

Special Paper**C.A. COULSON'S WORK ON A CONTOUR-INTEGRAL APPROACH
TO THE LONDON THEORY OF MAGNETIC SUSCEPTIBILITY
OF CONJUGATED MOLECULES**

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(in final form 23 January 1989)**Abstract**

Mizoguchi has very recently cast London's theory of magnetic susceptibilities of conjugated molecules in terms of the Coulson contour-integral formulation of Hückel molecular-orbital theory. Since interest in this approach has been thus revived, we present here a previously unpublished document, dated May 16th, 1953, by the late Professor C.A. Coulson, FRS, in which he formulates the London theory in terms of his own contour-integral method. Coulson's treatment is based on bond-bond polarisabilities and it therefore provides an interesting parallel to certain aspects of the now-classic McWeeny polarisability method, advanced five years later. The Coulson polarisability formalism does not, however, provide for explicit computation of individual "ring-current" intensities, nor – since it preceded the experimental observations – for the direct calculation of "ring-current" secondary fields (and, hence, $^1\text{H-NMR}$ chemical shifts).

1. Introduction

Mizoguchi [1] has very recently cast London's theory [2–7] of magnetic susceptibilities of conjugated molecules in terms of the Coulson contour-integral formulation [8] of Hückel molecular-orbital (HMO) theory [9]. As has been

emphasized [7(a),10(a)], the Coulson contour-integral approach [8] was much favoured by its originator but, perhaps because of its rather esoteric nature, has been less generally and less enthusiastically adopted by other authors. Now it has been pointed out in a footnote on page 323 of [7] (and, earlier, elsewhere [10(a)]) that, in a previously unpublished document dated May 16th, 1953 and entitled *Diamagnetic Anisotropy of Aromatics*, the late Professor C.A. Coulson, FRS, formulated the London theory [2–4] in terms of his own contour-integral approach [8]. This document was discovered by one of us (R.B.M.) in 1974 when helping Mrs. Eileen Coulson to sort and evaluate her late husband's scientific papers; it was then deposited in file B38.6 of the Coulson material in the Contemporary Scientific Archives Collection of the Bodleian Library, University of Oxford. Mrs. Coulson very kindly allowed a Xerox copy of this item to be made, before the papers were deposited in the Bodleian. Since then, although the existence of this work has been mentioned by one of us in a thesis [10(a)] and in a review of the "ring-current" effect [7(a)], the document itself has, until now, remained unpublished.

The recent work of Mizoguchi [1] has, however, revived interest in the Coulson contour-integral approach to magnetic susceptibilities in conjugated molecules and, in order to demonstrate Coulson's independent (albeit private) contributions to the development of these ideas, thirty-five years ago, we take the opportunity to publish here his 1953 manuscript in its entirety. As has already been pointed out in the only previous public references to this work [10(a),7(a)], the document also advances an alternative approach, within the framework of the HMO method and the London approximations, for calculating overall magnetic susceptibilities of conjugated molecules. As will be seen, Coulson's treatment is based on bond-bond polarisabilities [11,6] and it therefore provides an interesting parallel to certain aspects of the now-classic [7(b)] McWeeny polarisability method, proposed five years later [6]; the Coulson polarisability formalism, as presented, does not, however, provide for explicit computation of individual "ring-current" intensities, as McWeeny's method [6] and that of Pople [5] do, nor, of course – since it preceded the experimental observations [12,13] – for the direct calculation of "ring-current" secondary fields (and, hence, $^1\text{H-NMR}$ chemical shifts [10,7]).

2. The Coulson manuscript

We now present, *verbatim*, Coulson's hand-written manuscript on the magnetic properties of conjugated molecules in the presence of an external magnetic field. Because of the *historical* nature of this account, we have left it entirely in terms of the unrationalised CGS system of magnetic units which Coulson and other contemporary authors used, and have thus resisted the temptation to modernise the document to make it conform with the so-called *Système International*, which is now becoming more widespread. Accordingly, Coulson here begins his treatment by considering the

secular equations appropriate to the situation in which the planar, conjugated molecule under study is immersed in a constant, external magnetic field \mathbf{H} , of magnitude H , which is assumed to be normal to the plane of the molecule. Having thus set the scene, we now allow Professor Coulson himself to continue the story, by quoting him directly.

Diamagnetic Anisotropy of Aromatics, May 16th, 1953.

According to London [4], the secular equations are now

$$\Delta(\epsilon) \equiv \begin{vmatrix} \alpha_1 - \epsilon & \beta_{12} & \beta_{13} & \dots & \beta_{1n} \\ \beta_{21} & \alpha_2 - \epsilon & \beta_{23} & \dots & \beta_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \beta_{n1} & \beta_{n2} & \beta_{n3} & \dots & \alpha_n - \epsilon \end{vmatrix} = 0, \quad (1)$$

where

$$\beta_{12} = \beta_{12}^0 e^{2\pi i f_{12}}. \quad (2)$$

The exponential arises from gauge invariance, as is shown, *inter alia*, in the second appendix in [14].

Also*,

$$f_{12} = \frac{eH}{hc} S_{12}, \quad (3)$$

where

S_{12} = area of triangle from origin to points 1 and 2, taken in the correct order – i.e., $f_{21} = -f_{12}$.

THEOREM 1

The roots of eq. (1) are independent of the origin of coordinates. Consider, for simplicity, the case of four atoms only.

