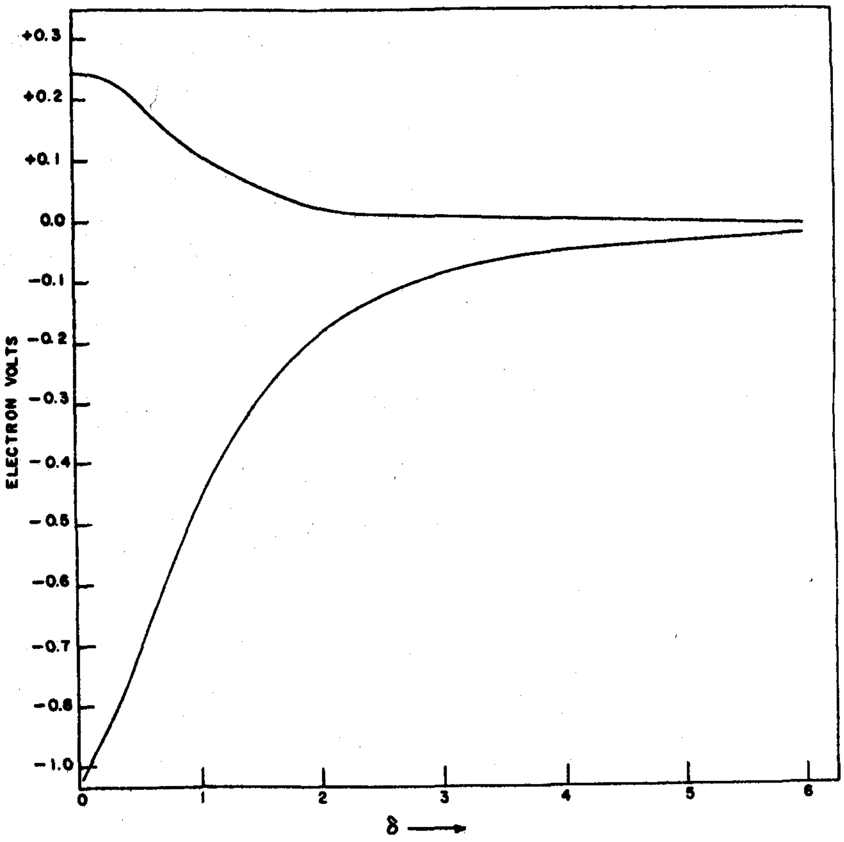

Fig. 7. Electron interaction (upper curve) and orbital energy (lower curve) shift as a function of resonance interaction in substituted benzenes, for longest wavelength transition.

low δ values, the electron interaction terms are seen to be quite significant; at high δ values, the orbital energy shift alone approximately determines the transition energy shift, corresponding to the case of "weak" substituents. The ionization potential shift is given for all cases considered by:

$$\Delta I = - \Delta e_3 \equiv (A_3 + 1) \qquad (4.5)$$

In Table 12 are listed the observed long wavelength transition energy shifts of compounds of interest to us in this thesis. We have, wherever possible, used the 0-0 frequency as determined from vapor spectra. In some cases, it has been necessary, however, to use solution spectra, and in these cases the spectra have been analyzed as carefully as possible to locate the most probable position of the 0-0 frequency, and this has been compared with that for benzene in the same solvent. This procedure eliminates the largest portion of the solvent effect.

In Table 13 are listed the available experimental data on ionization potentials. Ionization potentials obtained from spectroscopic information are generally reliable to 0.01 volt, and not infrequently even better. On the other

Table 12. $A_1 - B_1^+$ transition energy data for monosubstituted benzenes

Substituent	Δ^2E (ev)	$(\beta *)$
CH_3	-0.0750[a]	0.0140
C_2H_5	-0.0706[a]	0.0132
t-butyl	-0.0544[a]	0.0101
F	-0.0336[b]	0.00627
Cl	-0.1286[b]	0.0240
Br	-0.1355[b]	0.0253
I	-0.1612[c]	0.0301
OH	-0.2156[d]	0.0402
NH_2	-0.5028[d]	0.0938
SH	-0.03855[e]	0.0719
NH_3^+	(0.000)[h]	0.000
Pyridine	-0.00[i]	0.000
i-propyl	-0.0588	0.0110

a. See reference (50).

