NOTES ON THE SECULAR DETERMINANT IN MOLECULAR ORBITAL THEORY

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For a hydrocarbon molecule in which all the Coulomb terms are equivalent ($= \alpha$) and all the resonance integrals are also equal ($= \beta$), the secular determinant may be written in the form (1)

$$\Delta(x) \equiv \begin{vmatrix} x & \beta_{12} & \beta_{13} & \dots & \beta_{1n} \\ \beta_{21} & x & \dots & & \\ \dots & & & & \\ \beta_{n1} & \dots & & & x \end{vmatrix} = 0. \tag{1}$$

In this determinant x stands for $(\alpha - \epsilon)/\beta$, where ϵ is the energy of the molecular orbital, and each $\beta_{sr} = \beta_{rs}$ is either (a) unity, if r and s are neighbours, or (b) zero, if they are not. All overlap integrals between atomic orbitals are neglected. The present note is concerned with certain properties of the determinant $\Delta(x)$.

1. In some work by Miss J. Jacobs and the author, it has been found necessary to write down the first half-dozen terms in the power-series expansion of $\Delta(x)$. These are required in the asymptotic expansions of certain contour integrals (2). It appears that these coefficients may be obtained quite simply even for large molecules. Thus, let

$$\Delta(x) = x^n + C_1 x^{n-1} + C_2 x^{n-2} + \dots + C_n. \tag{2}$$

Then evidently, since x appears only on the leading diagonal,

$$C_1 = 0. \tag{3}$$

The coefficient C_2 is due to all those terms in the expansion of Δ in which we have taken $n-2$ of the leading-diagonal x factors, and is clearly of the form $C_2 = -\sum_{r,s} \beta_{rs}^2$. The only non-vanishing β_{rs} are for neighbouring atoms, which leads us to the result

$$C_2 = -1 \times \text{number of bonds in the molecule.} \tag{4}$$

For butadiene this would be 3, and for benzene 6.

In a similar way C_3 is of the form

$$C_3 = \sum_{r,s,t} \begin{vmatrix} 0 & \beta_{rs} & \beta_{rt} \\ \beta_{sr} & 0 & \beta_{st} \\ \beta_{tr} & \beta_{ts} & 0 \end{vmatrix} = 2\Sigma \beta_{rs}\beta_{st}\beta_{tr}.$$

The only non-vanishing contributions arise when all three atoms are neighbours of each other, in a configuration that we could represent diagrammatically by . Such configurations practically never occur, but when they do, they contribute 2 to C_3. Thus:

$$C_3 = 2 \times \text{number of distinct neighbour triangles.} \tag{5}$$

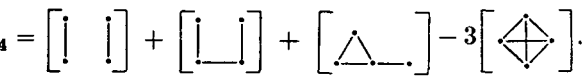
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Symbolically $C_3 = 2$ .

This analysis can be extended, and we can show that

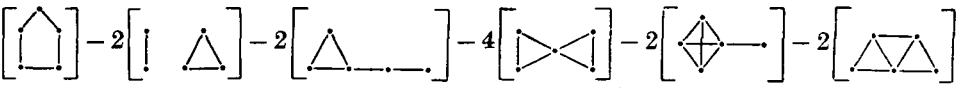
C_4 = total number of pairs of non-contiguous bonds
$-2 \times$ number of distinct neighbour squares 
$-6 \times$ number of distinct tetrahedrons. (6)

This may be written in the equivalent form

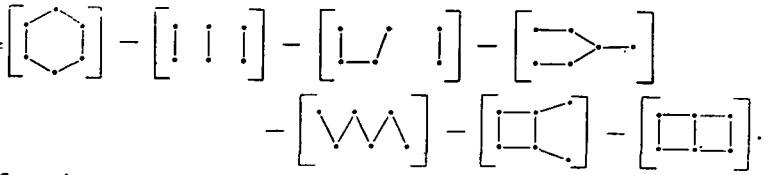
$C_4 =$ .

Such tetrahedrons will never occur in π-electron compounds, but might occur if, for example, the component atomic orbitals were of s character.

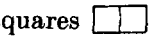
In a similar way

$C_5 = 2$  (7)

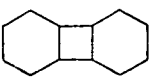
The calculation of C_6 in this manner is too involved. But if we restrict ourselves to those cases which occur in alternant hydrocarbons (3), then

$C_6 = -4$  (8)

An alternative form is

$C_6 = -1 \times$ total number of sets of three non-contiguous bonds
$-2 \times$ number of closed hexagons
$+2 \times$ number of double squares 
$+2 \times$ number of combinations of one square and a non-contiguous bond. (9)

There is no point in going further than this.