* (Explanatory note by B.O'L. and R.B.M.): In eq. (3), and throughout, $-e$ ($= -1.60210 \times 10^{-19}$ C, in SI units) is the charge on the electron, h ($= 6.6256 \times 10^{-34}$ Js) is Planck's constant, and c ($= 2.997925 \times 10^8$ ms⁻¹) is the speed of light *in vacuo*.

$$\Delta(\epsilon) \equiv \begin{vmatrix} \alpha_1 - \epsilon & \beta_{12}^\circ e^{2\pi i f_{12}} & \beta_{13}^\circ e^{2\pi i f_{13}} & \beta_{14}^\circ e^{2\pi i f_{14}} \\ \beta_{21}^\circ e^{2\pi i f_{21}} & \alpha_2 - \epsilon & \beta_{23}^\circ e^{2\pi i f_{23}} & \beta_{24}^\circ e^{2\pi i f_{24}} \\ \beta_{31}^\circ e^{2\pi i f_{31}} & \beta_{32}^\circ e^{2\pi i f_{32}} & \alpha_3 - \epsilon & \beta_{34}^\circ e^{2\pi i f_{34}} \\ \beta_{41}^\circ e^{2\pi i f_{41}} & \beta_{42}^\circ e^{2\pi i f_{42}} & \beta_{43}^\circ e^{2\pi i f_{43}} & \alpha_4 - \epsilon \end{vmatrix} \quad (4)$$

Divide column 2 by $e^{2\pi i f_{12}}$ and multiply row 2 by the same. Repeat the process with column and row 3 using $e^{2\pi i f_{13}}$, and column and row 4 using $e^{2\pi i f_{14}}$.

Recognising that $\beta_{ij}^\circ = \beta_{ji}^\circ$, we may write the result of this as:

$$\Delta(\epsilon) \equiv \begin{vmatrix} \alpha_1 - \epsilon & \beta_{12}^\circ & \beta_{13}^\circ & \beta_{14}^\circ \\ \beta_{12}^\circ & \alpha_2 - \epsilon & \beta_{23}^\circ e^{2\pi i(f_{23} - f_{13} + f_{12})} & \beta_{24}^\circ e^{2\pi i(f_{24} - f_{14} + f_{12})} \\ \beta_{13}^\circ & \beta_{23}^\circ e^{2\pi i(-f_{23} - f_{12} + f_{13})} & \alpha_3 - \epsilon & \beta_{34}^\circ e^{2\pi i(f_{34} - f_{14} + f_{13})} \\ \beta_{14}^\circ & \beta_{24}^\circ e^{2\pi i(-f_{24} - f_{12} + f_{14})} & \beta_{34}^\circ e^{2\pi i(-f_{24} - f_{13} + f_{14})} & \alpha_4 - \epsilon \end{vmatrix}$$

$$\equiv \begin{vmatrix} \alpha_1 - \epsilon & \beta_{12}^\circ & \beta_{13}^\circ & \beta_{14}^\circ \\ \beta_{12}^\circ & \alpha_2 - \epsilon & \beta_{23}^\circ e^{2\pi i A_{123}} & \beta_{24}^\circ e^{2\pi i A_{124}} \\ \beta_{13}^\circ & \beta_{23}^\circ e^{-2\pi i A_{123}} & \alpha_3 - \epsilon & \beta_{34}^\circ e^{2\pi i A_{134}} \\ \beta_{14}^\circ & \beta_{24}^\circ e^{-2\pi i A_{124}} & \beta_{34}^\circ e^{-2\pi i A_{134}} & \alpha_4 - \epsilon \end{vmatrix}, \quad (5)$$

where $A_{123} = (eH/hc) \times$ area of the triangle joining points, 1, 2, 3, in that order.

Proof of this latter statement, added by B.O'L. and R.B.M. (cf. pp. 318, 319, eq. (56) and fig. 5 of [7]):

Consider atoms 1, 2 and 3, and the arbitrary origin O , with the cycle traversed in the anticlockwise direction $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$, as defined by the arrows in fig. 1, where the letters K, L, M, N denote the moduli of the area segments indicated. It will be recalled from earlier in Coulson's treatment that S_{ij} is the *signed* (algebraical) area of the triangle formed by the origin and the atoms i and j of the conjugated network, counted positive if $i \rightarrow j$ is right-handed about the upward normal through O , and negative otherwise. Then,

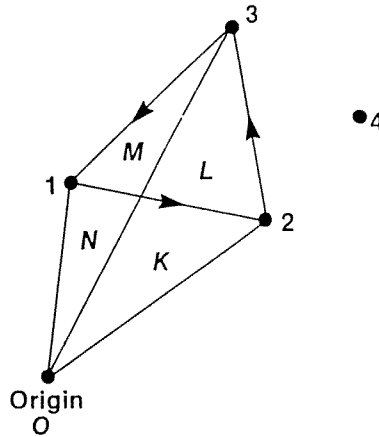


Fig. 1.

$$\begin{aligned}
 S_{12} + S_{23} + S_{31} &= -(N + K) + (K + L) + (M + N) \\
 &= L + M \\
 &= \text{area of triangle joining points 1, 2, 3.}
 \end{aligned}$$

Hence, considering the quantity $f_{12} + f_{23} - f_{13}$ appearing in the exponent of the (2, 3)-element of the first determinant in eq. (5), we have

$$\begin{aligned}
 f_{12} + f_{23} - f_{13} &= f_{12} + f_{23} + f_{31} \\
 &= \frac{eH}{hc} (S_{12} + S_{23} + S_{31}) \\
 &= \frac{eH}{hc} \times \text{area of triangle joining points 1, 2, 3} \\
 &= A_{123} ,
 \end{aligned}$$

as Coulson asserts.