b. See reference (6).

c. See reference (51).

d, e, h, i. See references (35), (36), (4), (34), respectively.

hand, electron impact values are usually only reliable only to a few tenths of a volt in the energy region of interest to us here. In the older literature, electron impact values are to be trusted even less than this because of improper understanding of the effect of space charges in the apparatus, and because of unreliable calibrations. By referring to comparative results of a single investigator, in which the same apparatus and closely similar conditions are used for successive determinations, one can hope to obtain reliable relative values even from electron impact data. It is for this reason, as well as for the theoretical viewpoint mentioned earlier, that we have considered only the magnitudes of shifts in ionization potentials as contrasted with their absolute magnitudes. For the purposes of the present paper, all electron impact data utilized are from the work of Morrison and Nicholson (20), who have measured the ionization potentials of a large number of compounds using a refined mass spectrometer. Even with these precautions, it is apparent from Table 13, in which the experimental ionization potential data are listed, that there is only moderate agreement between spectroscopic and electron impact data. Indeed, considering only shifts from the values found by the two methods from that of benzene respectively, in six cases for which comparative data exist, the shift in the ionization potential from that of benzene , from electron impact data, is less to the red than from spectroscopic data by an average of 0.23 ev, with values ranging from 0.07 to 0.53 ev difference in the shift. The fact that there is a consistent blue shift in the absolute magnitudes of ionization potentials from electron impact as compared with spectroscopic data, has been interpreted as a result of the electron impact values representing vertical ionization potentials whereas spectroscopic data yield adiabatic ionization potentials. From the framework of the calculations in which ground state orbitals, dimensions, etcetera, are employed exclusively, it would seem that vertical ionization potentials are the data that should be correlated with theory. It seems a little hard to believe, however, that the correction from vertical to adiabatic I's should vary as much as the above-indicated variation between spectroscopic and electron impact shifts, especially when confined to a closely related series of molecules. Consequently, we will adopt as more reliable the spectroscopic (and presumably adiabatic) I's and consider as uncertain the electron impact (despite their presumably vertical character) values. These

Table 13. Experimental ionization potential data for monosubstituted benzenes

Substituent	$I_{\text{spec.}}$[a]	$I_{\text{e.i.}}$[b]	$I_{\text{spec.}}$[a]	$I_{\text{e.i.}}$[b]	Ref.[c]
-H (benzene)	9.24	9.52	....	....	1,2
-F	9.20	9.67	-0.04	-0.15	2
-Cl	8.77	9.42	-0.47	-0.10	2
-Br	....	9.41	....	-0.11	
-I	....	9.10	....	-0.42	
$-CH_3$	8.82	9.23	-0.42	-0.29	1,2
$-C_2H_5$	8.77	9.12	-0.47	-0.40	1,2
-n-Propyl	....	9.14	....	-0.38	
-i-Propyl	8.76	9.13	-0.48	-0.39	1,2
-n-Butyl	....	9.14	....	-0.38	
-s-Butyl	....	9.19	....	-0.33	

a. "$I_{\text{spec.}}$" is ionization potential obtained from spectroscopic data. The references in column 6 refer to data in this column only. All values in this table are in electron volts.

b. "$I_{\text{e.i.}}$" is ionization potential obtained by electron impact measurements from the data of Morrison and Nicholson, reference (20).

c. "1" is reference (39, 40).
"2" is reference (41).
"3" is reference (42, 43).

Table 13. (Continued)

Substituent	$I^a_{spec.}$	$I^b_{e.i.}$	$I^a_{spec.}$	$I^b_{e.i.}$	Ref.[c]
-t-Butyl	8.5	9.35	-0.7	-0.17	1,2
$-CF_3$	9.72	....	-0.44	....	2
-OH	....	9.03	....	-0.49	
-CHO	....	9.82	....	-0.30	
-CN	....	9.95	....	-0.43	
$-CH{=}CH_2$	....	8.86	....	-0.66	
$-C\equiv CH$	....	9.15	....	-0.37	
(Pyridine)	8.7	....	0.5	....	3

will henceforth be carefully distinguished. The problem clearly emphasizes the need for much improved information on ionization potentials.

