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Graph Theory and Molecular Orbitals. XVI. on π-Electron Charge Distribution[1]

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An integral formula is derived exhibiting the dependence of the π-electron charge density (in the framework of Hückel theory) on the coefficients of the characteristic polynomial of the molecular graph and one of its subgraphs. Several simple consequences of this formula are demostrated.

The π-electron charge density is one of the most important pieces of information about a conjugated molecule which can be obtained from simple Hückel MO calculations[2]. This quantity was first introduced by Coulson[3] and was later successfully correlated with a number of experimental findings (*e. g.*, reactivity towards electrophilic and nucleophilic reagents in aromatic substitution reactions[4], proton NMR shifts[5], *etc.*). Besides, there is a close relationship between the π-electron charge distribution and the dipole moment of a conjugated molecule[6].

A well-known result is a uniform charge distribution in alternant hydrocarbons regardless any detail in their structure.[7] No analogous regularity exists for non-alternant hydrocarbons. The above results were also quite recently obtained using graph-theoretical considerations and proof-techniques[8,9].

In this work we would like to present some additional results leading to the further understanding of the dependence of π-electron charge density on structural features of the molecule. We use here the formalism of graph theory as it was developed in earlier papers of this series[10]. Thus, in case the molecular graph G possesses N vertices, $\mathbf{A} \equiv \mathbf{A}(G)$, its adjacency matrix will be defined as

$$A_{pq} = \begin{cases} 1 \text{ if vertices } p \text{ and } q \text{ are adjacent} \\ 0 \text{ otherwise} \end{cases} \tag{1}$$

The characteristic polynomial of G is

$$P(x) \equiv \det \left| x\mathbf{1} - \mathbf{A} \right| \tag{2}$$

Its roots (*i. e.* graph spectrum) are denoted as $x_1, x_2, \ldots, x_N$. For graphs without self-loops, as are the molecular graphs corresponding to conjugated hydrocarbons,

$$\sum_{j=1}^{N} x_j = 0 \tag{3}$$

Let G_r be a subgraph of G obtained after removal of the vertex r and all incident edges to it from the graph G. Let further G_h be a graph obtained by introducing a self-loop with a weight h on the vertex r of the graph G[11-13]. The weight h is to be understood as a variable parameter. In matrix notation this means that

$$A_{pq}(G_h) = A_{pq}(G) \tag{4}$$

for all p and q, except for $p = q = r$, when

$$A_{rr}(G_h) = h \text{ and } A_{rr}(G) = 0 \tag{5}$$

Therefore, for a graph with a self-loop with weight h,

$$\sum_{j=1}^{N} x_j = h \tag{6}$$

Of course,

$$G_h = G \text{ for } h = 0 \tag{7}$$

We denote the characteristic polynomial of G_r and G_h by P_r and P_h, respectively. The following relation

$$P_h = P - h\,P_r \tag{8}$$

was proved elsewhere[12,13].

