The Calculation of Resonance and Localisation Energies in Aromatic Molecules.

By C. A. Coulson.

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A simple method is described whereby the π-electron resonance energy of an aromatic or conjugated molecule, and the localisation energies required in the discussion of chemical reactivity, may be obtained by means of one single numerical integration, without the need for explicit calculation of any of the energies of the separate molecular orbitals. The overlap integral may be included in these calculations.

It is often desired to calculate the resonance energy, or one of the possible localisation energies, for the π-electrons in an aromatic or conjugated molecule. For example, Coulson, Moser, and Barnett (preceding paper) required the para-localisation energy for various possible positions of reaction between maleic anhydride and Clar's six-ringed polynuclear hydrocarbon 1 : 13 : 12-6 : 16 : 7-dibenzonaphthacene (zethrene). One way of making all these calculations is by direct solution of the appropriate secular determinants to give the energies of all the allowed molecular orbitals. But this is tedious, and may be avoided in the following manner. First, let us consider alternant hydrocarbons, since these are at present by far the best understood.

If we make the usual assumptions of simple molecular-orbital theory, that (i) all Coulomb terms have the same value α, (ii) all resonance integrals between neighbours have the same value β, (iii) all other resonance integrals are zero, and (iv) all overlap integrals between adjacent atomic orbitals have the same value S, and all other overlap integrals are zero, then, as Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025) and others have shown, the energies of the allowed molecular orbitals take the form

$$\varepsilon_j = \alpha + m_j\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$\gamma = \beta - \alpha S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and m_j, which varies from one level to another, is related to the corresponding energy $(\alpha + k_j\beta)$ obtained with neglect of overlap, by the equation

$$m_j = k_j/(1 + k_jS) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is convenient to measure energy from a zero corresponding to $\varepsilon = \alpha$. This means that the term α in (1) may be omitted, so that $\varepsilon_j = m_j\gamma$.

The ε_j are found as roots of the secular determinant, and $z = k_j\beta$ is a root of the equation

$$\Delta(z) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\Delta(\varepsilon)$ is the familiar secular determinant without overlap integrals. In general β and γ are both negative, and all the levels for which $k_j > 0$ (and therefore also $m_j > 0$) are doubly filled. Those for which $k_j < 0$ are empty. There may or may not be certain zero-energy orbitals, and these may have 0, 1, or 2 electrons in them. But their presence makes no difference to the total π-electron energy E which, by the method introduced by the author (*Proc. Camb. Phil. Soc.*, 1940, **36**, 201), may be expressed as a contour integral :

$$E = \frac{\gamma}{\pi i}\oint\frac{z}{\beta + Sz}\,\frac{\Delta'(z)}{\Delta(z)}\,\mathrm{d}z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In this integral, which is valid for the case where $S = 0$ as well as $S \neq 0$, Δ' denotes $\mathrm{d}\Delta/\mathrm{d}z$ and the contour consists of the complete imaginary axis and the infinite semicircle to its left. For an alternant hydrocarbon $\Delta'(z)/\Delta(z)$ is an odd function of z so that, as de Heer (*Phil. Mag.*, 1950, **41**, 370) shows, (5) may be written as

$$E = \frac{\beta\gamma}{\pi i}\oint \frac{z}{\beta^2 - S^2z^2}\,\frac{\Delta'(z)}{\Delta(z)}\,\mathrm{d}z = \frac{\beta\gamma}{\pi i}\oint \frac{z}{\beta^2 - S^2z^2}\,\frac{\mathrm{d}}{\mathrm{d}z}\log\Delta(z)\,\mathrm{d}z \quad . \quad . \quad . \quad (6)$$

Now let Δ_{Kek} stand for the secular determinant appropriate to a single Kekulé structure, and E_{Kek} the corresponding energy. Then $E - E_{\mathrm{Kek}}$ is merely the resonance energy R. So

$$R = E - E_{\mathrm{Kek}} = \frac{\beta\gamma}{\pi i}\oint \frac{z}{\beta^2 - S^2z^2}\,\frac{\mathrm{d}}{\mathrm{d}z}\log\left(\frac{\Delta}{\Delta_{\mathrm{Kek}}}\right)\mathrm{d}z$$

Integration by parts, and the fact that, at large z, $\Delta/\Delta_{\mathrm{Kek}} \longrightarrow 1$ allows this to be written (cf. Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188)

$$R = -\frac{\beta\gamma}{\pi i}\oint \frac{\beta^2 + S^2z^2}{(\beta^2 - S^2z^2)^2}\log\left(\frac{\Delta}{\Delta_{\mathrm{Kek}}}\right)\mathrm{d}z \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This shows, as was noticed by de Heer, that the overlap integral exerts only a minor influence on the energies, since it appears only in the first factor under the integral, and occurs only as S^2 and higher powers. With $S \approx 0{\cdot}25$, these additional terms would be expected to be small.