We now return to Coulson's account.

This shows that the origin of coordinates is irrelevant, since it disappears completely from eq. (5) and so the roots do not depend in any way upon it. As a matter of fact, eq. (5) is the form taken by eq. (4) when the origin is supposed to be at atom 1.

INEQUALITY OF β_{12} AND β_{21}

The quantities such as β_{12} are complex; but since Δ is Hermitian, all the roots ϵ are real. If we put

$$\beta_{12} = \beta_{12}^{\circ} + \delta\beta_{12}, \quad (6)$$

then, to square form in H ,

$$\begin{aligned} \delta\beta_{12} &= \beta_{12}^{\circ} \left\{ e^{2\pi i f_{12}} - 1 \right\} \\ &= \beta_{12}^{\circ} \left\{ \frac{2\pi i e H}{hc} S_{12} - \frac{2\pi^2 e^2 H^2}{h^2 c^2} S_{12}^2 \right\} \\ &= \beta_{12}^{\circ} \left\{ 2\pi i f_{12} - 2\pi^2 f_{12}^2 \right\}. \end{aligned} \quad (7)$$

We do not need to go beyond square terms since the susceptibility follows from

$$E(H) = E(0) - \frac{1}{2} \chi H^2. \quad (8)$$

It will be noticed that $\delta\beta_{12} \neq \delta\beta_{21}$. They are merely complex conjugates. This means that although we want to use perturbation expansions, such as those developed by Coulson and Longuet-Higgins [11], we shall have to develop a slightly different technique from that applicable when β_{12} is real and $\delta\beta_{12} = \delta\beta_{21}$.

MODES OF CALCULATION

There are essentially four ways of proceeding:

- (i) *direct solution of the secular determinant*, as in London [3,4];
- (ii) *manipulation of the secular determinant* in a form suitable to each particular symmetry type. This is a line followed by McWeeny (polyphenyls [14] and hexagonal symmetry type [15]) and he uses the contour-integral method.

$$E = \frac{2}{2\pi i} \oint \left\{ \frac{z \Delta'(z)}{\Delta(z)} - n \right\} dz, \quad (9)$$

with $\Delta(z)$ expanded in powers of

$$\theta = \frac{2\pi e}{hc} S;$$

($S = \frac{1}{6}$ area of benzene);

(iii) *expansion of Δ directly*, as in the work of Mayot et al. [16]. These authors write

$$\Delta = \Delta(z, H) = \Delta_0(z) + \omega \Delta_1(z) + \omega^2 \Delta_2(z) + \dots, \quad (10)$$

where

$$\omega = kH, \quad (11)$$

and is therefore proportional to H . k is a convenient constant without significance. Then,

$$E(H) = \frac{2}{2\pi i} \oint \left\{ z \frac{\partial}{\partial z} \ln \Delta - n \right\} dz. \quad (12)$$

(This is eq. (44) of [11].) In (9) and (12), n = number of carbon atoms, and all α 's are supposed equal (to zero). We suppose now that all orbitals are doubly filled. (Odd electrons can be treated separately.) Thus,

$$\begin{aligned} E(H) - E(0) &= \frac{2}{2\pi i} \oint z \frac{\partial}{\partial z} \ln \left(\frac{\Delta}{\Delta_0} \right) dz \\ &= \frac{2}{2\pi i} \oint z \frac{\partial}{\partial z} \ln \left\{ 1 + \omega \frac{\Delta_1}{\Delta_0} + \omega^2 \frac{\Delta_2}{\Delta_0} + \dots \right\} dz \\ &= \frac{2}{2\pi i} \oint z \frac{\partial}{\partial z} \left\{ \omega \frac{\Delta_1}{\Delta_0} + \omega^2 \left(\frac{\Delta_2}{\Delta_0} - \frac{\Delta_1^2}{2\Delta_0^2} \right) \dots \right\} dz. \quad (13) \end{aligned}$$

Now changing the sign of H is equivalent simply to interchanging rows and columns in eq. (1) and hence Δ is unaltered. Therefore, $\Delta(z, H)$ is an even function of H . Hence,

$$\Delta_1(z) \equiv 0. \quad (14)$$

This means that we can write

$$\begin{aligned} E(H) - E(0) &= \frac{2}{2\pi i} \oint z \frac{\partial}{\partial z} \left\{ \omega^2 \frac{\Delta_2}{\Delta_0} \dots \right\} dz \\ E(H) &= E(0) + \frac{2\omega^2}{2\pi i} \oint z \frac{\partial}{\partial z} \left(\frac{\Delta_2}{\Delta_0} \right) dz + \text{higher powers of } H. \end{aligned}$$

Hence,

$$\chi = - \frac{4k^2}{2\pi i} \oint z \frac{d}{dz} \left(\frac{\Delta_2}{\Delta_0} \right) dz . \tag{15}$$