We now turn to the numerical values of the empirical parameters. These were determined by a two-cycle iterative procedure, where necessary, and should be regarded as only approximate. In no case should the qualitative order be changed by fubther iteration. The work including the overlap integrals is still in progress; but enough has been done in this direction to show that the order will not be changed by their inclusion. They are given in Tables 14 and 15.

It is interesting to note that the empirical parameters, by and large, are in the order that chemical intuition would lead us to expect. However, Jaffe has found that Hammett sigma constant data requires the reverse resonance order of resonance interaction for the halogens than Tables 14 and 15, although making use of questionable assumptions. It is possible that variation of the ring-substituent exchange integral in a series of substituents of different electronegativity and radii, may be such as to reverse our resonance parameter order (54), and further work is needed on this point.

Table 14. Resonance parameters [d] for substituted benzenes (overlap integrals neglected)

X	δ^a	δ^b	δ^c
CH_3	4.8	4.8	3.9
C_2H_5	5.0	5.0	4.1
i-propyl	5.5	5.5	4.5
t-butyl	5.7	5.7	4.8
F	7.5	7.5	6.2
Cl	3.5	3.5	2.9
Br	3.4	3.4	2.8
I	3.2	3.1	2.6
OH	2.8	2.7	2.1
NH_2	1.6	1.5	0.9
SH	1.9	1.8	1.3
NH_3^+	10	10	10
Pyridine	....	....	....

a. All electron interaction terms assumed to cancel ("weak" substituent case).

b. Ground state - excited state electron interaction terms included, but excited state mixing neglected.

c. All electron interaction terms included.

d. Assuming inductive parameter is zero.

Table 15. Empirical parameters for substituted benzenes (overlap integrals neglected)[d]

X	δ^a	δ_1^a	δ^b	δ_1^b	δ^c	δ_1^c
CH_3	4.8	0.00	4.8	0.00	4.1	0.10
C_2H_5	5.0	-0.01	5.0	-0.01	4.2	0.08
i-propyl	5.5	-0.02	5.5	-0.02	4.5	0.02
t-butyl	5.7	(-0.05)	5.7	(-0.05)	4.6	-0.1
F	7.0	0.23	7.0	0.23	6.0	0.25
Cl	3.5	0.21	3.5	0.21	3.1	0.19
NH_3^+	...	0.5--0.8	...	0.5--0.8	...	0.5--0.8
Pyridine	...	+0.3	...	+0.3	...	+0.3

d. The notation is that of the preceding table.

V. CONCLUSIONS

The major conclusions derived from the foregoing research may be listed as follows:

1. The naive MO theory presents an inadequate understanding of the properties of substituted hydrocarbons.

2. The naive MO theory can be combined with the rigorous SCF theory so that the advantages of both are retained.

3. Solutions of the secular equation (overlap included) can be obtained simply for substituted hydrocarbons from solutions with overlap neglected.

4. The notions of "weak" and "strong" substituents provide useful qualitative descriptions of substituted hydrocarbons.

5. Transitions from non-bonding orbitals to delocalized orbitals are successfully treated by the foregoing methods.

6. The Sklar-Herzfeld procedure is fundamentally and practically incorrect.

7. Inductive and resonance interactions in substitu-

ted hydrocarbons are intimately dependent upon each other, and not additive as heretofore assumed.

VI. SUMMARY

It is shown in Chapter II how the conventional naive semi-empirical molecular orbital approach for conjugated hydrocarbons may be complemented by means of theoretically computed electron repulsion integrals in a manner suggested by the more rigorously founded SCF procedure. This is shown to give satisfying results in three examples, with a considerable reduction in labor as compared to the complete ASMO method. The method is carried over in a natural and simple manner to substituted hydrocarbons, providing unambiguous methods of evaluating empirical resonance and inductive parameters. The concept of "weak" and "strong" substituents is developed, and it is shown how these provide simple intuitive approaches to the estimation of interaction parameters in the theory. The inductive and resonance effects upon the energy levels are shown to be far from additive, and indeed are dependent upon each other. The dependence is analyzed, and it is indicated which ones are important (and determinable) from various experimental situations.