The integration in (7) is straightforward, but must be done numerically. The contribution from the infinite semicircle vanishes so that it may be written

$$R = -\frac{\beta\gamma}{\pi}\int_{-\infty}^{\infty} \frac{\beta^2 - S^2y^2}{(\beta^2 + S^2y^2)^2}\log\left(\frac{\Delta(iy)}{\Delta_{\mathrm{Kek}}(iy)}\right)\mathrm{d}y \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Numerical integration in the range $0 \leqslant |y/\beta| < 6$ and an estimate of the contribution from $|y/\beta| > 6$ in the same manner as used by Coulson and Jacobs (*J.*, 1949, 2805) usually provides a resonance energy of sufficient accuracy. But on account of the first factor in the integrand, the estimation of the contribution from $|y/\beta| > 6$ is not quite so simple as when $S = 0$. If there are n double bonds in the molecule, then $\Delta_{\mathrm{Kek}}(z) = (z^2 - \beta^2)^n$. Also we may use the expansion of $\Delta(z)$ obtained by the author (*Proc. Camb. Phil. Soc.*, 1949, **43**, 202), *viz.* :

$$\Delta(z) = z^{2n} - C_2\beta^2z^{2n-2} + C_4\beta^4z^{2n-4} - \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where C_2 = number of carbon–carbon bonds in the molecule, and C_4 = total number of pairs of non-contiguous bonds, etc. This means that

$$\log\left(\frac{\Delta(iy)}{\Delta_{\mathrm{Kek}}(iy)}\right) = \frac{C_2 - n}{(y/\beta)^2} + \frac{2C_4 - C_2{}^2 + n}{2(y/\beta)^4} + \ldots \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and the method of Coulson and Jacobs (*loc. cit.*) will apply.

It is possible, however, to reduce the contribution from $|y/\beta| > 6$ to negligible proportions as follows. In writing down Δ_{Kek}, let us suppose that the resonance integral is not β, but $x\beta$, where x is some constant to be chosen later. The corresponding overlap integral must be xS instead of S. No such modifications, however, are made in Δ. The form taken by (8) is now

$$R = \frac{\gamma}{\pi}\int_{-\infty}^{\infty} \frac{1 - S^2t^2}{(1 + S^2t^2)^2}\log\frac{\Delta(it)}{(t^2 + x^2)^n}\,\mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where we have introduced the dimensionless variable $t = y/\beta$. The expansion similar to (10) gives

$$\log\frac{\Delta(it)}{(t^2 + x^2)^n} = \frac{C_2 - nx^2}{t^2} + \frac{2C_4 - C_2{}^2 + nx^4}{2t^4} + \ldots \quad . \quad . \quad . \quad . \quad (12)$$

If we now choose x so that

$$C_2 - nx^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

then (12) simplifies to

$$\log\frac{\Delta(it)}{(t^2+x^2)^n} = \frac{2C_4 - C_2^2 + C_2^2/n}{2t^4} + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Explicit calculation for a variety of systems shows that the error resulting from complete neglect of that part of the integral in (11) which arises from $|t| > 6$ is less than $0{\cdot}01\gamma$. With this choice (13) for x, the energy of a Kekulé structure is

$$E_{\text{Kek}} = 2 \times \frac{nx\gamma}{1+Sx} = \frac{2\sqrt{(nC_2)}}{1+Sx}\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus the total energy of the π-electrons in the original molecule is

$$E = \frac{2\sqrt{(nC_2)}\gamma}{1+Sx} + \frac{2\gamma}{\pi}\int_0^\infty \frac{1-S^2t^2}{(1+S^2t^2)^2}\log\frac{\Delta(it)}{(t^2+x^2)^n}\,\mathrm{d}t \quad . \quad . \quad . \quad (16)$$

where $x^2 = C_2/n$ and the effective range of integration is only $0 < t < 6$. Numerical integration presents no difficulties.

FIG. 1.

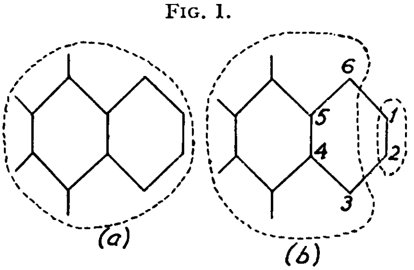
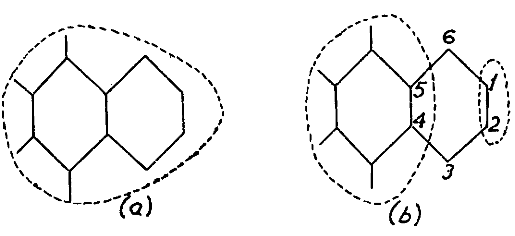


FIG. 2.