That is,

$$\begin{aligned} \chi &= - \frac{4k^2}{2\pi i} \left[\frac{z \Delta_2(z)}{\Delta_0(z)} \right]_{\text{round contour}} + \frac{4k^2}{2\pi i} \oint \frac{\Delta_2(z)}{\Delta_0(z)} dz \\ &= 0 + \frac{4k^2}{2\pi} \int_{-\infty}^{+\infty} \frac{\Delta_2(iy)}{\Delta_0(iy)} dy . \end{aligned} \tag{16}$$

The above equation is effectively expression (9) of [16]. It could, of course, also be obtained from the alternative expansion of the energy given in eq. (44) of [11] :

$$\begin{aligned} E(H) - E(0) &= \frac{1}{\pi} \int_{-\infty}^{+\infty} \left\{ \left(iy \frac{\Delta'}{\Delta} - n \right) - \left(iy \frac{\Delta'_0}{\Delta_0} - n \right) \right\} dy \\ &= \frac{1}{\pi} \int_{-\infty}^{+\infty} iy \left(\frac{\Delta'_0 + \omega^2 \Delta'_2 \dots}{\Delta_0 + \omega^2 \Delta_2 \dots} - \frac{\Delta'_0}{\Delta_0} \right) dy \\ &= \frac{1}{\pi} \int_{-\infty}^{+\infty} iy \left(\frac{\omega^2 \Delta_0 \Delta'_2 - \omega^2 \Delta_2 \Delta'_0 \dots}{\Delta_0^2 + \omega^2 \Delta_0 \Delta_2 \dots} \right) dy \\ E(H) - E(0) &= \frac{\omega^2}{\pi} \int_{-\infty}^{+\infty} iy \frac{\Delta_0 \Delta'_2 - \Delta_2 \Delta'_0}{\Delta_0^2} dy + \text{higher powers of } H. \\ \chi &= - \frac{2k^2}{\pi} \int_{-\infty}^{+\infty} iy \frac{\Delta_0 \Delta'_2 - \Delta_2 \Delta'_0}{\Delta_0^2} dy \\ &= - \frac{2k^2}{\pi} \int_{-\infty}^{+\infty} iy \frac{d}{idy} \left(\frac{\Delta_2}{\Delta_0} \right) dy \\ &= \frac{2k^2}{\pi} \int_{-\infty}^{+\infty} \frac{\Delta_2(iy)}{\Delta_0(iy)} dy , \end{aligned} \tag{17}$$

which is just eq. (16) again. Neither of these proofs is the same as that used by Mayot et al. [16], who worked from eq. (10):

$$\begin{aligned} \Delta &= \Delta(z, H) = \Delta_0(z) + \omega \Delta_1(z) + \omega^2 \Delta_2(z) + \dots \\ &= \Delta_0(z) + \omega^2 \Delta_2(z) + \dots \text{ since } \Delta_1(z) \equiv 0. \end{aligned}$$

This means that the roots are

$$z_i(H) = z_i(0) - \frac{\omega^2 \Delta_2(z_i)}{\Delta'_0(z_i)} + \dots \quad (18)$$

Whence,

$$\epsilon_i(H) - \epsilon_i(0) = - \frac{\omega^2 \Delta_2(\epsilon_i)}{\Delta'_0(\epsilon_i)} \quad (19)$$

So,

$$\begin{aligned} E(H) - E(0) &= -2\omega^2 \sum_{\text{occupied}} \frac{\Delta_2(\epsilon_i)}{\Delta'_0(\epsilon_i)} \\ &= - \frac{2\omega^2}{2\pi i} \oint \frac{\Delta_2(z)}{\Delta_0(z)} dz, \end{aligned}$$

which is merely eq. (16) all over again. The major objection to this is that it requires an explicit expansion of Δ in powers of H . And, except when there is symmetry, this is not a very easy matter to obtain. For this reason we put forward method (iv):

(iv) *The new method*

Let us work in terms of the $\delta\beta_{rs}$ defined in eqs. (6) and (7). Then,

$$\begin{aligned} \delta E &= \sum_{\text{bonds}} \left[\frac{\partial E}{\partial \beta_{rs}} \delta\beta_{rs} + \frac{\partial E}{\partial \beta_{sr}} \delta\beta_{sr} \right] \\ &+ \frac{1}{2} \sum_{\text{bonds}} \left[\frac{\partial^2 E}{\partial \beta_{rs}^2} (\delta\beta_{rs})^2 + 2 \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{sr}} \delta\beta_{rs} \delta\beta_{sr} + \frac{\partial^2 E}{\partial \beta_{sr}^2} (\delta\beta_{sr})^2 \right]. \end{aligned}$$

$$\begin{aligned}
 & + \sum_{\text{adjacent bonds}} \left[\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} \delta \beta_{rs} \delta \beta_{st} + \frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{st}} \delta \beta_{sr} \delta \beta_{st} \right. \\
 & \quad \left. + \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ts}} \delta \beta_{rs} \delta \beta_{ts} + \frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{ts}} \delta \beta_{sr} \delta \beta_{ts} \right] \\
 & + \sum_{\text{non-contiguous bonds}} \left[\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}} \delta \beta_{rs} \delta \beta_{tu} + \frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{tu}} \delta \beta_{sr} \delta \beta_{tu} \dots + \dots \right] \\
 & + \text{higher powers of the } \delta \beta. \tag{20}
 \end{aligned}$$

In this expansion, it has been assumed that there are no triangles of bonds. This is a trivial restriction and we could easily add an appropriate extra term if there were such.

