# The electronic structure of conjugated systems

## I. General theory

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This paper develops the general theory of conjugated systems by the method of molecular orbitals. The electron densities and bond orders appear as first-order derivatives of the energy of the mobile electrons with respect to the energy integrals in the secular equations; and various other relations are established which confirm the appropriateness of the definitions. A set of new quantities are introduced and discussed for the first time, namely, the mutual polarizability of two atoms or two bonds or an atom and a bond, and it is shown that they are important in determining the effect of structural changes on chemical reactivity, and also in calculating force constants and interaction terms for the vibration of bonds. Formulae are derived for the calculation of the total energy, electron densities, bond orders and mutual polarizabilities, and the relation of these quantities to other physical and chemical properties is briefly discussed.

## Notation

The notation used in this and later papers is summarized below; the numbers in brackets denote the equations in which the quantities are defined mathematically:

| | | |
|---|---|---|
| $n$ | number of atomic orbitals. | |
| $r, s, t, u$ | atoms of a conjugated system. | |
| $\phi_r$ | the atomic orbital for atom $r$. | |
| $\psi, \psi_j$ | any (the $j$th) molecular orbital. | |
| $c_r, c_{rj}$ | the coefficient of $\phi_r$ in $\psi, \psi_j$. | (1) |
| $n_j$ | the number of electrons in $\psi_j$. | |
| $E$ | the energy of a molecular orbital. | (3) |
| $H$ | the effective Hamiltonian operator for a $\pi$-electron | (3) |
| $H_{rr}$ | the coulomb integral for $\phi_r$. | (5) |
| $H_{rs} = \beta_{rs}$ | the resonance integral between $\phi_r$ and $\phi_s$. | (5) |
| $S_{rs}$ | the overlap integral between $\phi_r$ and $\phi_s$. | (6) |
| $H_{CC}$ | the coulomb integral for a carbon atom in benzene. | |
| $\alpha_r$ | the coulomb term for atom $r$. | (11) |
| $\epsilon = E - H_{CC}$ | the binding energy of a mobile electron. | (11) |
| $\epsilon_j$ | the value of $\epsilon$ for an electron in $\psi_j$. | |
| $\mathscr{E}$ | the total binding energy of the mobile electrons. | (26) |
| $q_r$ | the electron density at atom $r$. | (9) |
| $p_{rs}$ | the mobile order of bond $rs$. | (13) |
| $\Delta(\epsilon)$ | the secular determinant for a conjugated system, regarded as a function of $\epsilon$. | (14) |
| $\Delta'(\epsilon)$ | $= \partial\Delta(\epsilon)/\partial\epsilon$. | |

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$\Delta_{r,t}$, $\Delta_{rs,tu}$  where $r < s$, $t < u$, denote $\Delta$ with rows $r$ (and $s$) and columns $t$ (and $u$) struck out.

$\pi_{r,t}$, $\pi_{rs,tu}$  denote the mutual polarizabilities of atoms $r$ and $t$ and bonds $rs$ and $tu$.                                                    (46), (49)

$\pi_{rs,t}$, $\pi_{t,rs}$  denote the polarizability of bond $rs$ by atom $t$ and vice versa.  (47), (48)

$\delta$          denotes increment.

$H'$, $c'$, $\psi'$  denote increments in $H$, $c$, $\psi$.

Every determinant occurring in an integral with respect to $y$ is to be taken as a function of $iy$, the limits of integration, except where otherwise stated, being $-\infty$ to $+\infty$.

## INTRODUCTION

Theoretical treatments of unsaturated molecules begin by dividing the electrons into three classes, as follows:

(a) those which are not concerned with bond formation—the inner shell electrons;

(b) those which are engaged in the formation of $\sigma$ bonds, i.e. localized bonds having maximum density along the line joining two adjacent atoms;

(c) the $\pi$-electrons, whose orbitals are antisymmetric with respect to the plane of the $\sigma$ bonds at any atom. These electrons are variously called $\pi$, $p_h$, mobile, and unsaturation electrons. The part of the molecule in which they move is called a conjugated system.

The inner-shell electrons and $\sigma$-electrons are supposed to have their energies and distributions governed solely by the atomic orbital, or pair of orbitals, in which they move; and all effects depending on conjugation of unsaturation electrons, such as resonance energies and variations in bond order and electron density, are ascribed to the $\pi$-electrons. This series of papers will be concerned solely with these $\pi$-electrons; and it will be supposed, as is customary, that they may be treated quite independently of the underlying framework composed of the nuclei and the other types of electrons (a) and (b). This implies that the $\pi$-electrons are given a wave function of their own, from which their properties may be determined. Very little work has been published on the general theory of these $\pi$-electrons, although a large number of papers have appeared describing particular applications in the field of pure hydrocarbons; and a few calculations have been made of the energy, bond orders and electron densities in specific cases where there is one, or at most two, heteroatoms (e.g. quinones (Coulson 1946), Würster's salts (Goeppert-Mayer & McCallum 1942), pyridine, pyrrole and similar systems with one nitrogen atom (Wheland & Pauling 1935; Wheland 1942; Longuet-Higgins & Coulson 1947)). It is our intention in these papers to develop certain aspects of the theory of mobile electrons in a perfectly general way, applicable to hydrocarbons and heterosystems alike. Our first paper will be almost entirely theoretical; later papers will give applications to specific problems.

In calculating the energy and distribution of the $\pi$-electrons we here follow the method of molecular orbitals. That is, we express the $\pi$-electronic part of the wave

function as a simple product, each term of which represents a wave function for a single electron moving in the field of the nuclei and the other electrons. Such a wave function is called a *molecular orbital* (m.o.). (In a molecule in its ground state it can be shown that no great change in the total energy or electron distribution would result from taking, instead, the more accurate antisymmetric determinantal product. Such a procedure would, however, introduce quite unmanageable complexities into our analysis.) The total energy of the $\pi$-electrons is thus given by the sum of the energies of the electrons in these m.o.; in the ground state the occupied m.o. are those of lowest energy, each m.o. accommodating two electrons with opposed spins. If there is an odd number of electrons, at least one m.o. must contain only one electron. This implies the existence of an uncompensated spin, so that the molecule will be paramagnetic and behave chemically as a free radical.

In calculating the form of the m.o. one may express them arbitrarily as linear combinations of atomic orbitals (a.o.). If there are $n$ distinct a.o. $\phi_r$ $(r = 1, 2, ..., n)$ out of which the m.o. $\psi$ are constructed, the $j$th m.o. may be written

$$\psi_j = \sum_{r=1}^{n} c_{rj}\phi_r. \tag{1}$$

The $c_{rj}$ are numerical coefficients to be determined presently. (It is convenient to omit the suffix $j$ from $\psi_j$ and $c_{rj}$ in much of the following discussion, when there is no danger of confusion.) Remember in (1) that out of the $n$ a.o. $\phi_r$ exactly $n$ m.o. $\psi_j$ can be formed, so that the suffix $j$ ranges from 1 to $n$. These m.o. are generally labelled in such a way that $j = 1$ is the most binding, i.e. has lowest energy value, and $j = n$ is the most antibonding, i.e. has highest energy value. The whole set of m.o. may, by analogy with the $K, L, ...$ shells of atomic structure, be referred to as the $\pi$ molecular shell, or the mobile shell.

Although no assumption need be made about the precise form of $\phi_r$, it is convenient to regard it as the $2pz$ wave function for the $r$th atom (or $3pz$ for Cl, etc.), since such wave functions are antisymmetric with respect to the plane of the $\sigma$ bonds and have an axis of symmetry perpendicular to that plane. It should perhaps be mentioned here that the $2pz$ a.o. of covalently attached hydrogen have too great energy to take part appreciably in the formation of these m.o. Hyperconjugation with a methyl group, as recently discussed by Mulliken, Rieke & Brown (1941), is, however, included in the analysis by treating the $H_3$ group as a single a.o. conjugating with the rest of the molecule.