The modified semi-empirical method of Chapter II is applied to the general problem of the prediction of spectra of substituted conjugated hydrocarbons. It is shown that the new method has many of the advantages of the more rigorous ASMO approach in, for example, distinguishing between states of different multiplicity, without the attendant disadvantages of overly lengthy computation, too large singlet-triplet separations, and the like. The case of limited configuration interaction arising from degenerate or near-degenerate levels in the parent hydrocarbon is discussed in detail from the viewpoint of "strong" and "weak" substituents introduced in Chapter II. It is shown that this is a factor of major importance in molecules to which it is applicable and that a consideration of its effect can be used for the assignment of transitions. A method is suggested in which empirical parameters determined from $\pi - \pi$ spectra can be used in the prediction of $n - \pi$ spectra. Brief attention is given to the problem of polysubstitution, and to the calculation of delocalization energies and π-electron moments.

In Chapter IV, the procedure outlined in Chapter II is applied to substituted benzenes. Several of the conclusions derived there are verified for these compounds. Empirical parameters are evaluated for a series of substituents from the long wavelength transition and ionization potential.

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VIII. LITERATURE CITED

1. I. G. Ross, thesis, University of London, 1951.
2. M. J. Dewar, Proc. Cambridge Phil. Soc., 45, 638 (1949).
3. C. A. Coulson and H. C. Longuet-Higgins, Proc. Royal Soc. (London) A191, 16 (1947).
4. A. L. Sklar, J. Chem. Phys. 7, 984 (1939).
5. K. F. Herzfeld, Chem. Rev. 41, 233 (1947).
6. F. A. Matsen, J. Am. Chem. Soc. 72, 5243 (1950).
7. C. C. J. Roothaan, Revs. Mod. Phys. 23, 69 (1951).
8. R. G. Parr and B. L. Crawford, J. Chem. Phys. 16, 526 (1948).
9. C. C. J. Roothaan and R. G. Parr, J. Chem. Phys. 17, 1001 (1949).
10. R. G. Parr and R. S. Mulliken, J. Chem. Phys. 18, 1338 (1950).
11. R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466 (1953).
12. R. Pariser and R. G. Parr, J. Chem. Phys. 21, 767 (1953).
13. M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).
14. C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948).
15. R. Pariser, J. Chem. Phys. 21, 568 (1953).
16. R. S. Mulliken, J. Chem. Phys. 19, 912 (1951).