An example of the use of these formulae is diphenylene: 

Here the secular determinant for the π-electrons is

$$\Delta(x) = x^{12} + C_1 x^{11} + C_2 x^{10} + C_3 x^9 + C_4 x^8 + \ldots,$$

where

$C_1 = 0$,
$C_2 = -1 \times$ number of bonds $= -14$,
$C_3 = 2 \times$ number of triangles $= 0$,
$C_4 =$ number of non-contiguous pairs of bonds $- 2 \times$ number of squares $= 71 - 2 = 69$,
$C_5 = 2 \times$ number of pentagons $= 0$,
$C_6 = -1 \times$ number of sets of three non-contiguous bonds
$-2 \times$ number of hexagons $+ 2 \times$ number of configurations 
$= -162 - 4 + 12 = -154$.

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Now the complete determinant is known to be

$$(x^3+3x^2-3)(x^3-3x^2+3)(x^3+x^2-2x-1)(x^3-x^2-2x+1)$$
$$= x^{12}-14x^{10}+69x^8-154x^6+162x$$

agreeing with our present calculations as far as they go.

The analysis just described proves particularly convenient for discussing the difference between one secular determinant and that for a related molecule of nearly similar geometrical shape.

2. Our second paragraph concerns the roots of the secular determinant (1). These may all be shown to lie between $\pm X$, where X is the greatest of x_s, where

$$x_s = \sum_r |\beta_{rs}| \quad (s = 1, 2, \ldots, n).$$

The terms β_{ss}, being zero, are not involved in these summations. This result is essentially the same as a theorem which Prof. I. Schur of Berlin attributed to his predecessor, G. Frobenius. I am indebted to Dr W. Ledermann for drawing my attention to the theorem. In our case the proof is extremely simple. If x is a solution of (1), then there is a non-vanishing set of coefficients c_s which satisfy the secular equations

$$\sum_r \beta_{rs} c_s = -x c_r \quad (r = 1, 2, \ldots, n).$$

Let $|c_m|$ be the largest of the $|c_s|$. Then from the mth equation

$$|x||c_m| \leqslant \sum_s |\beta_{ms}||c_s| \leqslant \sum_s |\beta_{ms}||c_m|,$$

so that

$$|x| \leqslant \sum_s |\beta_{ms}|, \quad \text{i.e.} \quad |x| \leqslant x_m.$$

Since we cannot tell without calculation which is the mth row, our theorem amounts to what was stated at first:

$$|x| \leqslant \max \quad (x_1, x_2, \ldots, x_n).$$

The equality sign occurs in the infinite polyene chain where the extreme values $x = \pm 2$ occur, and in the infinite graphite layer where x attains the values ± 3. These, together with ethylene and the cyclic C_nH_n, are the only examples where the equality sign is found.

3. We are sometimes interested in the coefficients of the atomic orbitals in the lowest of the molecular orbitals. If this orbital is

$$\psi = c_1\phi_1 + c_2\phi_2 + \ldots + c_n\phi_n, \tag{10}$$

then all the coefficients c_r will be of the same sign. For the c_r are such as to render stationary the energy expression

$$\sum_{r,s} c_r c_s \beta_{rs} / \Sigma c_r^2. \tag{11}$$

In the case of the lowest energy level, the expression (11) will be an absolute maximum. Suppose, however, that all the c_r are not of the same sign. Then the hypothetical function

$$\psi' = |c_1|\phi_1 + |c_2|\phi_2 + \ldots + |c_n|\phi_n \tag{12}$$

leads to an energy expression $\sum_{r,s} |c_r||c_s|\beta_{rs}/\Sigma c_r^2$,

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which is greater than (11). This is not possible, so that the theorem is proved; all the coefficients must have the same sign.

Incidentally, on account of the orthogonality of all the molecular orbitals found from (1) this wave function (10) is the only one without changes of sign in the coefficients. This is a particular case of a general theorem regarding the number of nodes in solutions of eigenvalue problems.

The results in §§ 2, 3 hold even if the β_{rs} are not all equal, provided only that they have the same sign. The results in § 1 may be adjusted to cover this situation, but they lose most of their value when thus modified.

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