The coefficients $c_r$ and the energy $E$ of each m.o. are determined by minimizing the latter with respect to the former; that is

$$\partial E/\partial c_r = 0 \quad (r = 1, 2, ..., n), \tag{2}$$

where

$$E = \int \psi^* H \psi \, dv \Big/ \int \psi^* \psi \, dv. \tag{3}$$

$H$ is here the effective Hamiltonian operator for each $\pi$-electron. The set of conditions (2) leads to the 'secular equations'

$$(H_{rr} - ES_{rr})c_r + \sum_{s}' (H_{rs} - S_{rs}E)c_s = 0, \tag{4}$$

where $H_{rs}$ is the matrix component of $H$ in the system $\phi_r$, and is defined by

$$H_{rs} = \int \phi_r^* H \phi_s \, dv \quad \text{and} \quad S_{rs} = \int \phi_r^* \phi_s \, dv. \tag{5}$$

There is one equation of type (2) for each of the $n$ values of $r$; and the $\phantom{'}$ after the summation sign denotes that the term with $s = r$ is omitted from the sum. Neglecting overlap between a.o., i.e. putting

$$S_{rs} = 0 \tag{6}$$

for $r \neq s$, and supposing each a.o. to be normalized, so that

$$S_{rr} = 1, \tag{7}$$

then

$$(H_{rr} - E) c_r + \sum_s' H_{rs} c_s = 0. \tag{8}$$

Now in a given molecule the coulomb integrals $H_{rr}$ will depend upon the density of electrons near atom $r$. The number of electrons on atom $r$ is defined as

$$q_r = \sum_j n_j c_{jr}^2, \tag{9}$$

where $n_j$ is the number of electrons (either 0, 1 or 2) in the $j$th m.o. $H_{rr}$ would be expected to depend on $q_r$. But it will be supposed that in fact $H_{rr}$ depends only on the nature of atom $r$, e.g. whether it is carbon or nitrogen. There are many cases where this is quite a fair assumption. Thus, Coulson & Rushbrooke (1940) have shown that in hydrocarbons containing no odd-numbered unsaturated rings, the assumption that all the $H_{rr}$ are equal leads to the conclusion that in the ground state all the $q_r$ are equal, and hence also the $H_{rr}$, so that the hypothesis is at least self-consistent. For other systems in general all the $q_r$ will not be equal (Longuet-Higgins & Coulson 1947), even for the atoms of one kind; in any particular case it might be possible to allow for the variation of $H_{rr}$ with $q_r$ in order to make a truly self-consistent field, but in the general case this is quite impossible and it will be necessary to be content with the approximation that $H_{rr}$ depends solely on the nature of atom $r$. As it appears that the charges $q_r$ on atoms of one kind do not vary greatly from molecule to molecule, it is unlikely that the assumption introduces greater errors than are already inherent in the whole scheme of calculation.

It will be found best to measure the energy of a m.o. in terms of its difference from $H_{CC}$, which denotes the coulomb integral for the carbon atom in, say, benzene. The secular equations (8) then become

$$(\alpha_r - \epsilon) c_r + \sum_s' \beta_{rs} c_s = 0 \quad (r = 1, 2, ..., n), \tag{10}$$

where

$$\alpha_r = H_{rr} - H_{CC}, \quad \epsilon = E - H_{CC} \quad \text{and} \quad \beta_{rs} = H_{rs}. \tag{11}$$

$\beta_{rs}$ is often referred to as the 'resonance integral' between the a.o. $\phi_r$ and $\phi_s$; for non-bonded atoms it is very small and may be taken to be zero. For hydrocarbons where the $H_{rr}$ are all equal to $H_{CC}$, the secular equations are therefore

$$-\epsilon c_r + \sum_s' \beta_{rs} c_s = 0 \quad (r = 1, 2, ..., n). \tag{12}$$

It is desirable, in what follows, to have some physical interpretation for the quantities $H_{rr}$ and $\alpha_r$. According to (8), $H_{rr}$ is the energy of an electron in an orbit for which all the $c_s$ are zero except $c_r$, i.e. an electron confined to nucleus $r$. At first sight one would expect this to be equal to the ionization energy of the corresponding atom; but this is not quite so, because (i) the Hamiltonian $H$ involves the field from the other atoms, so that at best $H_{rr}$ would measure the energy of removal of the electron from nucleus $r$ in the presence of the other atoms, and (ii) when one electron is removed there is a considerable reorganization of the remaining electrons (see, for example, the case of methane treated by Coulson (1937), where the actual ionization energy is shown to be about one-quarter of the corresponding $H_{rr}$). It is not possible at present to calculate this energy with any accuracy. The most, therefore, that can be said with regard to $H_{rr}$ is that if the atom $r$ is particularly electronegative, so that it is difficult to remove its electrons, $H_{rr}$ will have a larger numerical value (its sign is necessarily relative to zero energy at infinity). Thus $\alpha_r$, which is the difference $H_{rr} - H_{CC}$, will certainly be closely related to the difference in ionization potential of the two atoms, and it may be regarded as a measure of this difference, since the two will vary in the same way. Nor must $\alpha_r$ be put equal to the difference in electron affinity of the two atoms, though it does seem quite likely that $H_{rr}$ is more intimately related to the electron-affinity scale introduced by Mulliken (1934). In view of the importance which will later be attached to this quantity $\alpha_r$, it is a pity that no more precise interpretation can be given to it. The matter, however, will not be pursued further just now.

Fortunately, the situation is more satisfactory as regards the other parameter in (10). This is the resonance integral $\beta_{rs}$, and, as shown by Lennard-Jones (1937) and others, $2\beta_{rs}$ may be taken as the difference in energy between a pure single and a pure double bond connecting atoms $r$ and $s$. It is a negative quantity whose magnitude increases along the series C=C, C=N, C=O.

The secular equations (10) determine the energies of the m.o. and the coefficients $c_{rj}$, from which the numbers of electrons on the different nuclei may be calculated. These numbers $q_r$ have been successfully correlated with the chemical reactivities of different positions in a number of molecules (see, for example, Longuet-Higgins & Coulson 1947). The coefficients may also be used for calculating the mobile orders $p_{rs}$ of unsaturated bonds. For according to the theory developed by Coulson (1939) each of the $\pi$-electrons makes a separate contribution, positive or negative, to every one of the bond orders. If $r$ and $s$ are neighbouring atoms, an electron in the $j$th m.o. (see equation (1)), which is assumed to be real and not complex, makes a contribution $c_{rj}c_{sj}$ to the bond $r$-$s$. So the total mobile bond order is

$$p_{rs} = \sum_j n_j c_{rj} c_{sj}. \tag{13}$$

If $r$ and $s$ are not neighbours, the mobile bond order is taken to be zero. Experimental bond lengths and force constants have been successfully correlated with bond orders calculated in this way (Lennard-Jones & Coulson 1939; Gordy 1946).

The exact significance of the overlap integrals $S_{rs}$ occurring in (4) has recently been discussed by Wheland (1941) and by Mulliken, Rieke and Brown (1941), who point out that in practice this overlap is not negligible. However, although its inclusion makes a difference to the calculation of energies, it does not affect the relative values of the coefficients $c_{rj}$. The secular equations (8), in which overlap is neglected, have therefore been taken as our starting point in the present theory.

<center>GENERAL THEORY</center>

The secular equations for a conjugated system of $n$ atomic orbitals are, by (10),

$$(\alpha_r - \epsilon)\, c_r + \sum_s{}' \beta_{rs} c_s = 0 \quad (r = 1, 2, \ldots, n). \tag{10}$$

$\alpha_r$ and $\beta_{rs}$ $(= \beta_{sr}^*)$ are fixed quantities characteristic of the molecule; $\epsilon$ and the coefficients $c_r$ are the unknowns. By choosing a purely real form for every atomic wave function $\phi_r$, which is always permitted except when dealing with certain magnetic properties, one ensures that the $\beta_{rs}$ and the $c_r$ are real also. The condition for consistency of the $n$ equations (10) is that the 'secular determinant' shall vanish, viz. that

$$\Delta(\epsilon) \equiv \begin{vmatrix} \alpha_1 - \epsilon & \beta_{12} & \beta_{13} & \cdots & \cdots \\ \beta_{21} & \alpha_2 - \epsilon & \beta_{23} & \cdots & \cdots \\ \beta_{31} & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \alpha_n - \epsilon \end{vmatrix} = 0. \tag{14}$$

In general this equation has $n$ roots $\epsilon_j$ $(j = 1, 2, \ldots, n)$. Each of these is substituted back in turn into the secular equations (10) to give the corresponding sets of coefficients $c_{1j}, c_{2j}, \ldots, c_{nj}$, or rather their ratios—their absolute magnitudes are fixed by the normalization condition, viz.