Before we can go further, we need expressions for

$$\frac{\partial E}{\partial \beta_{rs}}, \quad \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} \quad \text{and} \quad \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}}.$$

These will necessarily be different from the corresponding expressions in [11], though, when all the β 's are real, so that $\beta_{rs} = \beta_{sr}$, we should have simple relations between them all. Our analysis here follows closely the analysis in [11].

Thus, let ϵ be a root of $\Delta(\epsilon, \beta_{rs}) = 0$. Then,

$$\left(\frac{\partial E}{\partial \beta_{rs}} \right)_{\Delta=0} = - \left(\frac{\partial \Delta}{\partial \beta_{rs}} \right) / \left(\frac{\partial \Delta}{\partial \epsilon} \right) = (-1)^{r+s+1} \left(\frac{\Delta_{r,s}}{\Delta'} \right), \tag{21}$$

where we must now be careful to distinguish* $\Delta_{r,s}$ and $\Delta_{s,r}$. These are complex conjugates of each other. It will be noticed that a factor of 2 is missing in eq. (21) as compared with eq. (32) of [11]. This is to be expected, since, in the latter, we are really concerned with

*Explanatory note by B.O'L. and R.B.M: $\Delta_{r,s}$ means the determinant Δ with the r th row and the s th column deleted.

$$\frac{\partial E}{\partial \beta_{rs}} + \frac{\partial E}{\partial \beta_{sr}}$$

and then we put $\beta_{rs} = \beta_{sr}$ so that $\Delta_{r,s} = \Delta_{s,r}$.

By addition of the set of relations (21) we have:

$$\frac{\partial E}{\partial \beta_{rs}} = (-1)^{r+s+1} 2 \sum_{\substack{\text{occupied} \\ \text{roots}}} \frac{\Delta_{r,s}}{\Delta'} \tag{22}$$

$$= \frac{2(-1)^{r+s+1}}{2\pi i} \oint \frac{\Delta_{r,s}(z)}{\Delta(z)} dz . \tag{23}$$

When we put all the β_{rs} real in this latter integral, as is required when we substitute into eq. (20), we see, from eq. (35) of [11], that

$$\left(\frac{\partial E}{\partial \beta_{rs}} \right)_{H=0} = p_{rs} . \tag{24}$$

But when dealing with second-order derivatives we must not put $H = 0$ until the end; so we must proceed from eq. (23):

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{rs}^2} &= \frac{2(-1)^{r+s+1}}{2\pi i} \oint \frac{\Delta_{r,s}(z)}{\Delta^2(z)} (-1)^{r+s+1} \Delta_{r,s}(z) dz \\ &= \frac{2}{2\pi i} \oint \left(\frac{\Delta_{r,s}}{\Delta} \right)^2 dz . \end{aligned} \tag{25}$$

When we put $H = 0$, and compare with eq. (57) of [11], this gives

$$\left(\frac{\partial^2 E}{\partial \beta_{rs}^2} \right)_{H=0} = \pi_{r,s} = \left(\frac{\partial^2 E}{\partial \beta_{sr}^2} \right)_{H=0} \tag{26}$$

by symmetry

Similarly*,

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{sr}} &= \frac{2(-1)^{r+s+1}}{2\pi i} \oint \left(\frac{\Delta_{rs,rs}(-1)^{r+s-1}}{\Delta} - \frac{\Delta_{r,s} \Delta_{s,r}(-1)^{r+s}}{\Delta^2} \right) dz \\ &= \frac{2}{2\pi i} \oint \left(\frac{\Delta_{rs,rs}}{\Delta} + \frac{\Delta_{r,s} \Delta_{s,r}}{\Delta^2} \right) dz \\ &= \frac{2}{2\pi i} \oint \frac{\Delta_{r,r} \Delta_{s,s}}{\Delta^2} dz, \end{aligned} \tag{27}$$

or, using Jacobi relations (see eq. (56) of [11]):

$$\Delta \cdot \Delta_{rs,rs} = \Delta_{r,r} \Delta_{s,s} - \Delta_{r,s} \Delta_{s,r}.$$

We can verify that eqs. (27) and (25) fit, for, on putting $H = 0$, we get:

$$\begin{aligned} \left(\frac{\partial^2 E}{\partial \beta_{rs}^2} + \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{sr}} \right)_{H=0} &= \frac{2}{2\pi i} \oint \frac{\Delta_{r,s}^2 + \Delta_{r,r} \Delta_{s,s}}{\Delta^2} dz \\ &= \pi_{r,s,rs} \text{ by eq. (63) of [11].} \end{aligned} \tag{28}$$

This is just what should have been expected. Hence,

$$\left(\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{sr}} \right)_{H=0} = \pi_{r,s,rs} - \pi_{r,s}. \tag{29}$$

Further,

$$\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} = \frac{2(-1)^{r+s+1}}{2\pi i} \oint \left(\frac{\Delta_{rs,st}(-1)^{s+t}}{\Delta} - \frac{\Delta_{r,s} \Delta_{s,t}(-1)^{s+t}}{\Delta^2} \right) dz, \tag{30}$$

and it is supposed, for convenience, that $r < s < t$. Hence,

* Explanatory note by B.O'L. and R.B.M.: $\Delta_{rs,tu}$ means that the rows r and s , together with the columns t and u , have been removed from the determinant Δ . It is also supposed, where necessary in this notation, that $r < s$, $t < u$ [11].

