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Application of Coulson's Contour Integral Method to Linear Finite Polymers

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Coulson's contour integration method has been applied to calculate the charge and bond order matrices and total energies of conjugated systems composed of fragments whose Hückel secular equations have been solved. Integral formulas have been derived for the calculation of these quantities for two coupled conjugated systems and for linear polymers. A rapid method for the numerical evaluation of the integral formulas is presented and applied to a linear finite polyene.

Coulson [1] introduced in 1940 an integration method with which molecular orbital calculations can be performed without direct reference to the eigenvalues and eigenvectors of the secular problem. Recently, Linderberg [2] showed that this technique is useful in conjunction with computers. The purpose of this paper is to show that the contour integration method is particularly useful in calculating the properties of large molecules composed of fragments whose Hückel secular equations have been solved.

The results of Coulson and Linderberg are presented here in a somewhat different notation. For simplicity, overlap is not included and the coefficients of the atomic orbitals are assumed to be real. The calculations are performed in terms of a Hückel bond matrix $\boldsymbol{B}$ obtained from the normal Hückel matrix $\boldsymbol{H}$ by the transformation

$$\boldsymbol{B}=\frac{1}{\beta_0}(\boldsymbol{H}-\alpha_0\boldsymbol{I}) \tag{1}$$

where α_0 and β_0 stand for the standard resonance parameter for the carbon-carbon bond and the Coulomb parameter of carbon, respectively. The equations of Coulson are converted into two general integral formulas.

Theorem 1. *The charge and bond order matrix* $\boldsymbol{P}$ *is given by the formula*

$$\boldsymbol{P}=\frac{1}{\pi i}\oint_{\text{occ}}(z\boldsymbol{I}-\boldsymbol{B})^{-1}\,dz \tag{2}$$

where "occ" means that the complex integral is taken over the contour enclosing the eigenvalues of $\boldsymbol{B}$ *corresponding to the occupied orbitals.*

The integrand is expanded as a sum of dyads

$$(z\boldsymbol{I}-\boldsymbol{B})^{-1}=\sum_j\frac{1}{z-\varepsilon_j}\boldsymbol{c}_j\boldsymbol{c}_j^T \tag{3}$$

where ε_j and $\boldsymbol{c}_j$ are, respectively, the eigenvalues and eigenvectors of $\boldsymbol{B}$. Application of the Cauchy integral formula gives

$$\frac{1}{2\pi i}\oint_{\text{occ}}(z\boldsymbol{I}-\boldsymbol{B})^{-1}dz=\frac{1}{2\pi i}\sum_j \boldsymbol{c}_j\boldsymbol{c}_j^T\oint_{\text{occ}}\frac{dz}{z-\varepsilon_j}=\sum_j \boldsymbol{c}_j\boldsymbol{c}_j^T=\frac{1}{2}\boldsymbol{P}.$$

Theorem 2. *The total π-electron energy in units of β_0 and assuming that $\alpha_0=0$ is given by the formula*

$$E=\frac{1}{\pi i}\oint_{\text{occ}} z\,\mathrm{tr}(z\boldsymbol{I}-\boldsymbol{B})^{-1}dz. \tag{4}$$

This theorem is proved by dyadic expansion like the preceding.

Two Systems Coupled by One Bond

Let $\boldsymbol{B}_1$ and $\boldsymbol{B}_2$ be the Hückel bond matrices of two conjugated systems S_1 and S_2 containing n and m atoms, respectively. The bond matrix of the coupled system is

$$\boldsymbol{B}=\begin{pmatrix}\boldsymbol{B}_1 & \boldsymbol{K}\\ \boldsymbol{K}^T & \boldsymbol{B}_2\end{pmatrix}.$$

Two new matrices are now defined by

$$\boldsymbol{G}_1=(z\boldsymbol{I}-\boldsymbol{B}_1)^{-1}$$
$$\boldsymbol{G}_2=(z\boldsymbol{I}-\boldsymbol{B}_2)^{-1}.$$