$$c_{1j}^2 + c_{2j}^2 + c_{3j}^2 + \ldots + c_{nj}^2 = 1. \tag{15}$$

Since the matrix of $\Delta$ is Hermitean, the $\epsilon_j$ are all real, and in most of the succeeding analysis it will be assumed that they are all distinct: this is true in general, and makes the proofs much less cumbersome, while few of the conclusions depend on it (see Appendix 2). It can be proved that if $\epsilon_j \neq \epsilon_k$, then

$$\sum_r c_{rj} c_{rk} = 0. \tag{16}$$

Therefore since all the $\epsilon_j$ are different, all the m.o. are orthogonal, and this fact can be combined with (15) in the equation

$$\sum_r c_{rj} c_{rk} = \delta_{jk}. \tag{17}$$

Further, except when the contrary is stated, we shall discuss only molecules in which all the electrons are paired, so that each occupied m.o. contains exactly two electrons. Lastly, the zero of energy can be chosen in such a way that $\epsilon$ is negative for each of the occupied m.o. and positive for each of the unoccupied m.o. In the

ground state of the molecule the occupied m.o. will be measured from 1 to $m$, and the unoccupied from $m+1$ to $n$, so that

$$\epsilon_1 < \epsilon_2 < \ldots < \epsilon_m < 0 < \epsilon_{m+1} < \ldots < \epsilon_n. \tag{18}$$

### Total mobile bond orders and $\pi$-electron densities

According to the definitions (9) and (13), the total mobile order of a bond $r$-$s$ is given by

$$p_{rs} = 2 \sum_{j=1}^{m} c_{rj} c_{sj}, \tag{19}$$

and the total density of $\pi$-electrons around atom $r$ by

$$q_r = 2 \sum_{j=1}^{m} c_{rj}^2. \tag{20}$$

In this form both $p_{rs}$ and $q_r$ are given as a sum over the occupied m.o. But we propose to show now how both these quantities may be determined directly from the secular determinant introduced in (14). From this certain important deductions can be made concerning both their absolute magnitudes and their variations with changes in the fundamental parameters $\alpha$ and $\beta$.

Now it follows from equation (3) and the definitions of $\alpha_r$, $\beta_{rs}$ and $\epsilon$ in (11) that for any linear combination of the $\phi_r$

$$\epsilon = \left( \sum_r c_r^2 \alpha_r + 2 \sum\sum_{r<s} c_r c_s \beta_{rs} \right) \Big/ \sum_t c_t^2. \tag{21}$$

Therefore

$$\delta\epsilon = \sum_r \left\{ \frac{c_r^2}{\sum_t c_t^2} \right\} \delta\alpha_r + \sum\sum_{r<s} \left\{ \frac{2c_r c_s}{\sum_t c_t^2} \right\} \delta\beta_{rs} + \sum_r \delta c_r \frac{\partial\epsilon}{\delta c_r}.$$

But for a m.o. by (2) and (15)

$$\partial\epsilon/\partial c_r = 0, \quad \sum_t c_t^2 = 1.$$

Therefore

$$\delta\epsilon = \sum_r c_r^2 \delta\alpha_r + \sum\sum_{r<s} 2 c_r c_s \beta_{rs}$$

for any small changes in $\alpha_r$, $\beta_{rs}$ and $c_r$. But for a m.o. $\epsilon$ may be obtained in terms of $\alpha_r$, $\beta_{rs}$ as a root of the secular determinant, and hence $\left( \dfrac{\partial\epsilon}{\partial\alpha_r} \right)_{\Delta=0}$ may be written for its variation with $\alpha_r$. It follows that

$$\left( \frac{\partial\epsilon}{\partial\alpha_r} \right)_{\Delta=0} = c_r^2, \quad \left( \frac{\partial\epsilon}{\partial\beta_{rs}} \right)_{\Delta=0} = 2 c_r c_s. \tag{22, 23}$$

Summation of (22) and (23) over the occupied m.o. gives

$$q_r = 2 \sum_{j=1}^{m} c_{rj}^2 = 2 \sum_{j=1}^{m} \left( \frac{\partial\epsilon_j}{\partial\alpha_r} \right)_{\Delta=0} = \left( \frac{\partial\mathscr{E}}{\partial\alpha_r} \right)_{\Delta=0} \tag{24}$$

and

$$p_{rs} = 2 \sum_{j=1}^{m} c_{rj} c_{sj} = \sum_{j=1}^{m} \left( \frac{\partial\epsilon_j}{\partial\beta_{rs}} \right)_{\Delta=0} = \frac{1}{2} \left( \frac{\partial\mathscr{E}}{\partial\beta_{rs}} \right)_{\Delta=0}, \tag{25}$$

where $\mathscr{E}$ is the sum of the $\pi$-electron energies, i.e.

$$\mathscr{E} = \sum_{j=1}^{m} 2\epsilon_j. \tag{26}$$

Equation (24) suggests that the electron density at a position is closely related to its chemical reactivity, since the approach of a charged reagent will alter the coulomb integral of the position in question, and the resulting changes in $\mathscr{E}$ will be very important in determining the activation energy for reaction. This suggestion is supported by the results of calculations for various particular molecules (Wheland & Pauling 1935; Longuet-Higgins & Coulson 1947). Continuing with the argument, then

$$\left(\frac{\partial \epsilon_j}{\partial \alpha_r}\right)_{\Delta=0} = -\left(\frac{\partial \Delta}{\partial \alpha_r}\right) \bigg/ \left(\frac{\partial \Delta}{\partial \epsilon}\right), \tag{27}$$

and

$$\left(\frac{\partial \epsilon_j}{\partial \beta_{rs}}\right)_{\Delta=0} = -\left(\frac{\partial \Delta}{\partial \beta_{rs}}\right) \bigg/ \left(\frac{\partial \Delta}{\partial \epsilon}\right), \tag{28}$$

in which, after differentiation, $\epsilon$ is given the value $\epsilon_j$. And

$$\frac{\partial \Delta}{\partial \alpha_r} = \Delta_{r,r}, \quad \frac{\partial \Delta}{\partial \beta_{rs}} = 2(-)^{r+s} \Delta_{r,s}, \tag{29, 30}$$

where $\Delta_{r,r}$ and $\Delta_{r,s}$ are the determinants obtained by striking out from $\Delta$ the $r$th row and $r$th or $s$th columns respectively. (The factor 2 arises from the fact that $\beta_{sr} = \beta_{rs}$.) Thus, from equations (24) to (30),

$$q_r = -2 \sum_{j=1}^{m} \frac{\Delta_{r,r}(\epsilon_j)}{\Delta'(\epsilon_j)}, \tag{31}$$

$$p_{rs} = (-)^{r+s+1} 2 \sum_{j=1}^{m} \frac{\Delta_{r,s}(\epsilon_j)}{\Delta'(\epsilon_j)}, \tag{32}$$

where $\Delta'(\epsilon_j)$ denotes $\left[\dfrac{\partial \Delta(\epsilon)}{\partial \epsilon}\right]_{\epsilon=\epsilon_j}$.

The sums in (31) and (32) can be converted into integrals as follows: Consider the complex integral (33)

$$\frac{1}{2\pi i} \int_{\gamma} \frac{\Delta_{r,s}(z)}{\Delta(z)} \, dz, \tag{33}$$

where the path of integration $\gamma$ (figure 1) is the imaginary axis from $-\infty i$ to $+\infty i$, and the infinite semicircle to the left of the $y$-axis. At large distances from the origin the integrand is of order $z^{-2}$, provided that $r \neq s$. So the integral over the large semicircle vanishes and hence (33) reduces to

$$\frac{1}{2\pi i} \int_{-\infty i}^{\infty i} \frac{\Delta_{r,s}(z)}{\Delta(z)} \, dz. \tag{34}$$