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} &= \frac{2(-1)^{r+t+1}}{2\pi i} \oint \frac{\Delta \cdot \Delta_{rs, st} - \Delta_{r,s} \Delta_{s,t}}{\Delta^2} dz \\ &= \frac{2(-1)^{r+t}}{2\pi i} \oint \frac{\Delta_{r,t} \Delta_{s,s}}{\Delta^2} dz, \end{aligned} \tag{31}$$

or, using the Jacobi relation given in eq. (56) of [11], with the form

$$\Delta \cdot \Delta_{rs, st} = \Delta_{r,s} \Delta_{s,t} - \Delta_{r,t} \Delta_{s,s}. \tag{32}$$

We can put this in the form

$$\left(\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} \right)_{H=0} = \pi_{rs, st} - \pi_{rt, s} \tag{33}$$

since, from eq. (61) of [11], we have

$$\pi_{rs, st} = (-1)^{r+t} \frac{2}{2\pi i} \oint \frac{\Delta_{r,t} \Delta_{s,s} + \Delta_{r,s} \Delta_{s,t}}{\Delta^2} dz \tag{34}$$

and, from eq. (59) of [11],

$$\pi_{rt, s} = (-1)^{r+t} \frac{2}{2\pi i} \oint \frac{\Delta_{r,s} \Delta_{t,s}}{\Delta^2} dz \tag{35}$$

and

$$\Delta_{t,s} = \Delta_{s,t} \text{ when } H = 0.$$

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{st}} &= \frac{\partial}{\partial \beta_{st}} \left\{ \frac{2(-1)^{r+s+1}}{2\pi i} \oint \frac{\partial}{\partial \beta_{st}} \left(\frac{\Delta_{s,r}}{\Delta} \right) dz \right\} \\ &= \frac{2(-1)^{r+s+1}}{2\pi i} \oint -\frac{\Delta_{s,r}}{\Delta^2} (-1)^{s+t} \Delta_{s,t} dz \\ &= \frac{2(-1)^{r+t}}{2\pi i} \oint \frac{\Delta_{s,r} \Delta_{s,t}}{\Delta^2} dz; \end{aligned} \tag{36}$$

$$\left(\frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{st}} \right)_{H=0} = \pi_{rt,s}, \text{ from eq. (59) of [11].} \tag{37}$$

And

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ts}} &= \frac{2(-1)^{r+s+1}}{2\pi i} \oint - \frac{\Delta_{r,s}(-1)^{t+s}}{\Delta^2} \Delta_{t,s} dz \\ &= \frac{2(-1)^{r+t}}{2\pi i} \oint \frac{\Delta_{r,s} \Delta_{t,s}}{\Delta^2} dz \\ &= \pi_{rt,s}, \text{ as before.} \end{aligned} \tag{38}$$

And

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{ts}} &= \frac{\partial}{\partial \beta_{ts}} \left\{ \frac{2(-1)^{r+s+1}}{2\pi i} \oint \frac{\Delta_{s,r}}{\Delta} dz \right\} \\ &= \frac{2(-1)^{r+s+1}}{2\pi i} \oint \left(\frac{\Delta_{st,sr}(-1)^{t+s+1}}{\Delta} - \frac{\Delta_{s,r} \Delta_{s,t}(-1)^{s+t}}{\Delta^2} \right) dz \\ &= \frac{2(-1)^{r+t}}{2\pi i} \oint \frac{\Delta \cdot \Delta_{st,sr} + \Delta_{s,r} \Delta_{s,t}}{\Delta^2} dz. \end{aligned} \tag{39}$$

But,

$$\Delta \cdot \Delta_{st,sr} = \Delta_{s,s} \Delta_{t,r} - \Delta_{s,r} \Delta_{t,s}, \tag{40}$$

so that

$$\left(\frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{ts}} \right)_{H=0} = \frac{2(-1)^{r+t}}{2\pi i} \oint \frac{\Delta_{s,s} \Delta_{t,r}}{\Delta^2} dz \tag{41}$$

$$= \pi_{rs,st} - \pi_{rt,s} \tag{42}$$

$$= \left(\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} \right)_{H=0}, \text{ as in eq. (33).} \tag{43}$$

On the whole, we should expect that this latter equality would hold. Also that

$$\left(\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{st}} + \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ts}} \right)_{H=0} = \pi_{rs,st} - \pi_{rt,s} + \pi_{rt,s} = \pi_{rs,st}, \quad (44)$$

which is eminently reasonable, since the left-hand side of eq. (44) may be written as:

$$\begin{aligned} \left(\frac{\partial}{\partial \beta_{st}} + \frac{\partial}{\partial \beta_{ts}} \right) \frac{\partial E}{\partial \beta_{rs}} &= \left(\frac{\partial}{\partial \beta_{st}} + \frac{\partial}{\partial \beta_{ts}} \right) p_{rs} \\ &= \pi_{rs,st} \quad \text{when } H = 0. \end{aligned} \quad (45)$$