17. P. O. Lowdin, J. Chem. Phys. 18, 365 (1950).

18. L. Pauling, J. Am. Chem. Soc. 58, 94 (1936).

19. R. S. Mulliken, J. Chim. Phys. 46, 695 (1949).

20. G. Wheland and L. Pauling, J. Am. Chem. Soc. 57, 2086 (1935).

21. H. H. Jaffe, J. Chem. Phys. 20, 285 (1952).

22. G. Wheland, J. Am. Chem. Soc. 64, 902 (1942).

23. L. Goodman and H. Shull, Unpublished work.

24. R. S. Mulliken and C. A. Rieke, J. Am. Chem. Soc. 63, 1770 (1941).

25. C. A. Coulson, Proc. Royal Soc. (London) A195, 933 (1952)

26. H. C. Longuet-Higgins and R. G. Sowden, J. Chem. Soc., 1404 (1952).

27. F. A. Matsen, J. Am. Chem. Soc. 72, 5252 (1950).

28. R. G. Parr and B. L. Crawfors, J. Chem. Phys. 16, 1049 (1948).

29. I. Fischer, Arkiv. f. Fysik, 5, 26 (1952).

30. R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys. 17, 1248 (1949).

31. B. H. Chirgwin and C. A. Coulson, Proc. Royal Soc. (London) A201, 196 (1950).

32. M. Kasha, Disc. Faraday Soc. 9, 14 (1950).

33. J. R. Platt, J. Chem. Phys. 19, 101 (1951).

34. H. Stephenson, thesis, Duke University, 1952.

35. H. Sponer and E. Teller, Revs. Mod. Phys. 13, 76 (1941).

36. W. W. Robertson and F. A. Matsen, J. Am. Chem. Soc. 72, 5250 (1950).

37. G. P. Nordheim and H. Sponer, J. Chem. Phys. 20, 285 (1952).

38. D. P. Craig, Proc. Royal Soc. (London) A200, 401, (1950).

39. J. D. Morrison, J. Chem. Phys. 19, 1305 (1951).

40. J. D. Morrison and J. Nicholson, J. Chem. Phys. 20, 1021 (1952).

41. W. Price, Chem. Revs. 41, 257 (1947).

42. G. Hammond, A. Walsh and A. Teegan, Disc. Faraday Soc. 9, 58 (1950).

43. W. Price and A. Walsh, Proc. Royal Soc. (London) A191, 22, 32 (1947).

44. C. A. Coulson and J. De Heer, J. Chem. Soc., 483 (1952).

45. R. S. Mulliken and R. G. Parr, J. Chem. Phys. 19, 1271 (1951).

46. L. Goodman and H. Shull, to be published.

47. L. Goodman and H. Shull, Presented at the Symposium on Molecular Spectroscopy, Columbus, Ohio, June 12, 1953.

48. J. R. Platt, J. Chem. Phys. 18, 1168 (1950).

49. H. McConnell, J. Chem. Phys. 20, 700 (1952).

50. F. Matsen, W. Robertson and C. Chuoke, Chem. Revs. 41, 273 (1947).

51. W. Beckering, Unpublished work.

52. A. Sutton, Acta Cryst. 3, 56 (1950).

53. Y. Syrkin and M. Dyatkina, Sructure of Molecules (Interscience, New York, 1950).

54. L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, N. Y., 1948), 2nd edition.

55. R. S. Mulliken, J. Chem. Phys. 3, 506 (1935).

56. R. S. Mulliken, J. Chem. Phys. 8, 234 (1940).

57. R. S. Mulliken, J. Chem. Phys. 8, 382 (1940).

IX. APPENDICES

A. Orthogonalized Orbitals for Aniline and Trans-1-aminobutadiene

The matrix form of the orthogonalized orbitals, calculated by Lowdin's procedure (17) is given below. Note that all overlap integrals have been included, both between carbon AO's and between the substituent and all the various hydrocarbon AO's. For aniline, the overlap integrals are from Fischer (29); for aminobutadiene, they have been calculated from formulas given by Mulliken, Rieke, Orloff and Orloff (30), assuming the same C-N bond distance and Z value as in aniline:

Aniline

$$\begin{bmatrix} \Phi_1^o \\ \Phi_3^o \\ \Phi_5^o \\ \Phi_6^o \\ \Phi_{NH_2}^o \end{bmatrix} = \begin{bmatrix} 1.0026 & 0.0037 & 0.0038 & 0.0062 & -0.0433 \\ 0.0037 & 1.0045 & 0.0055 & 0.0091 & -0.0631 \\ 0.0038 & 0.0055 & 1.0056 & 0.0092 & -0.0640 \\ 0.0062 & 0.0091 & 0.0092 & 1.0151 & -0.1053 \\ -0.0433 & -0.0631 & -0.0639 & -0.1053 & 1.0350 \end{bmatrix} \begin{bmatrix} \Phi_1 \\ \Phi_3 \\ \Phi_5 \\ \Phi_6 \\ \Phi_{NH_2} \end{bmatrix}$$

Trans-1-aminobutadiene

$$\begin{bmatrix} \Phi_1^0 \\ \Phi_2^0 \\ \Phi_3^0 \\ \Phi_4^0 \\ \Phi_{NH_2}^0 \end{bmatrix} = \begin{bmatrix} 1.0030 & 0.0036 & 0.0029 & 0.0037 & -0.0424 \\ 0.0036 & 1.0050 & 0.0040 & 0.0050 & -0.0580 \\ 0.0029 & 0.0040 & 1.0032 & 0.0040 & -0.0466 \\ 0.0037 & 0.0050 & 0.0040 & 1.0050 & -0.0583 \\ -0.0424 & -0.0580 & -0.0466 & -0.0583 & 1.0161 \end{bmatrix} \begin{bmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \\ \Phi_4 \\ \Phi_{NH_2} \end{bmatrix}$$