Now by Cauchy's theorem (33) equals the sum of the residues of the integrand at its poles within $\gamma$. Clearly, the poles of the function $\Delta_{r,s}/\Delta$ are the roots of $\Delta = 0$,

i.e. points on the real axis for which $z = \epsilon_1, \epsilon_2, ..., \epsilon_n$. These are all simple poles, since $\Delta$ has no repeated roots; therefore the residue at $\epsilon_j$ is $\Delta_{r,s}(\epsilon_j)/\Delta'(\epsilon_j)$. Further, by (18) the poles within the contour $\gamma$ are just those corresponding to the occupied m.o., and those outside correspond to the unoccupied m.o. Therefore (33) equals

$$\sum_{j=1}^{m} \Delta_{r,s}(\epsilon_j)/\Delta'(\epsilon_j).$$

It follows from (32) that

$$p_{rs} = (-)^{r+s+1} \frac{2}{2\pi i} \int_{-\infty i}^{\infty i} \frac{\Delta_{r,s}(z)}{\Delta(z)} dz$$

$$= (-)^{r+s+1} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,s}(iy)}{\Delta(iy)} dy, \tag{35}$$

which may be written as

$$-\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\partial}{\partial \beta_{rs}} \log \Delta(iy)\, dy. \tag{36}$$
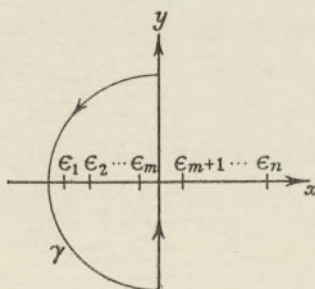


FIGURE 1

A similar expression for $q_r$ may be found by considering the integral

$$\frac{1}{2\pi i} \int_{\gamma} \frac{\Delta_{r,r}(z)}{\Delta(z)} dz. \tag{37}$$

At large distances from the origin the integrand tends to $-1/z$. Hence the part of the integral round the infinite semicircle equals $-\frac{1}{2}$. Now the sum of the residues of $\Delta_{r,r}(z)/\Delta(z)$ at its simple poles within $\gamma$ (there being no poles on $\gamma$) equals

$$\sum_{j=1}^{m} \Delta_{r,r}(\epsilon_j)/\Delta'(\epsilon_j).$$

Therefore by Cauchy's theorem

$$\frac{1}{2\pi i} \int_{-\infty i}^{\infty i} \frac{\Delta_{r,r}(z)}{\Delta(z)} dz - \frac{1}{2} = \sum_{j=1}^{m} \frac{\Delta_{r,r}(\epsilon_j)}{\Delta'(\epsilon_j)}.$$

Therefore by (31)

$$q_r = 1 - \frac{1}{\pi i} \int_{-\infty i}^{\infty i} \frac{\Delta_{r,r}(z)}{\Delta(z)} dz$$

$$= 1 - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,r}(iy)}{\Delta(iy)} dy. \tag{38}$$

This may also be written

$$q_r = 1 - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\partial}{\partial \alpha_r} \log \Delta(iy)\, dy. \tag{39}$$

Provided the integrals are given their principal values, (35) and (38) still represent $p_{rs}$ and $q_r$ in an 'odd molecule' for which

$$\left. \begin{aligned} \epsilon_j < 0, \quad n_j = 2 \quad (j = 1, 2, ..., (m-1)), \\ \epsilon_m = 0, \quad n_m = 1, \\ \epsilon_k > 0, \quad n_k = 0 \quad (k = (m+1), ..., n). \end{aligned} \right\} \tag{40}$$

The values of $\alpha_r$ can always be adjusted so that $\epsilon = 0$ for the m.o. containing one electron. In this case the integrand in (33) has a pole on $\gamma$, at $z = 0$. The contour of integration is therefore modified to $\gamma'$, which differs from $\gamma$ in traversing a small semicircle $c$ centred at the origin (figure 2). As before, the integral over $\gamma'$ equals the sum of the residues at $\epsilon_1$ to $\epsilon_{m-1}$, and the integral over the large semicircle is zero; but the integral over $c$ equals $-\frac{1}{2}$ times the residue at $\epsilon_m$, i.e. at the origin. Therefore the integral over the straight part of the contour equals

$$\frac{1}{2\pi i} P \int_{-\infty i}^{\infty i} \frac{\Delta_{r,s}(z)}{\Delta(z)}\, dz = \sum_{j=1}^{m-1} \frac{\Delta_{r,s}(\epsilon_j)}{\Delta'(\epsilon_j)} + \frac{1}{2} \frac{\Delta_{r,s}(0)}{\Delta'(0)}.$$

But, by analogy with (32), the right-hand side of this is $(-)^{r+s+1} \frac{1}{2} p_{rs}$. Therefore

$$p_{rs} = \frac{(-1)^{r+s+1}}{\pi} P \int_{-\infty}^{\infty} \frac{\Delta_{r,s}(iy)}{\Delta(iy)}\, dy. \tag{35a}$$
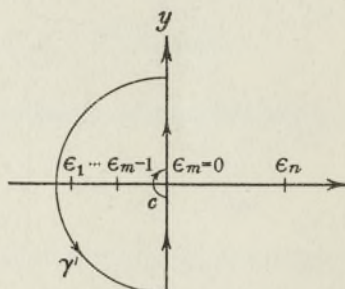


FIGURE 2

A similar argument shows that

$$q_r = 1 - \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\Delta_{r,r}(iy)}{\Delta(iy)}\, dy. \tag{38a}$$

A corresponding integral formula for $\mathscr{E}$ may be obtained from the integral

$$\frac{1}{2\pi i} \int_{\gamma} \left\{ z \frac{\Delta'(z)}{\Delta(z)} - n \right\} dz.$$

On account of the fact that (see equation (14))

$$\Delta(z) = (-)^n \left\{ z^n - \left( \sum_r \alpha_r \right) z^{n-1} + ... \right\},$$

it follows that the integrand equals $\left(\sum_r \alpha_r\right) z^{-1} + O(z^{-2})$. The contribution from the infinite semicircle is therefore $\frac{1}{2}\sum_r \alpha_r$. But the poles within $\gamma$ are at $\epsilon_j$ $(j = 1, 2, ..., m)$, and the residue at $\epsilon_j$ is $\epsilon_j$. Therefore

$$\frac{1}{2\pi i}\int_{-\infty i}^{\infty i}\left\{z\frac{\Delta'(z)}{\Delta(z)} - n\right\}dz + \tfrac{1}{2}\sum_r \alpha_r = \sum_{j=1}^{m}\epsilon_j = \tfrac{1}{2}\mathscr{E}.$$

Therefore
$$\mathscr{E} = \sum_r \alpha_r + \frac{1}{\pi}\int_{-\infty}^{\infty}\left\{iy\frac{\Delta'(iy)}{\Delta(iy)} - n\right\}dy. \tag{41}$$

This equation also holds for molecules having an orbital of zero energy containing 0, 1 or 2 electrons, since these contribute nothing to $\mathscr{E}$, nor does the integrand develop a pole at $z = 0$, since $z\Delta'(z)/\Delta(z) = O(1)$. Equation (41) is a generalization of a formula previously obtained (Coulson 1940) for hydrocarbons in which each $\alpha_r$ is zero.

Three integral formulae have now been obtained; before proceeding further it is convenient to list them together:

$$p_{rs} = -\frac{1}{2\pi}\int\frac{\partial}{\partial\beta_{rs}}\log\Delta\,dy = (-)^{r+s+1}\frac{1}{\pi}\int\frac{\Delta_{r,s}}{\Delta}dy, \tag{42}$$

$$q_r = 1 - \frac{1}{\pi}\int\frac{\partial}{\partial\alpha_r}\log\Delta\,dy = 1 - \frac{1}{\pi}\int\frac{\Delta_{r,r}}{\Delta}dy, \tag{43}$$

$$\mathscr{E} = \sum_r \alpha_r + \frac{1}{\pi}\int\left\{y\frac{\partial}{\partial y}\log\Delta - n\right\}dy = \sum_r \alpha_r + \frac{1}{\pi}\int\left\{iy\frac{\Delta'}{\Delta} - n\right\}dy. \tag{44}$$

Here and later every determinant which occurs in an integral is to be taken as *a function of iy, not y*, and the limits of integration, when not given, are $-\infty$ to $+\infty$.

These three formulae, besides certain applications which will be considered later, enable us to calculate in one step the total $\pi$-electronic energy, the total mobile charge on a particular nucleus, or the total mobile order of any particular bond, without the need of solving the secular determinant for each of the separate molecular orbitals; and as one of the writers has shown (Coulson 1940) this single integration may often be achieved numerically to a high degree of accuracy without great labour. The mobile charges may be used (e.g. Longuet-Higgins, unpublished work) to estimate the resonance dipole moment, and the active centres for cationoid and anionoid attack; and the bond order, which measures the double-bond character of a bond, will indicate its reactivity as well as its length and force constant.