Lastly,

$$\begin{aligned} \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}} &= \frac{2(-1)^{r+s+1}}{2\pi i} \oint \left(\frac{(-1)^{t+u} \Delta_{rt,su}}{\Delta} - \frac{\Delta_{r,s} (-1)^{t+u} \Delta_{t,u}}{\Delta^2} \right) dz \\ &\quad \text{in the case where } r < t, s < u, \\ &= \frac{2(-1)^{r+s+t+u+1}}{2\pi i} \oint \frac{\Delta \cdot \Delta_{rt,su} - \Delta_{r,s} \Delta_{t,u}}{\Delta^2} dz \\ &= \frac{2(-1)^{r+s+t+u}}{2\pi i} \oint \frac{\Delta_{r,u} \Delta_{s,t}}{\Delta^2} dz. \end{aligned} \quad (46)$$

This does not go too well, since by itself it is not expressible in terms of the various functions (polarisabilities) used in [11]. But it will probably help to combine it with $\partial^2 E / \partial \beta_{rs} \partial \beta_{ut}$.

$$\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ut}} = \frac{2(-1)^{r+s+t+u}}{2\pi i} \oint \frac{\Delta_{r,t} \Delta_{s,u}}{\Delta^2} dz, \quad (47)$$

in the case where $r < u, s < t$.

Whence,

$$\left(\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}} + \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ut}} \right)_{H=0} = \pi_{rs,tu}, \quad \text{from eq. (61) of [11].} \quad (48)$$

Also,

$$\frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}} = \frac{\partial^2 E}{\partial \beta_{sr} \partial \beta_{ut}} \Bigg)_{\text{all at } H=0}, \quad \text{from eq. (46).} \quad (49)$$

Combining all these various bits:

$$\begin{aligned} \delta E = & \sum_{\text{bonds}} p_{rs} (\delta \beta_{rs} + \delta \beta_{sr}) \\ & + \frac{1}{2} \sum_{\text{bonds}} \pi_{r,s} ((\delta \beta_{rs})^2 + (\delta \beta_{sr})^2) + \sum_{\text{bonds}} (\pi_{rs,rs} - \pi_{r,s}) \delta \beta_{rs} \delta \beta_{sr} \\ & + \sum_{\substack{\text{adjacent bonds} \\ rs, st}} (\pi_{rs, st} - \pi_{rt, s}) (\delta \beta_{rs} \delta \beta_{st} + \delta \beta_{sr} \delta \beta_{ts}) \\ & + \sum_{\substack{\text{adjacent bonds} \\ rs, st}} \pi_{rt, s} (\delta \beta_{sr} \delta \beta_{st} + \delta \beta_{rs} \delta \beta_{ts}) \\ & + \sum_{\substack{\text{pairs of non-contiguous} \\ \text{bonds } rs, tu}} \left[2 \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}} \delta \beta_{rs} \delta \beta_{tu} + 2 \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ut}} \delta \beta_{rs} \delta \beta_{ut} \right] \\ & + \dots \end{aligned} \quad (50)$$

So, to terms of square degree in H :

$$\begin{aligned} \delta E = & \sum_{\text{bonds}} p_{rs} \beta_{rs}^{\circ} (-4\pi^2 f_{rs}^2) + \frac{1}{2} \sum_{\text{bonds}} 2\pi_{r,s} (\beta_{rs}^{\circ})^2 (-4\pi^2 f_{rs}^2) \\ & + \sum_{\text{bonds}} (\pi_{rs,rs} - \pi_{r,s}) 4\pi^2 f_{rs}^2 (\beta_{rs}^{\circ})^2 \\ & + \sum_{\substack{\text{adjacent bonds} \\ rs, st}} (\pi_{rs, st} - \pi_{rt, s}) (-8\pi^2 \beta_{rs}^{\circ} \beta_{st}^{\circ} f_{rs} f_{st}) \\ & + \sum_{\substack{\text{adjacent bonds} \\ rs, st}} \pi_{rt, s} (8\pi^2 \beta_{rs}^{\circ} \beta_{st}^{\circ} f_{rs} f_{st}) \\ & + \sum_{\substack{\text{pairs of bonds} \\ rs, tu \\ \text{with no common} \\ \text{atoms}}} 2(-4\pi^2 \beta_{rs}^{\circ} \beta_{tu}^{\circ} f_{rs} f_{tu}) \left\{ \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{tu}} - \frac{\partial^2 E}{\partial \beta_{rs} \partial \beta_{ut}} \right\}. \end{aligned} \quad (51)$$

In eq. (51), the contents of the curly brackets may, from eqs. (46) and (47), be written as

$$\frac{2(-1)^{r+s+t+u}}{2\pi i} \oint \frac{\Delta_{r,u}\Delta_{s,t} - \Delta_{r,t}\Delta_{s,u}}{\Delta^2} dz,$$

which, from eq. (56) of [11], is

$$\frac{2(-1)^{r+s+t+u+1}}{2\pi i} \oint \frac{\Delta_{rs,tu}}{\Delta} dz.$$

Whence, from the above*, with eqs. (8) and (3):

$$\begin{aligned} 2 \frac{h^2 c^2}{e^2} \chi &= \sum_{\text{bonds}} 4\pi^2 p_{rs} \beta_{rs} S_{rs}^2 + \sum_{\text{bonds}} 4\pi^2 \beta_{rs}^2 \pi_{r,s} S_{rs}^2 \\ &+ \sum_{\text{bonds}} 4\pi^2 \beta_{rs}^2 S_{rs}^2 (\pi_{r,s} - \pi_{rs,rs}) \\ &+ \sum_{\text{adjacent bonds}} 8\pi^2 \beta_{rs} \beta_{st} (\underbrace{\pi_{rs,st} - \pi_{rt,s}}_{=0}) S_{rs} S_{st} - 8\pi^2 \beta_{rs} \beta_{st} S_{rs} S_{st} \underbrace{\pi_{rt,s}}_{=0} \\ &+ \sum_{\substack{\text{pairs of non-} \\ \text{adjacent bonds} \\ rs, tu}} 8\pi^2 \beta_{rs} \beta_{tu} S_{rs} S_{tu} \pi_{rs}^{tu}, \end{aligned} \tag{52}$$

where

$$\pi_{rs}^{tu} \equiv \frac{2(-1)^{r+s+t+u+1}}{2\pi i} \oint \frac{\Delta_{rs,tu}}{\Delta} dz. \tag{53}$$