The characteristic polynomial P may be written in the form

$$P \equiv P(x) = \sum_{n=0}^{N} a_n x^{N-n} \tag{9}$$

This enables us to define another polynomial, H,

$$H \equiv H(x) = (i\,x)^N P(1/ix) \tag{10}$$

where $i = \sqrt{-1}$. Then

$$H = \sum_n i^n a_n x^n \tag{11}$$

which can be also presented as

$$H = U + i\,V \tag{12}$$

where

$$U \equiv U(x) = \sum_n (-)^n a_{2n} x^{2n} \tag{13}$$

$$V \equiv V(x) = \sum_n (-)^n a_{2n+1} x^{2n+1} \tag{14}$$

In an analogous way we define the polynomials H_r, U_r, V_r, and H_h, U_h, V_h,

$$H_r = (ix)^{N-1} P_r(1/ix) = U_r + i\,V_r \tag{15}$$

$$H_h = (ix)^N P_h(1/ix) = U_h + i\,V_h \tag{16}$$

Because of the relation (8),

$$H_h = H - i\,h\,x\,H_r \tag{17}$$

and therefore,

$$U_h = U + h\,x\,V_r \tag{18}$$

$$V_h = V - h\,x\,U_r \tag{19}$$

which finally gives

$$|H_h| = [(U + h\,x\,V_r)^2 + (V - h\,x\,U_r)^2]^{1/2} \tag{20}$$

We note that the dependence of the coefficients a_n on the molecular graph structure is nowadays completely elucidated[14–18]. Therefore, the topological properties of the polynomials H, U, V, *etc.*, are also well understood[1]. For later discussion it will be important that the polynomials U and U_r are positive for all values of x. This is a consequence of the relation

$$(-)^n\,a_{2n} \geqslant 0 \tag{21}$$

which holds for an arbitrary graph[1].

A Topological Formula for π-Electron Charge Density

In Hückel theory the π-electron charge density (Q_r) on the atom r is related to the π-electron energy[19] as follows

$$Q_r = \frac{\partial E_\pi}{\partial \alpha_r} \tag{22}$$

where α_r is the Coulomb integral[2,4,6] corresponding to the atom (vertex) r, and E_π is the total π-electron energy. When the corresponding graph-theoretical terminology is used[10], the Eq. (22) is given by,

$$Q_r = \frac{\partial E_\pi(G)}{\partial A_{rr}} \tag{23}$$

The above equation may be further transformed by taking into account Eqs. (4), (5), and (7):

$$Q_r = \left[\frac{\partial E_\pi(G_h)}{\partial h}\right]_{h=0} \tag{24}$$

In[1] it is shown that the following equation is valid for graphs having no self-loops (that is, for graphs whose spectra fulfill Eq. (3)):

$$E_\pi(G) = (1/\pi)\int_{-\infty}^{+\infty} \frac{\ln|H|}{x^2}\,dx \tag{25}$$

Using Eq. (6) the above formula may be easily extended to include graphs possessing self-loops. Namely,

$$E_\pi(G_h) = h + (1/\pi)\int_{-\infty}^{+\infty} \frac{\ln|H_h|}{x^2}\,dx \tag{26}$$

A detailed analysis shows that

$$\frac{\partial E_\pi(G_h)}{\partial h} = 1 + (1/\pi)\int_{-\infty}^{+\infty} \frac{\partial}{\partial h}\,\frac{\ln|H_h|}{x^2}\,dx \tag{27}$$

which combined with Eq. (20) and substituted back into Eq. (23) yields a topological formula for π-electron charge density:

$$Q_r = 1 + (1/\pi) \int_{-\infty}^{+\infty} \frac{UV_r - VU_r}{U^2 + V^2} \frac{dx}{x} \tag{28}$$

Expression (28) exhibits the exact analytical form of the dependence of Q_r on the coefficients of the characteristic polynomials P and P_r. Another form of Eq. (28) is

$$Q_r = 1 + (1/\pi) \int_{-\infty}^{+\infty} \frac{P_r(ix)}{P(ix)} dx \tag{29}$$

This elegant formula was first obtained by Coulson and Longuet-Higgins[19], but using a very different way of reasoning. It can be shown that Eqs. (28) and (29) are completely equivalent. However, the form of Eq. (28) is more convenient for the following discussion.

It results from Eqs. (28) and (29) that Q_r is uniquely determined with (and that it can be calculated from) the spectra of graph G and G_r. It is interesting to compare this conclusion with the original definition of charge density[3], which is based solely on the coefficients of MO's (*i. e.* eigenvectors of the graph G).

DISCUSSION

The form of Eq. (28) indicates that the dependence of Q_r on the molecular topology is rather complicated. This is inded the case[8,9,20]. However, in the present discussion we wish to show some properties of the charge distribution which follow straightforwardly from our formula and the topological behaviour of the polynomials H and H_r.