B. Mathematical Form of Solutions of the Secular Equation

Here we consider the mathematical problem of including the overlap integrals in the secular equation (2.3). Direct solution of the exact secular equation introduces considerable additional labor, and the matrix method developed by Chirgwin and Coulson (31) and Lowdin (18) breaks down for hetero molecules, since the matrix $\underline{H}$ does not commute with the matrix $\underline{S}$, as is readily ascertained by direct examination. Lowdin (17) has developed another method, where, through calculation of a matrix $\underline{H}'$ ($\underline{H}' = \underline{(1 + S)^{1/2}H(1 + S)^{1/2}}$), the solutions corresponding to overlap included may be obtained from those without overlap, even though $\underline{H}$ and $\underline{S}$ do not commute; however, for the class of molecules treated here, $\underline{H}'$ is unwieldly. By examination of the general solutions of equation (2.3) we shall see how the overlap integrals may be included in a computationally simple and straightforward manner.

The secular determinant (2.3), under the conditions:

$$
\begin{aligned}
H_{jx} &= C_{js}\beta \quad , \; j \neq x \\
H_{xx} &= \alpha + \delta\beta \\
H_{ij} &= \delta_s C_{is} C_{js}\beta \, , \; i \neq j \neq x \\
H_{jj} &= \alpha + n_j\beta + C_{js}^2\delta_s\beta \quad , \; j \neq x \\
S_{jx} &= 0 \; , \; j \neq x
\end{aligned}
\qquad (B.1)
$$

becomes, with the substitution $A = \dfrac{\alpha - E}{\beta}$, for simplicity,

$$
\begin{vmatrix}
(A+n_1+C_{1s}^2\delta_s)\beta & \cdots\cdots & C_{1s}C_{js}\delta_s\beta & \cdots\cdots & C_{1s}\beta \\
\vdots & & \vdots & & \vdots \\
C_{js}C_{1s}\delta_s\beta & \cdots\cdots & (A+n_j+C_{js}^2\delta_s)\beta & \cdots & C_{js}\beta \\
\vdots & & \vdots & & \vdots \\
C_{1s}\beta & \cdots\cdots & C_{js}\beta & \cdots\cdots & (A+\delta)\beta
\end{vmatrix} = 0 \qquad (B.2)
$$

The solution of the determinant (B.2) may be written in the following form:

$$\delta = F_j - A_j \ , \tag{B,3}$$

where

$$F_j = \frac{\sum_{k=1}^{N} c_{ks}^2 \prod_{i \neq k=1}^{N} (A_j + n_i)}{\prod_{i=1}^{N} (A_j + n_i) + \delta_s \sum_{k=1}^{N} c_{ks}^2 \prod_{i \neq k=1}^{N} (A_j + n_i)} \tag{B.4}$$

and

$$A_j = \frac{\alpha - E_j}{\beta} \ ,$$

giving convenient relations for plotting A_j as a function of δ. The wave functions corresponding to these orbital energies are given by equation (2.2), where:

$$a_{ji} = \left(\frac{B_i}{B_x}\right)_j \left[\sum_{i=1}^{N+1} \left(\frac{B_i}{B_x}\right)_j^2\right]^{-1/2} \tag{B.5}$$