In the case of alternant hydrocarbons:

$$\begin{aligned} \frac{2h^2 c^2}{4\pi^2 e^2} \chi &= \sum_{\text{bonds}} \left\{ p_{rs} \beta_{rs} S_{rs}^2 + \pi_{r,s} \beta_{rs}^2 S_{rs}^2 + (\pi_{r,s} - \pi_{rs,rs}) \beta_{rs}^2 S_{rs}^2 \right\} \\ &+ \sum_{\text{adjacent bonds}} 2\beta_{rs} \beta_{st} \pi_{rs,st} S_{rs} S_{st} + \sum_{\text{non-adjacent bonds}} 2\beta_{rs} \beta_{tu} S_{rs} S_{tu} \pi_{rs}^{tu}, \end{aligned} \tag{54}$$

*In the derivation that follows, Coulson noted that $\pi_{rt,s} = \partial p_{rt} / \partial \alpha_s$ is zero for pairs of adjacent bonds rs and st .

$$\begin{aligned}
&= \sum_{\text{bonds}} \left\{ p_{rs} \beta_{rs} + (2\pi_{r,s} - \pi_{rs,rs}) \beta_{rs}^2 \right\} S_{rs}^2 \\
&+ \sum_{\substack{\text{adjacent} \\ \text{bonds}}} 2\beta_{rs} \beta_{st} \pi_{rs,st} S_{rs} S_{st} + \sum_{\substack{\text{non-adjacent} \\ \text{bonds}}} 2\beta_{rs} \beta_{tu} S_{rs} S_{tu} \pi_{rs}^{tu} . \quad (55)
\end{aligned}$$

As an afterthought in these notes, Coulson roughly outlined an alternative route to eq. (55) which, in some ways, he considered simpler as a method. However, he found this approach somewhat unsatisfactory in view of the non-vanishing of the majority of the terms involved and the need to evaluate too many integrals. Accordingly, his definitive treatment is the one presented here.

3. Conclusion and comparison with recent work

In conclusion, it might be useful if we were to set Coulson's 1953 contributions in the context of subsequent and, in particular, modern developments. The connection between Coulson's work and that of McWeeny [6] was outlined in section 1. Here, we note that, in the treatment that we have presented in this paper, Coulson concentrates on summations over *bonds* – *not* over *circuits* or *rings*, as McWeeny [6,7(b),17,18] and Mizoguchi [1] do. The latter author, expanding on his previous work [19–21], takes [1] the established formula (eq. (13) of ref. [17]) for the bond current that arises in McWeeny's method and writes the quantities (bond orders and imaginary bond-bond polarisabilities*) on the right-hand side of this equation in the language of the Coulson contour-integral formalism [8]; he does this *via* polynomial expressions (obtained earlier in his paper [1]) for (a) the sum of the bond order of a given bond and the imaginary self bond-bond polarisability* for that bond, and (b) the mutual, imaginary bond-bond polarisability* for two distinct bonds. By these means, Mizoguchi shows [1] that what he calls the "driving force" for the current in a particular bond is the presence of the several *circuits* that contain that bond. (In this sense, Mizoguchi's method has echoes of previous approaches invoking the idea of 'conjugation circuits' [22–31].) In his treatment [1], Mizoguchi also investigates the dependence of imaginary bond-bond polarisabilities on molecular topology and presents certain connections and relations amongst imaginary bond-bond polarisabilities and bond orders, similar to some independently arrived at by one of the present authors and Haigh [10(b),32]. It was the work of Pople [5], and McWeeny's unitary transformation of 1958 [6,7(b),17,18,33], that explicitly intro-

*Imaginary bond-bond polarisability is explicitly defined in the Appendix (pp. 446,447) of ref. [18]. Its relation to the real bond-bond polarisability (defined by Coulson and Longuet-Higgins [11]) is discussed in detail on p. 314 of ref. [6] and on p. 322 of ref. [7].

duced the chemically intuitive idea of individual 'rings' into London's Gauge-Invariant LCAO-MO method [2–4], and it is not surprising, therefore, that Coulson's 1953 manuscript reported here deals solely with summations over *bonds*; it is, however, important to end this account by emphasizing that the formalisms of London [2–4], Pople [5], McWeeny [6,7(b),17,18] and Mizoguchi [1] – as well as Coulson's approach, detailed here – will all give *entirely equivalent numerical results* when applied, as is the custom, to evaluate the *ratio* of the London ("ring-current") magnetic-susceptibility of a given conjugated molecule to the corresponding quantity calculated, by the same method, for benzene. This is because *all* these methods (a) are based on a simple HMO wave function, (b) invoke the so-called 'London Approximations' [7(b)], and (c) make the same assumptions about molecular geometry.

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