### MUTUAL POLARIZABILITIES OF ATOMS AND BONDS

To some extent the above applications of the theory of molecular orbitals are familiar. But there is another application which has not been widely applied hitherto, and which promises to yield important results. Suppose that by some means one is able to alter the energy integral $\alpha_r$ of one atom to a different value $\alpha_r + \delta\alpha_r$. This

may be achieved, for example, by replacing a boundary hydrogen atom by a methyl group or other radical—the effect of alkylation has been much discussed in relation to the change in energy levels, and hence of colour, in certain conjugated dye molecules—or it may be achieved by replacing one group by another with different electron affinity, for example, CH in benzene by N, giving pyridine. But however it arises this change in $\alpha_r$ will cause changes in the charge densities around all the nuclei. In particular, if the change may be treated in first approximation as a perturbation applied to atom $r$, the change of electron density on atom $s$ is

$$\delta q_s = \frac{\partial q_s}{\partial \alpha_r} \delta \alpha_r = \pi_{s,r} \delta \alpha_r, \quad \text{say.} \tag{45}$$

Values of $\pi_{s,r}$ will therefore tell what differences in electron distribution are to be expected between pairs of molecules related in this way. Now according to (24)

$$\pi_{s,r} = \frac{\partial q_s}{\partial \alpha_r} = \frac{\partial^2 \mathscr{E}}{\partial \alpha_r \partial \alpha_s} = \frac{\partial^2 \mathscr{E}}{\partial \alpha_s \partial \alpha_r} = \frac{\partial q_r}{\partial \alpha_s} = \pi_{r,s}, \tag{46}$$

so thus follows the theorem: 'A change in electron affinity at atom $r$ produces the same change in electron density at atom $s$ as a similar change at atom $s$ would produce at atom $r$.' This symmetry suggests that both $\pi_{s,r}$ and $\pi_{r,s}$ should be referred to as the *mutual polarizability of atoms r and s*.

As has been seen, one would expect the magnitudes and signs of these mutual polarizabilities to be of importance in determining how a substituent will affect the electron density and hence the chemical reactivity at different positions in a conjugated molecule. There is, however, another rather practical use to which these mutual polarizabilities can be put—and the others shortly to be introduced. It arises from the fact that the secular equations are vastly easier to solve for pure hydrocarbons than for systems such as pyridine or indole. Thus for indole it is necessary to solve a determinantal equation of the ninth degree, whereas in the corresponding hydrocarbon (benz-pentadienyl) the secular determinant factorizes into a quartic and a quintic. Once the wave functions have been calculated for the appropriate hydrocarbon, it is possible with little further labour to estimate the charge shifts in the related hetero-molecules, as we hope to do in a later paper.

But when $\alpha_r$ is changed, not only do the electron densities $q_s$ change, so also do the bond orders $p_{st}$. A polarizability may be introduced, called the bond-atom polarizability $\pi_{st,r}$, to measure this change. In fact

$$\delta p_{st} = \frac{\partial p_{st}}{\partial \alpha_r} \delta \alpha_r = \pi_{st,r} \delta \alpha_r, \quad \text{say.} \tag{47}$$

This will be discussed later.

The effects represented by $\pi_{s,r}$ and $\pi_{st,r}$ result from a change in the coulomb energy integral $\alpha_r$ at some atom; and to the extent to which first-order perturbation theory is valid any number of such changes may be superposed at different atoms. But, of course, the effect of changing one of the resonance integrals $\beta_{rs}$ across a bond $r$-$s$ could be studied equally well. A particularly important way in which this occurs

is during the process of vibration; for as the molecule vibrates, the bond lengths are changing, and hence also the resonance integrals. An alteration in $\beta_{st}$, say, will cause a change in electron density at atom $r$ which is measured by the atom-bond polarizability

$$\pi_{r,st} = \frac{\partial q_r}{\partial \beta_{st}}, \tag{48}$$

and a change in the order of bond $ru$ measured by

$$\pi_{ru,st} = \frac{\partial p_{ru}}{\partial \beta_{st}}. \tag{49}$$

Now changes in the charge density—and hence electric moment—as a result of vibration are responsible for the absorption of infra-red light, so that the intensity of absorption in a given vibrational transition is related in part to the coefficients $\pi_{r,st}$. And changes in bond order imply changes in energy, so that cross-terms in the potential energy function for vibrations are closely dependent upon the magnitudes of the quantities $\pi_{ru,st}$. A fuller account of this effect is being given in a later paper.

Relationships similar to (46) may be found for $\pi_{st,r}$ and $\pi_{r,st}$. Thus

$$\pi_{st,r} = \frac{\partial p_{st}}{\partial \alpha_r} = \frac{1}{2}\frac{\partial^2 \mathscr{E}}{\partial \alpha_r \partial \beta_{st}} = \frac{1}{2}\frac{\partial q_r}{\partial \beta_{st}} = \tfrac{1}{2}\pi_{r,st}. \tag{50}$$

This is, the polarizability of a bond by an atom equals half the polarizability of the atom by the bond. Similarly

$$\pi_{rs,tu} = \frac{\partial p_{rs}}{\partial \beta_{tu}} = \frac{1}{2}\frac{\partial^2 \mathscr{E}}{\partial \beta_{tu} \partial \beta_{rs}} = \frac{\partial p_{tu}}{\partial \beta_{rs}} = \pi_{tu,rs}. \tag{51}$$

Here again, therefore, one may speak of the *mutual polarizability of a pair of bonds*.

Integral formulae for $\pi_{r,s}$, $\pi_{rs,t}$ and $\pi_{rs,tu}$ may be obtained by differentiation of the integrals in (42) and (43). Thus

$$\pi_{r,s} = -\frac{1}{\pi}\int \frac{\partial^2}{\partial \alpha_r \partial \alpha_s}\log \varDelta \, dy, \tag{52}$$

$$\pi_{rs,t} = -\frac{1}{2\pi}\int \frac{\partial^2}{\partial \alpha_t \partial \beta_{rs}}\log \varDelta \, dy, \tag{53}$$

$$\pi_{rs,tu} = -\frac{1}{2\pi}\int \frac{\partial^2}{\partial \beta_{rs} \partial \beta_{tu}}\log \varDelta \, dy. \tag{54}$$

More useful relationships are obtained by using the alternative forms of the integrands in (38) and (39), as follows:

$$\pi_{r,s} = -\frac{1}{\pi}\int \frac{\partial}{\partial \alpha_s}\left\{\frac{\varDelta_{r,r}}{\varDelta}\right\} dy$$

$$= -\frac{1}{\pi}\int \frac{\varDelta \cdot \varDelta_{rs,rs} - \varDelta_{r,r}\varDelta_{s,s}}{\varDelta^2} dy, \tag{55}$$

where the letters before and after the comma in each suffix denote respectively rows and columns omitted from $\varDelta$, and as agreed on p. 49 all the determinants are

functions of $iy$, not $y$. Thus, for example, $\Delta_{rs,tu}$ means that the rows $r$ and $s$, together with the columns $t$ and $u$, have been removed from the determinant $\Delta$. It is also supposed, where necessary in this notation, that $r < s$, $t < u$. If $r > s$, then in order to preserve consistency in the analysis $\Delta_{rs,tu}$ must be interpreted as $-\Delta_{sr,tu}$. But on account of the symmetric nature of $\Delta$, then $\Delta_{r,s} = \Delta_{s,r}$.