It is easily shown that

$$\boldsymbol{G}=\begin{pmatrix}\boldsymbol{G}_1^{-1} & -\boldsymbol{K}\\ -\boldsymbol{K}^T & \boldsymbol{G}_2^{-1}\end{pmatrix}^{-1}=\begin{pmatrix}(\boldsymbol{I}-\boldsymbol{G}_1\boldsymbol{K}\boldsymbol{G}_2\boldsymbol{K}^T)^{-1}\boldsymbol{G}_1 & \boldsymbol{G}_1\boldsymbol{K}(\boldsymbol{I}-\boldsymbol{G}_2\boldsymbol{K}^T\boldsymbol{G}_1\boldsymbol{K})^{-1}\boldsymbol{G}_2\\ \boldsymbol{G}_2\boldsymbol{K}^T(\boldsymbol{I}-\boldsymbol{G}_1\boldsymbol{K}\boldsymbol{G}_2\boldsymbol{K}^T)^{-1}\boldsymbol{G}_1 & (\boldsymbol{I}-\boldsymbol{G}_2\boldsymbol{K}^T\boldsymbol{G}_1\boldsymbol{K})^{-1}\boldsymbol{G}_2\end{pmatrix}.$$

It is assumed that atom p in the system S_1 is bonded to atom q in the system S_2. Let the resonance parameter for the bond be k. The elements of $\boldsymbol{K}$ are then

$$K_{ij}=\delta_{ip}\delta_{jq}k.$$

With this matrix we obtain

$$(\boldsymbol{I}-\boldsymbol{G}_1\boldsymbol{K}\boldsymbol{G}_2\boldsymbol{K}^T)_{ij}=\delta_{ij}-(\boldsymbol{G}_1)_{ip}(\boldsymbol{G}_2)_{qq}\delta_{jp}k^2.$$

This matrix is inverted by partitioning [3]:

$$((\boldsymbol{I}-\boldsymbol{G}_1\boldsymbol{K}\boldsymbol{G}_2\boldsymbol{K}^T)^{-1})_{ij}=\delta_{ij}+\frac{k^2(\boldsymbol{G}_1)_{ip}(\boldsymbol{G}_2)_{qq}\delta_{jp}}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}}.$$

Hence

$$((\boldsymbol{I}-\boldsymbol{G}_1\boldsymbol{K}\boldsymbol{G}_2\boldsymbol{K}^T)^{-1}\boldsymbol{G}_1)_{ij}=(\boldsymbol{G}_1)_{ij}+\frac{k^2(\boldsymbol{G}_1)_{ip}(\boldsymbol{G}_1)_{pj}(\boldsymbol{G}_2)_{qq}}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}}. \tag{5}$$

Analogously we find that

$$((\boldsymbol{I}-\boldsymbol{G}_2\boldsymbol{K}^T\boldsymbol{G}_1\boldsymbol{K})^{-1}\boldsymbol{G}_2)_{ij}=(\boldsymbol{G}_2)_{ij}+\frac{k^2(\boldsymbol{G}_2)_{iq}(\boldsymbol{G}_2)_{qj}(\boldsymbol{G}_1)_{pp}}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}} \tag{6}$$

and

$$(\boldsymbol{G}_2\boldsymbol{K}^T(\boldsymbol{I}-\boldsymbol{G}_1\boldsymbol{K}\boldsymbol{G}_2\boldsymbol{K}^T)^{-1}\boldsymbol{G}_1)_{ij}=\frac{k(\boldsymbol{G}_2)_{iq}(\boldsymbol{G}_1)_{pj}}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}}. \tag{7}$$

Application of Theorem 1 gives the differences in bond orders and electron densities between coupled and uncoupled systems. For instance, for the atoms of the system S_1 we obtain

$$(\Delta\boldsymbol{P}_1)_{ij}=\frac{1}{\pi i}\oint_{\text{occ}}\frac{k^2(\boldsymbol{G}_1)_{ip}(\boldsymbol{G}_1)_{pj}(\boldsymbol{G}_2)_{qq}}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}}dz. \tag{8}$$

The total π-energy difference is given by

$$\Delta E=\frac{1}{\pi i}\oint_{\text{occ}}\frac{k^2 z}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}}[(\boldsymbol{G}_2)_{qq}(\boldsymbol{G}_1^2)_{pp}+(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2^2)_{qq}]dz. \tag{9}$$

Polymers

Recurrence relations for obtaining the elements of the matrix $\boldsymbol{G}$ for polymers are easily derived from Eqs. (5–7). In the case of identical monomer units, explicit formulas may be derived. Assuming that S_1 represents the monomer unit and S_2 the polymer, we derive from Eq. (5)

$$(\boldsymbol{G}_2)_{qq}^{(n+1)}=(\boldsymbol{G}_1)_{qq}+\frac{k^2(\boldsymbol{G}_1)_{qp}^2(\boldsymbol{G}_2)_{qq}^{(n)}}{1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}^{(n)}}. \tag{10}$$