The quantity $(B_i/B_x)_j$ is the unnormalized ratio of the coefficients of Φ_i and Φ_x in Ψ_j, and is given by

$$\left(\frac{B_i}{B_x}\right)_j = \frac{C_{is} \prod\limits_{k \neq i=1}^{N} (A_j + n_k)}{\prod\limits_{k=1}^{N} (A_j + n_k) + \delta_s \sum\limits_{k=1}^{N} C_{ks}^2 \prod\limits_{l \neq k=1}^{N} (A_j + n_l)} \qquad (i \neq x)$$

$$\text{and} \qquad \left(\frac{B_{N+1}}{B_x}\right)_j = 1 \tag{B.6}$$

Up to this point, we have not indicated whether the carbon-carbon overlaps have been included in the energies H_{jj} and wave functions Φ_j of the parent hydrocarbon. In actuality, equations (B.3) and (B.6) apply, regardless of whether these overlaps have been included or not. If they have not been included, the method developed by Chirgwin, Coulson and Wheland (22,31) may be used to utilize the easily obtained solutions with neglect of overlap: If $H^{o}_{jj}=\alpha+n^{o}_{j}\beta$ are the hydrocarbon orbital energies, overlap neglected, then

$$H'_{jj} = \alpha + \frac{n^{o}_{j}(\beta - \alpha S_c)}{1 + n^{o}_{j}S_c} \qquad (B.7)$$

are the orbital energies, overlap included. S_c is the overlap integral between neighboring carbon atoms. The quantity $(\beta - \alpha S_c)$ is Mulliken and Rieke's γ, and is the hydrocarbon quantity which is actually evaluated empirically, (24). Inclusion of overlap just renormalizes the wave functions as follows:

$$\Phi_j = \frac{1}{(1 + n^{o}_{j}S_c)^{1/2}} \sum C^{o}_{ju}\phi_u \qquad (B.8)$$

where C^{o}_{ju} refers to the coefficients obtained with neglect of overlap. With these transformations, the δ values and wave functions of the substituted hydrocarbon may be found from orbital energies found with these overlaps neglected, by substituting in equations (B.4) and (B.6):

$$n_i = \frac{n_i^o}{1 + S_c n_i^o}$$

$$C_{is} = \frac{C_{is}^o}{(1 + S_c n_i^o)^{1/2}} \qquad \text{(B.9)}$$

for the corresponding quantities with overlap neglected. Relations (B.3) and (B.5) now determine the orbital energies and wave functions as functions of δ, with carbon-carbon overlaps included.

We now consider the solutions with the overlap integrals S_{jx} included. This is carried out with the following set of assumptions:

$$S_{jx} = C_{js}s, \qquad s = \phi_1\phi_x dv$$

$$H_{jx} = C_{js}R\beta$$

$$H_{xx} = \alpha + \delta\beta \tag{B.10}$$

$$H_{ij} = \delta_s C_{is} C_{js}\beta, \qquad i \neq j \neq x$$

$$H_{jj} = \alpha + n_j\beta + C_{js}^2 \delta_s \beta , \qquad j \neq x$$

Then equation (B.3) no longer holds. Instead, A_j is determined as a function of δ, by

$$\delta = (f_j - 1 + R)^2 F_j - A_j , \tag{B.11}$$

where

$$f_j = 1 - s\left(\frac{\alpha}{\beta} - A_j\right) . \tag{B.12}$$

If A_j is known as a function of δ (overlap neglected), substitution of equation (B.3) in (B.12) gives a relation determining δ' (overlap included) from δ and the corresponding A_j values:

$$\delta = (f_j - 1 + R)^2(\delta - A_j) - A_j \qquad \text{(B.13)}$$

The wave functions coefficients, a'_{ji}, corresponding to equation (B.13) are now determined by equation (B.14):

$$a'_{ji} = \left(\frac{B_i}{B_x}\right)'_j \left[\sum_{i=1}^{N+1}\left(\frac{B_i}{B_x}\right)'^{2}_j + 2\sum_{i=1}^{N} C_{is}\left(\frac{B_i}{B_x}\right)^{s}_j\right]^{-1/2}, \qquad \text{(B.14)}$$

where

$$\left(\frac{B_i}{B_x}\right)'_j = \left(\frac{B_i}{B_x}\right)_j (f_j - 1 + R) \qquad i \neq x$$

$$\left(\frac{B_{N+1}}{B_x}\right)' = 1 \qquad \text{(B.15)}$$

The expressions (B.13) and (B.14), with (B.15), provide convenient methods of determining δ' values and wave functions in terms of those without overlap. One notes that equation (B.14) does not amount to a renormalization of ψ_j, since