Now by Jacobi's formula for the adjugate to a determinant

$$\Delta \cdot \Delta_{rs,tu} = \Delta_{r,t}\Delta_{s,u} - \Delta_{r,u}\Delta_{s,t}. \tag{56}$$

Putting $t = r$, $u = s$ in (56) and substituting in (55), it follows that

$$\pi_{r,s} = \frac{1}{\pi}\int\left\{\frac{\Delta_{r,s}}{\Delta}\right\}^2 dy. \tag{57}$$

Again, from (42), $\qquad \pi_{rs,t} = (-)^{r+s+1}\frac{1}{\pi}\int\frac{\partial}{\partial\alpha_t}\left\{\frac{\Delta_{r,s}}{\Delta}\right\}dy$

$$= (-)^{r+s+1}\frac{1}{\pi}\int\frac{\Delta\cdot\Delta_{rt,st} - \Delta_{r,s}\Delta_{t,t}}{\Delta^2}dy, \tag{58}$$

assuming for the moment that both $r$ and $s$ are less than $t$. In view of (56) and the fact that $\Delta_{t,s} = \Delta_{s,t}$, this becomes

$$\pi_{rs,t} = (-)^{r+s}\frac{1}{\pi}\int\frac{\Delta_{r,t}\Delta_{s,t}}{\Delta^2}dy. \tag{59}$$

Finally, from (42), $\qquad \pi_{rs,tu} = (-)^{r+s+1}\frac{1}{\pi}\int\frac{\partial}{\partial\beta_{tu}}\left\{\frac{\Delta_{r,s}}{\Delta}\right\}dy. \tag{60}$

But it is easily seen by writing down the form of $\Delta_{r,s}$ that if $r$ and $s$ are each less than $t$ and $u$, then

$$\frac{\partial\Delta_{r,s}}{\partial\beta_{tu}} = (-)^{t+u}\{\Delta_{rt,su} + \Delta_{ru,st}\}$$

and $\qquad\qquad\qquad \frac{\partial\Delta}{\partial\beta_{tu}} = (-)^{t+u}2\Delta_{t,u}.$

So under these conditions it follows from (56) that

$$\pi_{rs,tu} = (-)^{r+s+t+u}\frac{1}{\pi}\int\frac{\Delta_{r,u}\Delta_{s,t} + \Delta_{r,t}\Delta_{s,u}}{\Delta^2}dy. \tag{61}$$

Equations (57), (59) and (61), in which it is understood that all the determinants are functions of $iy$, have been proved under certain conditions of inequality between the indices $r$, $s$, $t$ and $u$ (e.g. $r < t$, $s < u$). It is not difficult to prove, however, that they are actually valid for all relative values of these indices. In particular, (57) holds even if $r = s$, so that the *self-polarizability of atom $r$* satisfies the equation

$$\pi_{r,r}\left(= \frac{\partial q_r}{\partial\alpha_r}\right) = \frac{1}{\pi}\int\left\{\frac{\Delta_{r,r}}{\Delta}\right\}^2 dy. \tag{62}$$

And (61) is true if $r = t$, $s = u$; so that the *self-polarizability of bond rs* is given by

$$\pi_{rs,rs}\left(= \frac{\partial p_{rs}}{\partial \beta_{rs}}\right) = \frac{1}{\pi} \int \frac{\Delta_{r,r}\Delta_{s,s} + \Delta_{r,s}^2}{\Delta^2} dy. \tag{63}$$

The self-polarizability of an atom measures the change of charge density at the atom when its electron affinity is altered; the self-polarizability of a bond measures the change of mobile order in the bond when its resonance integral is altered.

It is easy to prove that (57), (59) and (61) still hold for an odd molecule with one electron in an m.o. of zero energy, provided one takes the principal values of the integrals. One merely starts from equations (35 $a$) and (38 $a$) instead of (35) and (38); the reasoning follows exactly similar lines.

### FORMULAE FOR POLARIZABILITIES IN TERMS OF THE COEFFICIENTS

Equations (57), (59) and (61) give the three types of polarizability in terms of certain integrals, and for many purposes this is the most convenient form for them. But the m.o. is often known explicitly, and then it is desirable to have equivalent expressions in terms of the coefficients $c_{rj}$ of (1). These alternative expressions for $\pi_{r,s}$, $\pi_{rs,t}$ and $\pi_{rs,tu}$ may be derived by application of ordinary first-order perturbation theory to the secular equations.

Suppose there is a molecule in which the occupied m.o. are $\psi_1, \psi_2, \ldots, \psi_m$ and the unoccupied m.o. are $\psi_{m+1}, \ldots, \psi_n$, built up according to (1) from the component atomic orbitals $\phi_1, \ldots, \phi_n$. Notice what happens to the coefficients, electron densities and bond orders when the coulomb integral $\alpha_r$ is increased by a small amount $\delta\alpha_r$. (An increase in $\alpha_r$ corresponds, of course, to a decrease in electron affinity.) By first-order perturbation theory the perturbed wave functions can be expanded in the form

$$\psi_j + \psi_j' = \psi_j + \sum_{k=1}^{n}{}' \left\{ \frac{\int \int \psi_j H' \psi_k dv}{\epsilon_j - \epsilon_k} \right\} \psi_k,$$

which equals

$$\psi_j + \sum_{k=1}^{n}{}' \frac{c_{rj}c_{rk}\delta\alpha_r}{\epsilon_j - \epsilon_k} \psi_k,$$

since

$$\psi_j = \sum_{s=1}^{n} c_{sj}\phi_s \quad \text{and} \quad \int \phi_r H' \phi_r dv = \delta\alpha_r,$$

all other integrals of this type being zero. So

$$\psi_j' = \delta\alpha_r \sum_{k=1}^{n}{}' \left\{ \frac{c_{rj}c_{rk}}{\epsilon_j - \epsilon_k} \sum_{s=1}^{n} c_{sk}\phi_s \right\} = \sum_{s=1}^{n} c_{sj}'\phi_s, \quad \text{say,}$$

where

$$c_{sj}' = \delta\alpha_r c_{rj} \sum_{k=1}^{n}{}' \frac{c_{rk}c_{sk}}{\epsilon_j - \epsilon_k}.$$

Bearing in mind the fact that the occupied orbitals are those for which $1 \leqslant j \leqslant m$, the change in electron density at atom $s$ equals may be deduced as

$$\delta q_s = 2 \sum_{j=1}^{m} \{(c_{sj} + c'_{sj})^2 - c^2_{sj}\}$$

$$= 4 \sum_{j=1}^{m} c_{sj} c'_{sj}$$

since $c'_{sj}$ is small. Thus $\quad \delta q_s = 4 \delta \alpha_r \sum_{j=1}^{m} \sum_{k=1}^{n}{}' \frac{c_{rj} c_{sj} c_{rk} c_{sk}}{\epsilon_j - \epsilon_k}.$

From this it follows that

$$\pi_{s,r} = \frac{\partial q_s}{\partial \alpha_r} = 4 \sum_{j=1}^{m} \sum_{k=1}^{n}{}' \frac{c_{rj} c_{sj} c_{rk} c_{sk}}{\epsilon_j - \epsilon_k}.$$

But the summand here is antisymmetric in $j$ and $k$ so that $\sum\limits_{j=1}^{m} \sum\limits_{k=1}^{m}{}' = 0$. Therefore

$$\pi_{s,r} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{rj} c_{sj} c_{rk} c_{sk}}{\epsilon_j - \epsilon_k}. \tag{64}$$

In particular the self-polarizability of atom $r$ is

$$\pi_{r,r} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c^2_{rj} c^2_{rk}}{\epsilon_j - \epsilon_k}. \tag{64a}$$

Similarly, the change in order of bond $st$ equals

$$\delta p_{st} = 2 \sum_{j=1}^{m} \{(c_{sj} + c'_{sj})(c_{tj} + c'_{tj}) - c_{sj} c_{tj}\}$$

$$= 2 \sum_{j=1}^{m} (c_{sj} c'_{tj} + c_{tj} c'_{sj})$$

$$= 2 \delta \alpha_r \sum_{j=1}^{m} \sum_{k=1}^{n}{}' \frac{c_{rj} c_{rk} (c_{sj} c_{tk} + c_{tj} c_{sk})}{\epsilon_j - \epsilon_k}.$$

Therefore $\quad \pi_{st,r} = 2 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{rj} c_{rk} (c_{sj} c_{tk} + c_{tj} c_{sk})}{\epsilon_j - \epsilon_k}. \tag{65}$

Equations (64) and (65) show the effect of changing the coefficient $\alpha_r$; next note how a change of $\beta_{rs}$ to $\beta_{rs} + \delta \beta_{rs}$ alters the electron densities and bond orders. As before $\psi_j$ becomes $\psi_j + \psi'_j$, where now

$$\psi'_j = \sum_{k=1}^{n}{}' \left\{ \frac{\int \int \psi_j H' \psi_k \, dv}{\epsilon_j - \epsilon_k} \right\} \psi_k = \sum_{k=1}^{n}{}' \frac{(c_{rj} c_{sk} + c_{sj} c_{rk}) \delta \beta_{rs}}{\epsilon_j - \epsilon_k} \psi_k$$

$$= \sum_{t=1}^{n} c'_{tj} \phi_t,$$

where $\quad c'_{tj} = \delta \beta_{rs} \sum_{k=1}^{n}{}' \frac{c_{tk} (c_{rj} c_{sk} + c_{sj} c_{rk})}{\epsilon_j - \epsilon_k}.$