First, for all alternant systems it is always[17,18],

$$a_{2n+1} = 0 \tag{30}$$

and therefore it follows from Eq. (13),

$$V(x) = V_r(x) \equiv 0 \tag{31}$$

This leads, then, to

$$Q_r = 1 \tag{32}$$

Thus, the charge distribution in all alternant hydrocarbons (including free radicals) is uniform.

In non-alternants the charge density of a π-centre obviously depends both on the hydrocarbon itself and the π-centre position in the molecule. This fact is well reflected in formula (28). Namely, Eq. (28) may be also written as

$$Q_r = 1 + A_r + B_r \tag{33}$$

where

$$A_r = -(1/\pi) \int_{-\infty}^{+\infty} \frac{VU_r}{U^2 + V^2} \frac{dx}{x} \tag{34}$$

$$B_r = (1/\pi) \int_{-\infty}^{+\infty} \frac{U V_r}{U^2 + V^2} \frac{dx}{x} \tag{35}$$

Since the polynomials U, U_r (and of course, $U^2 + V^2$) are positive for all values of x, the sign of the integral A_r is determined with $V(x)$ only; that is to say solely from the molecular graph G. By analogy, the sign of the term B_r depends on the graph G_r only. Hence, A_r may be understood as being the »*molecular*« and B_r as being the »*positional*« contribution to the charge density. The actual numerical value of the π-electron charge density results from the delicate balance of these two contributions. As a simple illustration let us consider a non-alternant hydrocarbon molecule having only *one* odd-membered cycle Γ, while all other structural details are arbitrary. Let the size of Γ be γ. The coefficients a_{2n+1} of the characteristic polynomial of such graphs have the property

$$\text{sign}\,[(-)^n a_{2n+1}] = \begin{cases} 0 \text{ for } 2n+1 < \gamma \\ (-)^{(\gamma+1)/2} \text{ for } 2n+1 \geqslant \gamma \end{cases} \tag{36}$$

Therefore, from Eq. (13),

$$\text{sign}\left[\frac{V(x)}{x}\right] = (-)^{(\gamma+1)/2} \tag{37}$$

and finally from Eq. (34),

$$\text{sign}\,[A_r] = (-)^{(\gamma-1)/2} = \begin{cases} +1 \text{ if } \gamma = 4m+1 \\ -1 \text{ if } \gamma = 4m+3 \end{cases} \tag{38}$$

it is seen that the sign of A_r is not depending on r.

Let us now consider an atom r belonging to the cycle Γ. Graph G_r then contains no odd cycles and therefore[17,18] $V_r(x) \equiv 0$. Consequently, $B_r = 0$, and the only contribution to Q_r stems from A_r. The following rule follows, therefore, immediately from Eq. (38).

Rule

In a conjugated hydrocarbon containing only one odd-membered cycle all atoms belonging to this cycle are negatively charged ($Q_r > 1$) if the size of the cycle is $4m + 1$ and positively charged ($Q_r < 1$) if the size of the cycle is $4m + 3$.

This result is independent of any other detail in the molecular structure.

The case when the considered π-centre does not belong to Γ may be treated by analogy. However, G_r contains now the cycle Γ and therefore,

$$\text{sign}\left[\frac{V_r(x)}{x}\right] = (-)^{(\gamma+1)/2} \tag{39}$$

which combined with Eq. (35) yields,

$$\text{sign}\,[B_r] = \begin{cases} -1 \text{ if } \gamma = 4m+1 \\ +1 \text{ if } \gamma = 4m+3 \end{cases} \tag{40}$$

a result which is expected since the total charge of the neutral hydrocarbon is zero.

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SAŽETAK

Teorija grafova i molekularne orbitale. XVI. O raspodjeli π-elektronskog naboja

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Izvedena je integralna formula koja ukazuje na vezu između raspodjele π-elektronskog naboja u konjugiranom ugljikovodiku i koeficijenata karakterističnog polinoma pripadnog molekularnog grafa i jednog njegovog podgrafa. Prikazano je također i nekoliko jednostavnih posljedica ove topološke formule.

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