$$a'_{ji} = a_{ji}\left[\sum_{i=1}^{N+1}\left(\frac{B_i}{B_x}\right)_j^2 \Big/ \left(\sum_{i=1}^{N}\left(\frac{B_i}{B_x}\right)^2 + 2sC_{is}\left(\frac{B_i}{B_x}\right)_j \frac{1}{(f-1+R)} + \frac{1}{(f-1+R)^2}\right)\right]^{1/2} \qquad (i \neq x)$$

and

$$a'_{jx} = \frac{a_{jx}}{(f-1+R)}\left[\sum_{i=1}^{N+1}\left(\frac{B_i}{B_x}\right)_j^2 \Big/ \left(\sum_{i=1}^{N}\left(\frac{B_i}{B_x}\right)^2 + 2sC_i\left(\frac{B_i}{B_x}\right)_j \frac{1}{(f-1+R)} + \frac{1}{(f-1+R)^2}\right)\right]^{1/2}$$

that is, the coefficient of Φ_x is multiplied by a different factor than Φ_i, $(i \neq x)$. This result is to be expected since as mentioned earlier, H and S do not commute, which is the fundamental requirement that the wave functions are given solely by a renormalization.

Computationally, equations (B.13), (B.14) and (B.15) are easily handled, so that the wave functions and energy levels with overlap included may be found from the overlap neglected quantities with little effort. One notes several special cases of interest: if s is small (~0.1), or if is large (or both), the term multiplied by s , in equation (B.14) may be safely neglected, giving the result:

$$a'_{ji} = \left(\frac{B_i}{B_x}\right)'_j \left[\sum_{i=1}^{N+1} \left(\frac{B_i}{B_x}\right)'^2_j\right]^{1/2} \qquad (B.16)$$

thus providing an especially simple relation for weak substituents, or those having small overlap integrals. In all cases, equation (B.17) gives qualitatively valid coefficients, rapidly. If h_{sx} is taken equal to β (Matsen and Pauling), then $R \cong 1$, and

$$\delta' = f_j^2 (\delta - A_j) - A_j , \qquad (B.17)$$

or if Wheland's assumption is utilized, $h_{sx} = \frac{s\beta}{s_c}$ and $R = \frac{s}{s_c}$.

C. Inequality Relations Among Electron Repulsion Integrals

The proof of the lefthand inequality in equation (2.34) can be obtained in the same manner Roothaan (7) used for the other inequalities. The energy of a continuous charge distribution $\rho(x,y,z)$ is:

$$\int \frac{\rho^u \rho^v}{r^{uv}} \, dv^{uv} = \frac{1}{8\pi} \, E^2 dv \geqslant 0 , \qquad (C.1)$$

where $\rho^u = \rho(x^u,y^u,z^u)$, $E = \mathrm{Div}\,\rho$; the equal sign holding, if and only if, $\rho = 0$. Following Roothaan, let $\rho = e^2(I_i^* I_j - I_k^* I_l)$; then,

$$0 \leqslant \int \frac{(I_i^* I_j - I_k^* I_l)(I_i^* I_j - I_k^* I_l)}{r^{uv}} \, dv^{uv}$$

$$= K_{ij} - K_{kl} - 2M_{ijkl}.$$

Hence,

$$M_{ijkl} \leq \frac{1}{2}(K_{ij} + K_{kl}) \,, \qquad \text{(C.2)}$$

the equal sign holding, if and only if,

$$I_i^* I_j = I_k^* I_l \,. \qquad \text{(C.3)}$$

Next, let

$$\rho = e^2(I_i^* I_j - I_k^* I_l) \,;$$

then,

$$- M_{ijkl} \leq \frac{1}{2}(K_{ij} + K_{kl}) . \qquad \text{(C.4)}$$

And, since K_{ij} and K_{kl} are ≥ 0, we have established the inequality

$$|M_{ijkl}| \leq \frac{1}{2}(K_{ij} + K_{kl}) \,. \qquad \text{(C.5)}$$