This leads to a change in density on atom $t$ given by

$$\delta q_t = 4 \sum_{j=1}^{m} c_{tj} c'_{tj} = 4 \delta \beta_{rs} \sum_{j=1}^{m} \sum_{k=1}^{n}{}' \frac{c_{tj} c_{tk} (c_{rj} c_{sk} + c_{sj} c_{rk})}{\epsilon_j - \epsilon_k}.$$

This may be written

$$\pi_{t,rs} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{tj} c_{tk} (c_{rj} c_{sk} + c_{sj} c_{rk})}{\epsilon_j - \epsilon_k}. \tag{66}$$

Comparing this with (65) then $\pi_{t,rs} = 2\pi_{rs,t}$, in agreement with (50). Finally,

$$\pi_{tu,rs} = 2 \sum_{j=1}^{m} (c_{tj} c'_{uj} + c_{uj} c'_{tj}) / \delta \beta_{rs}$$

$$= 2 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{(c_{rj} c_{sk} + c_{sj} c_{rk})(c_{tj} c_{uk} + c_{uj} c_{tk})}{\epsilon_j - \epsilon_k}. \tag{67}$$

Equations (64) to (67) enable one to calculate all the atom and bond polarizabilities in a molecule in terms of the energies and coefficients of its molecular orbitals. These equations are the exact analogues of (57), (59) and (61), and may be verified directly by the evaluation of certain complex integrals. For instance, we may relate (64) to (57) by integrating

$$P \int_{-\infty i}^{\infty i} \int_{-\infty i}^{\infty i} \frac{\Delta_{r,s}(w) \Delta_{r,s}(z)}{\Delta(w) \Delta(z) (w-z)} \, dw \, dz$$

successively with respect to $w$ and $z$, using Cauchy's residue theorem. It should be noted that equations (64) to (67) do not hold for odd molecules with one electron in a m.o. of zero energy; the necessary modifications are, however, not difficult to make.

An interesting chemical implication of (67) is the following: If there are two conjugated systems initially separate, and they are then joined by a weak bond between atom $r$ of the first and atom $s$ of the second, then to a first approximation, in which only conjugation effects are considered, the order of any other bond $tu$ in either system is unaffected.

To prove this one takes as the basis of the perturbation calculation in (67) the separated conjugated systems. Then each suffix $j$ in a term of (67) will refer to an occupied m.o. in one of the two systems, and each suffix $k$ to an unoccupied m.o. Suppose that $j$ and $k$ refer to the same system. Then either $c_{rj}$ and $c_{rk}$, or else $c_{sj}$ and $c_{sk}$, must vanish, since $r$ and $s$ are in different systems; thus the first bracket in (67) is zero. But if $j$ and $k$ refer to different systems, and $tu$ is a bond in one of the systems, either $c_{tj}$ and $c_{uj}$, or else $c_{tk}$ and $c_{uk}$, must vanish; and so the second bracket is zero. Hence in all cases every term of (67) is zero and so $\pi_{rs,tu} = 0$, which establishes the theorem. This theorem tells us something about the condition when a reaction between conjugated systems is being initiated. For it shows that (steric conditions permitting) conjugation may begin to take place, with the introduction of resonance forces, without the reacting groups having to be deformed. It is only when the reaction complex is well on the way to being formed that serious changes in bond order occur in the two separate parts.

### INEQUALITIES AND IDENTITIES INVOLVING ELECTRON DENSITIES, BOND ORDERS AND ATOM AND BOND POLARIZABILITIES

The electron densities, bond orders and the various polarizabilities have been calculated independently of one another. But there are several identities and in-equalities between them that must now be described. These inequalities are useful in understanding certain experimental phenomena, as will be shown; and the identities provide useful checks upon the numerical working at various stages.

(i) The first inequality concerns the electron density $q_r$; this being a sum of square terms must obviously be positive. But we shall now show that it cannot exceed 2. For this purpose return to equation (17). This shows us that the molecular orbitals $\psi_j$ may be regarded as a set of unit orthogonal vectors in the $n$-space defined by the unit orthogonal vectors $\phi_r$, $c_{rj}$ being the cosine of the angle between $\psi_j$ and the base vector $\phi_r$. But the roles of $\phi$ and $\psi$ may be interchanged, and $\phi_r$ regarded as a unit vector relative to the set of orthogonal base vectors $\psi_j$; it follows that $\sum_{j=1}^{n} c_{rj}^2 = 1$, so that $\sum_{j=1}^{m} c_{rj}^2 \leqslant 1$. But $q_r = 2 \sum_{j=1}^{m} c_{rj}^2$, and so

$$0 \leqslant q_r \leqslant 2. \tag{68}$$

This inequality gives a simple explanation of the charge shifts in certain con-jugated systems. For example, in chlorobenzene there are six $\pi$-electrons from the benzene nucleus and two from the Cl atom. If the Cl atom were not conjugated with the ring, it would have exactly two of these electrons. But by (68) conjugation can only reduce this number, so that there is a charge drift into the ring. Our analysis shows that this migration would be expected even though Cl is more electronegative than carbon. In fact, it is only the magnitude of the electron drift, and not its
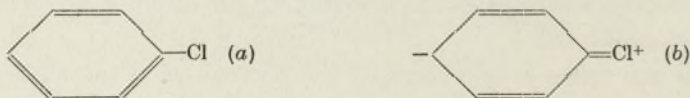


direction, which depends upon the nature of the attached group. The conventional valence-bond description of this phenomenon is that there is resonance between covalent structures of type (a) and ionic structures of type (b) in which charge has moved from Cl to the less electronegative C. We believe that the present explanation by the method of m.o. is a worth-while supplement to the resonance picture. A similar explanation is behind the drift of electrons away from the electronegative N atom in molecules such as pyrrole and indole (Longuet-Higgins & Coulson 1947).

(ii) It is worth noting that there is no condition analogous to (68) requiring $p_{rs}$ to be positive; in fact, generalizing the idea of bond order to apply to atoms which are not actually adjacent to one another, it is easy to show that the bond order between *para* positions in benzene is negative; the implications of this fact are discussed in a later paper.

(iii) By a direct application of Cauchy's inequality it can be proved that the order of a bond is not greater than the geometric mean of the electron densities at the atoms forming the bond. For Cauchy's inequality is that

$$\left\{ \sum_{j=1}^{m} c_{rj} c_{sj} \right\}^2 \leqslant \left\{ \sum_{j=1}^{m} c_{rj}^2 \right\} \left\{ \sum_{j=1}^{m} c_{sj}^2 \right\}, \tag{69}$$

so that

$$p_{rs}^2 \leqslant q_r q_s. \tag{70}$$

(iv) It follows from (18) and (64a) that

$$\pi_{r,r} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{rj}^2 c_{rk}^2}{\epsilon_j - \epsilon_k} < 0. \tag{71}$$

This means that an increase in $\alpha_r$ (i.e. a decrease in the electron affinity of atom $r$) results in a decrease of electron charge there, as would be expected.

(v) Similarly, from (67) it follows that

$$\pi_{rs,rs} < 0. \tag{72}$$

That is, an increase in the numerical value of $\beta_{rs}$—which is actually negative—leads to an increase of bond order, also as expected.

Equation (72) has an important application in the interaction of two conjugated systems. Imagine the systems to be initially isolated, and then to approach so that the atomic orbital $\phi_r$ of the first overlaps the atomic orbital $\phi_s$ of the second. Then $\beta_{rs}$ will decrease steadily from zero, and $p_{rs}$, which satisfies

$$p_{rs} = \int_0^{\beta_{rs}} \pi_{rs,rs} d\beta_{rs}, \tag{73}$$

will therefore increase steadily. But since $r$ and $s$ belong initially to separate systems, $p_{rs}$ is initially zero; its final value must therefore be positive. Hence *the mobile order of a bond between two otherwise disconnected systems must be positive.* Such a bond will later be referred to as a 'chain bond'. This conclusion is of obvious and fundamental importance from the chemical point of view. It explains, for instance, why the single bond connecting two aryl radicals, as in diphenyl or phenylethylene, is always partly double. Conjunction between the two groups across this bond will necessarily increase its bond order, and therefore presumably shorten it and increase its force constant. This conclusion is independent of whatever substituent groups there may be in the two halves, provided always that they do not interfere sterically with one another (as in various diphenyl $o$-$o'$ derivatives).