Here the same index q is used to label analogous positions in the monomer and n- and $n+1$-mers. Using the notation

$$Q_n=1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_2)_{qq}^{(n)}$$

we have

$$Q_{n+1}=a+\frac{b}{Q_n} \tag{11}$$

where

$$a=1-k^2(\boldsymbol{G}_1)_{pp}(\boldsymbol{G}_1)_{qq}+k^2(\boldsymbol{G}_1)_{qp}^2$$

$$b=-k^2(\boldsymbol{G}_1)_{qp}^2.$$

This formula shows that Q_n is given by a terminating continuous fraction

$$Q_n=a+\frac{b}{a+}\,\frac{b}{a+}\cdots\frac{b}{Q_1}. \tag{12}$$

Eq. (9) is now brought into a more amenable form. Performing integration by parts, we obtain

$$\Delta E = -\frac{1}{\pi i} \oint_{\text{occ}} \ln(1 - k^2 (G_1)_{pp} (G_2)_{qq}) dz\,. \tag{13}$$

The energy change that occurs when one monomer unit is joined to an $n-1$-mer is obtained from

$$\Delta E^{(n)} = -\frac{1}{\pi i} \oint_{\text{occ}} \ln Q_{n-1}\, dz\,. \tag{14}$$

Hence the total π-energy of a polymer composed of n identical monomer units is obtained from

$$E^{(n)} = nE^{(1)} + \sum_{m=2}^{n} \Delta E^{(m)} = nE^{(1)} - \frac{1}{\pi i} \oint_{\text{occ}} \ln \prod_{m=1}^{n-1} Q_m\, dz\,. \tag{15}$$

From formula (11), it follows that

$$R_1^{(n-1)} = Q_{n-1} Q_{n-2} = a_1 Q_{n-2} + b_1\,,$$

$$R_2^{(n-1)} = Q_{n-1} Q_{n-2} Q_{n-3} = (a_1^2 + b_1) Q_{n-3} + a_1 b_1\,,$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$R_m^{(n-1)} = \prod_{n-m-1}^{n-1} Q_i = a_m Q_{n-m-1} + b_m\,.$$

In these equations

$$a_1 = a,\; b_1 = b\,,$$

$$a_m = a \cdot a_{m-1} + b_{m-1}\,,$$

$$b_m = b \cdot a_{m-1}\,.$$

These simultaneous difference equations are transformed into a linear homogeneous second-order difference equation

$$a_{m+2} - a \cdot a_{m+1} - b \cdot a_m = 0\,. \tag{16}$$

The general solution of this equation is

$$a_m = \alpha r_1^m + \beta r_2^m$$

where r_1 and r_2 are solutions of the characteristic equation

$$r^2 - ar - b = 0$$

and α and β are coefficients determined by the initial conditions. In this case the initial conditions obviously lead to equations

$$\alpha r_1 + \beta r_2 = a\,,$$

$$\alpha + \beta = 1\,.$$

Hence the solutions are

$$a_m = \frac{r_1^{m+1} - r_2^{m+1}}{r_1 - r_2},$$

$$b_m = b\,\frac{r_1^m - r_2^m}{r_1 - r_2}.$$

Thus we get

$$R_{n-2}^{(n-1)} = \prod_{m=1}^{n-1} Q_m = a_{n-2}Q_1 + b_{n-2} = \frac{r_1^{n-1} - r_2^{n-1}}{r_1 - r_2} + b\,\frac{r_1^{n-2} - r_2^{n-2}}{r_1 - r_2}. \tag{17}$$

Then, on the strength of the fact that $Q_1 = r_1 + r_2 - r_1 r_2$ and $b = -r_1 r_2$, the expression for the total energy is

$$E^{(n)} = nE^{(1)} - \frac{1}{\pi i} \oint_{\mathrm{occ}} \ln \frac{r_1^n(1-r_2) - r_2^n(1-r_1)}{r_1 - r_2}\, dz. \tag{18}$$

To obtain an explicit formula for the calculation of the electron densities, Eq. (5) is written as

$$(G_1)_{ii}^{(n)} = (G_1)_{ii} + \frac{(G_1)_{ip}^2}{(G_1)_{pp}} \left(\frac{1}{Q_{n-1}} - 1 \right).$$