We have given this analysis in full. But our remaining applications of the method can be greatly abbreviated since they follow essentially the same basic idea.

Bond Localisation Energies.—The bond localisation energy (R. D. Brown, *Quart. Reviews*, 1952, **6**, 63) is defined as the energy necessary to localise a pair of π-electrons in a particular bond, which is supposed to be isolated from the rest of the resonating framework. Thus, in Fig. 1, the bond-localisation energy $E_{\text{bond loc.}}$ for the bond 1—2 is the difference in π-electron energies of the two systems shown as (*a*) and (*b*); in each case π-electrons are mobile within, but not across, the dotted lines. We are effectively comparing E for two systems. In the first system we take β as resonance integral for all the bonds: in the second we put $\beta_{16} = \beta_{23} = 0$, so that, in effect, no interaction can taken place across the bonds 1—6 and 2—3, leading to isolation of the two parts of the molecule. If Δ and Δ_b denote the secular determinants (without overlap) for these two systems, then by analogy with (8)

$$E_{\text{bond loc.}} = -\frac{\beta\gamma}{\pi}\int_{-\infty}^{\infty}\frac{\beta^2 - S^2y^2}{(\beta^2+S^2y^2)^2}\log\frac{\Delta(iy)}{\Delta_b(iy)}\,\mathrm{d}y \quad . \quad . \quad . \quad . \quad (17)$$

There are the same number of carbon atoms in both structures, and so the expression Δ/Δ_b tends to unity quite fast as $y \longrightarrow \infty$. We may now expand (17) in the form (10) and use the method of Coulson and Jacobs for numerical integration. Alternatively we may improve the convergence by a process analogous to that used in passing from (8) to (16). If we introduce a fictitious β and S for the localised bond, with values $x\beta$, xS, but keep all the other non-vanishing β and S unchanged, then it may be shown, after a little reduction that

$$\log\frac{\Delta(iy)}{\Delta_b(iy)} = \frac{(3-x^2)\beta^2}{y^2} + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If we choose $x = \sqrt{3}$ we find that the contribution from values of $|y/\beta| > 6$ in (17) is quite negligible. Numerical integration is now straightforward. We can write

$$E_{\text{bond loc.}} = \left[\frac{2\sqrt{3}S}{1 + \sqrt{3}S} - \frac{2S}{1 + S}\right]\gamma - \frac{2\beta\gamma}{\pi}\int_0^\infty \frac{\beta^2 - S^2y^2}{(\beta^2 + S^2y^2)^2}\log\frac{\Delta(iy)}{\Delta_b^*(iy)}\,dy \ . \quad (19)$$

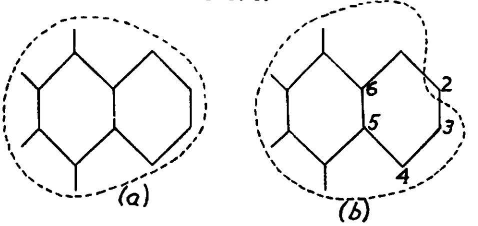
where Δ_b^* is the secular determinant for the fictitious system corresponding to Fig. 1*b* and in which β for the localised bond is replaced by $\beta\sqrt{3}$. The terms in square brackets in (19) are needed to correct for the false energy attributed to the isolated double bond 1—2 by the use of $x\beta$ instead of β. The relation between (19) and (16) is immediately clear if we recognise that a single Kekulé structure is one which we reach by successively localising double bonds in the manner of Fig. 1 until all the bonds are either single or double.

Para-localisation Energy.—The para-localisation energy is the energy required to localise two electrons on atoms which (Fig. 2) are *para* to each other. If we regard our previous bond-localisation as an ortho-process, then this is the corresponding para-process. Instead of (17) we shall have

$$E_{\text{para. loc.}} = -\frac{\beta\gamma}{\pi}\int_{-\infty}^{\infty} \frac{\beta^2 - S^2y^2}{(\beta^2 + S^2y^2)^2}\log\frac{\Delta(iy)}{\Delta_p(iy)}\,dy \quad . \ . \ . \ . \quad (20)$$

where Δ_p is the secular determinant for the system, such as in Fig. 2*b*, consisting of two isolated atoms (here 3 and 6) with one π-electron each, and the residual molecule (here ethylene and a smaller polynuclear hydrocarbon). The integration in (20) may be performed without difficulty; but it is a little more tedious since $\Delta_p(z)$ contains a factor z^2 arising from the isolated atoms (here 3 and 6). This factor causes a logarithmic infinity in the integrand near $z = 0$. We cannot merely leave this factor out because the convergence of (20) at large y then becomes too slow for convenience. But if, for mathematical convenience, we imagine the *para*-atoms to be joined by a fictitious bond with resonance integral $x\beta$, we avoid the logarithmic infinity at the origin, and we reduce the integrand to very small values at large y by putting $x = 2$. The new formula which replaces (20) is