It is convenient at this point to introduce a few identities:

(vi) In the first place (21) can be used for checking the charge distributions and bond orders. For summation over the occupied m.o. gives the very useful relation

$$\mathscr{E} = \sum_r \alpha_r q_r + 2 \sum \sum_{r<s} \beta_{rs} p_{rs}. \tag{74}$$

(vii) Secondly, it follows from (15) and (20) that $\sum_r q_r = 2m$, which is constant and does not depend on the values of $\alpha_r$ and $\beta_{rs}$. Hence from the definitions of $\pi_{r,s}$ and $\pi_{r,st}$

$$\sum_r \pi_{r,s} = 0 = \sum_r \pi_{r,st}. \tag{75}$$

(viii) Finally, by differentiating (74) with respect to $\alpha_r$ or $\beta_{tu}$ and then using (24) and (25), then

$$\sum_s \alpha_s \pi_{s,r} + 2 \sum\sum_{s<t} \beta_{st} \pi_{st,r} = 0, \tag{76}$$

$$\sum_s \alpha_s \pi_{s,tu} + 2 \sum\sum_{r<s} \beta_{rs} \pi_{rs,tu} = 0. \tag{77}$$

Equations (75) to (77) are useful in checking values of the polarizabilities.

The suitability of the definitions adopted for electron density and bond order is satisfactorily confirmed by the reasonableness of all these results, as judged by qualitative chemical ideas. In following papers of this series we hope to show how the various formulae introduced in this paper may be used to explain and correlate various experimental phenomena.

## APPENDIX 1

Integrals involving determinants of the type $\Delta_{r,s}$ occur frequently in the formulae given in this paper, for instance in equations (42), (57), (59) and (61). When they do, it is often convenient or illuminating to expand $\Delta_{r,s}$ by the following theorem:

When the $r$th row and $s$th column are struck out from $\Delta$, the secular determinant for a conjugated system, the resulting determinant $\Delta_{r,s}$ equals

$$(-)^{r+s} \Sigma(-)^l \beta_{rt}\beta_{tu} \cdots \beta_{vs} \Delta_{rtu \ldots vs, rtu \ldots vs}, \tag{78}$$

where atoms $r, t, u, \ldots, v, s$ lie along a continuous non-crossing chain, $l$ is the number of bonds in the chain, and $\Delta_{rtu \ldots vs, rtu \ldots vs}$ is the secular determinant for the rest of the molecule (taken equal to unity if $r, t, \ldots, s$ include all the atoms in the molecule), the summation being taken over all such chains.
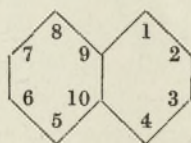


The theorem may be illustrated by the example of $\Delta_{1,6}$ for naphthalene. There are four chains of the specified kind between atoms 1 and 6, namely,

$$1\ 9\ 8\ 7\ 6, \quad 1\ 9\ 10\ 5\ 6, \quad 1\ 2\ 3\ 4\ 10\ 5\ 6 \quad \text{and} \quad 1\ 2\ 3\ 4\ 10\ 9\ 8\ 7\ 6.$$

$\Delta_{1,6}$ is therefore expressible as the sum of four terms, of which the second, for example, is $-\beta^4 \Delta_{1\ 9\ 10\ 5\ 6,\ 1\ 9\ 10\ 5\ 6}$. Since the corresponding route cuts the molecule in two, the latter determinant is itself the product of the secular determinants for the systems (7 8) and (2 3 4).

First prove that every term of $\Delta_{r,s}$ $(= \Delta_{s,r})$ must contain a factor of the type $\beta_{rt}\beta_{tu} \ldots \beta_{vs}$. Expand $\Delta_{s,r}$ in terms of row $r$. A typical term in the expansion is $\pm \beta_{rt}\Delta_{rs,rt}$, where $t \neq r$. If $t = s$, this is a factor of the required type. If $t \neq s$, expand $\Delta_{rs,rt}$ in terms of row $t$. A typical term is $\pm \beta_{tu}\Delta_{rst,rtu}$, where $u \neq r$ or $t$. If $u = s$, we have a factor of the required type; if $u \neq s$, we expand again. It is clear that as this process is continued every new letter introduced must differ from all of $r, t, u, \ldots$ so that ultimately the letter $s$ must be reached. When this happens the typical term will be of the form $\pm \beta_{rt}\beta_{tu} \ldots \beta_{vs}\Delta_{rtu \ldots vs, rtu \ldots vs}$. In this the $\beta$ part will be zero unless $rt, tu, \ldots, vs$ are all bonds; therefore there is one such term for each non-crossing chain of bonds from $r$ to $s$. If atoms $r, t, u, \ldots, v, s$ include all the atoms of the system, the factor multiplying the $\beta$'s will be unity.

Now in the expansion of $\Delta$, the sign of $\beta_{sr}\beta_{rt}\beta_{tu} \ldots \beta_{vs}\Delta_{rtu \ldots vs, rtu \ldots vs}$ is $+$ or $-$ according as the permutation $(rtu \ldots vs)$ is even or odd; that is, the sign is $(-)^l$, where $l$ is the number of bonds in the chain $rt, tu, \ldots, vs$. But $\Delta_{s,r}$ is $(-1)^{r+s}$ times the coefficients of $\beta_{sr}$ in the expansion of $\Delta$. It follows that

$$\Delta_{r,s} = \Delta_{s,r} = (-)^{r+s} \Sigma (-)^l \beta_{rt}\beta_{tu} \ldots \beta_{vs}\Delta_{rtu \ldots vs, rtu \ldots vs},$$

the summation being taken over all non-crossing chains of bonds between atoms $r$ and $s$.

Not only is this result useful in calculations involving $\Delta_{r,s}$, but it also suggests why the effects of a perturbation applied to a conjugated system die away at long distances—a fact which is hardly self-evident from the secular equations, although to be expected on physical grounds. For the highest power of $\epsilon$ occurring in $\Delta_{r,s}(\epsilon)$ is $\epsilon^{n-1-b}$, where $b$ is the number of conjugated bonds along the shortest route between atoms $r$ and $s$. This means that, for example, in equation (57), where $\pi_{r,s}$ is expressed as an integral, the integrand by (78) is of order $y^{-2b-2}$, so that the integral would be expected to be small for large values of $b$. This effect is well illustrated by the polyenes, which are discussed in a later paper.

### APPENDIX 2

It has been assumed throughout this paper that the roots of $\Delta$ are all distinct; this is nearly always true, but it is interesting to inquire how many of the equations depend upon this assumption.

If one applies to a molecule with degenerate energy levels any perturbation $H'$ which separates all the degenerate levels, all the expressions derived for $\mathscr{E}$ and its derivatives will certainly hold for the perturbed molecule. Supposing, as is reasonable, that $\mathscr{E}$ and its derivatives vary continuously with $H'$, their values for the unperturbed molecule will be the limits of the expressions as $H'$ tends to zero, *if such limits exist*.

Now the expressions for $\mathscr{E}$ and its derivatives are of two kinds. An example of the first is (38), viz.

$$q_r = 1 - \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\Delta_{r,r}(iy)}{\Delta(iy)}\,dy.$$

Both numerator and denominator in the integrand are continuous functions of $H'$, and the denominator cannot vanish since by hypothesis all the roots of $\varDelta$ are real and do not include zero. Therefore the limit of the right-hand side as $H'$ tends to zero is obtained simply by putting $H' = 0$ before integrating. Therefore formulae of this type hold for a molecule with multiple-energy levels. An example of the second type of expression is (64), viz.

$$\pi_{s,r} = 4 \sum_{j=1}^{m} \sum_{k=m+1}^{n} \frac{c_{rj} c_{sj} c_{rk} c_{sk}}{\epsilon_j - \epsilon_k}.$$

By hypothesis all the occupied m.o. have negative energies and the unoccupied m.o. positive energies, so the denominator cannot vanish; hence the right-hand side tends to a limit as $H'$ tends to zero, the terms $c_{rj}$ becoming the coefficients of the a.o. $\phi_r$ in the zeroth order m.o. $\psi_j$ appropriate to the perturbation $H'$.

It is therefore seen that any of the formulae for $\mathscr{E}$ and its derivatives which include the electron densities, bond orders and atom and bond polarizabilities, may be legitimately applied to molecules containing degenerate energy levels, provided the m.o. used as basis are correct zeroth order m.o. for any perturbation whatever which separates all the energies.

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