From Eq. (17) we derive

$$Q_{n-1} = \frac{R_{n-2}^{(n-1)}}{R_{n-3}^{(n-2)}} = \frac{r_1^n(1-r_2) - r_2^n(1-r_1)}{r_1^{n-1}(1-r_2) - r_2^{n-1}(1-r_1)}. \tag{19}$$

Hence the electron densities of the atoms of the terminal monomer unit in an n-mer are obtained from

$$(P_1)_{jj}^{(n)} = \frac{1}{\pi i} \oint_{\mathrm{occ}} \frac{(G_1)_{jp}^2 (r_1^{n-1} - r_2^{n-1})(1-r_1)(1-r_2)}{(G_1)_{pp}[r_1^n(1-r_2) - r_2^n(1-r_1)]}\, dz + (P_1)_{jj}^{(1)} \tag{20}$$

where $(P_1)_{jj}^{(1)}$ denotes the electron density of the atom j in the isolated monomer unit.

Numerical Calculation of Integrals

Proper choice of the integration path is essential to simplify the calculation of the integrals. The contour must enclose the eigenvalues corresponding to the occupied orbitals of both the coupled system and the subsystems. In the case of alternant hydrocarbons and most of their heteroanalogues, the "Coulson contour", i.e. the imaginary axis from $+\infty i$ to $-\infty i$ and the infinite semicircle to the right of the imaginary axis may be chosen. The integral taken over the infinite semicircle has a constant value. For example, by the substitution $z = iy$, Eq. (8) becomes

$$(\Delta P_1)_{ij} = \frac{1}{\pi} \int_{\infty}^{-\infty} \frac{k^2 (G_1)_{ip} (G_1)_{pj} (G_2)_{qq}}{1 - k^2 (G_1)_{pp} (G_2)_{qq}}\, dy. \tag{21}$$

The explicit expressions for the elements of the G-matrices are obtained by dyadic expansion (3).

Extremely cumbersome algebraic formulas are obtained when an attempt is made to separate the real and imaginary parts of the integrands. Therefore, the evaluation of the integrals is most easily performed using complex arithmetics with a computer. On substituting $y=x(1-x^2)^{-1/2}$, the integration limits change to $(-1,1)$ and we obtain generally

$$I=\frac{1}{\pi}\int_{-\infty}^{\infty} f(y)dy=\frac{1}{\pi}\int_{-1}^{1}(1-x^2)^{-1/2}(1+y(x)^2)f(y(x))dx \tag{22}$$

Chebyshev-Gauss quadrature utilizing the fact that $f(y)$ is an even function of y gives

$$I=\frac{1}{m}\sum_{i=1}^{m}\left(1+\tan^2\frac{2m-2i+1}{4m}\pi\right)f\left(\tan\frac{2m-2i+1}{4m}\pi\right). \tag{23}$$

This quadrature formula proved to be numerically very stable and rapidly converging.

Applications

The accuracy of the numerical integration was tested by applying Eq. (18) to the linear polyene $C_{60}H_{62}$. The total energy in this case is obtained from the explicit formula [4]:

$$E=\frac{2}{\sin\frac{\pi}{122}}-2=75.67619648\,.$$

Energy is expressed in units of β_0 and assuming that $\alpha_0=0$. The total π-energy was also computed using Eqs. (18) and (23) taking ethylene as the monomer unit. Approximate values of the energy $E^{(30)}$ at a number of integration abscissas are shown in Table 1. We see that the convergence is fairly rapid.

The significance of Theorems 1 and 2 lies in the fact that they provide analytical expressions for quantities otherwise derivable only by comparatively slow diagonalization procedures. The rapidity of the numerical integration may be utilized in computing changes in, e.g., charges, bond orders, and total π-energies by

Table 1. Numerical calculation of the total π-electron energy of the linear polyene $C_{60}H_{62}$

m	$E^{(30)}$
1	75.51
2	76.015
4	75.788
8	75.699
16	75.6785
32	75.67624
64	75.67619649

Eqs. (8) and (9) when two coupled systems are rotated about the connecting bond. Eqs. (18) and (20) are perhaps the first explicit expressions to be proposed for the calculation of Hückel energies and charges of arbitrary linear finite polymers.

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