FIG. 3.



$$E_{\text{para. loc.}} = \frac{4S\gamma}{1 + 2S} - \frac{2\beta\gamma}{\pi}\int_0^\infty \frac{\beta^2 - S^2y^2}{(\beta^2 + S^2y^2)^2}\log\frac{\Delta(iy)}{\Delta_p^*(iy)}\,dy \quad . \ . \ . \quad (21)$$

where

$$\Delta_p^*(iy) = \Delta_p(iy) \times (y^2 + 4\beta^2)/y^2 \quad . \ . \ . \ . \ . \ . \quad (22)$$

The first term on the right in (21) is needed to compensate for the fictitious bond which we have introduced between atoms 6 and 3. Despite its appearance $\Delta_p^*(iy)$ is finite at $y = 0$. In this way para-localisation energies are found by one single integration.

Atom-localisation Energy.—The atom localisation energy, $E_{\text{atom loc.}}$, was originally introduced by Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) in a discussion of the transition state in chemical reactions. According as the reaction is electrophilic, free-radical, or nucleophilic, we require to localise 2, 1, or 0 electrons on one particular atom (*e.g.*, atom 2 in Fig. 3). This means that we have $2n - 2$, $2n - 1$, or $2n$ electrons in the residual molecule shown within the broken lines in Fig. 3*b*. This is an odd alternant, so that the top occupied orbital has zero energy. As a result—a situation already recognised by several writers—the localisation energy, $E_{\text{atom loc.}}$, is the same for all three types of reaction. An analysis very similar to that which led up to (20) shows that we may write

$$E_{\text{atom loc.}} = -\frac{\beta\gamma}{\pi}\int_{-\infty}^{\infty}\frac{\beta^2 - S^2y^2}{(\beta^2 + S^2y^2)^2}\log\frac{\Delta(iy)}{\Delta_a(iy)}\,dy \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where Δ_a is the secular determinant Δ with (in the particular case of Fig. 3) $\beta_{21} = 0 = \beta_{23}$. Once again Δ_a involves a factor y^2 so that the numerical integration has to deal with a logarithmic infinity at $y = 0$. Just as in (21) this may be much simplified, both at $y = 0$ and $y = \infty$, by a transformation to

$$E_{\text{atom loc.}} = \frac{2\sqrt{2}S\gamma}{1 + \sqrt{2}S} - \frac{2\beta\gamma}{\pi}\int_{0}^{\infty}\frac{(\beta^2 - S^2y^2)}{(\beta^2 + S^2y^2)^2}\log\frac{\Delta(iy)}{\Delta_a^*(iy)}\,dy \quad . \quad . \quad (24)$$

where

$$\Delta_a^*(iy) = \Delta_a(iy) \times (y^2 + 2\beta^2)/y^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The advantage of equations (16), (19), (21), and (24) is that they reduce the calculation of the various resonance and localisation energies to the evaluation of one single integral. On account of the fact that in each case the integrand tends to zero very rapidly as y increases, the contribution from $|y/\beta| > 6$ is negligible for almost all purposes. Furthermore these energies are given directly, and are not obtained as the relatively small differences between two fairly large and nearly equal energies. This greatly increases the accuracy available with the same amount of numerical effort.

Non-alternants and Heteromolecules.—Our previous discussion has dealt solely with the case of alternant hydrocarbons. These are the systems most commonly studied, and most easily handled. When we are concerned with non-alternant hydrocarbons (*e.g.* fulvene, azulene) or heterocyclic systems (*e.g.*, pyridine) general formulations like our previous ones are no longer possible. But in any particular case formulæ which serve the same purpose may be found without difficulty. We can no longer use the relationships (1)—(3), but must deal all the time with the full secular determinant (Δ_0 say) involving S and the various α's. Instead of using (5) and (6) as our starting point, we must fall back on the more cumbrous formula

$$E = \frac{1}{\pi i}\oint\frac{z\Delta_0'(z)}{\Delta_0(z)}\,dz \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This leads to the resonance energy formula

$$R = \frac{1}{\pi i}\oint z\frac{d}{dz}\log\left(\frac{\Delta_0(z)}{\Delta_{0,\,\text{Kek}}(z)}\right)dz \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where $\Delta_{0,\,\text{Kek}}$ is the secular determinant, including S and α, for a Kekulé structure. This may be converted into

$$R = -\frac{1}{\pi i}\oint\log\left(\frac{\Delta_0(z)}{\Delta_{0,\,\text{Kek}}(z)}\right)dz \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

and so into an integral along the y-axis. But, on account of the complex character of $\Delta_0(iy)$, the whole analysis becomes more clumsy. For that reason we shall not here attempt to go beyond (28).

MATHEMATICAL INSTITUTE, OXFORD.

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