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The Nonexistence of Topological Formula for Total π-Electron Energy

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A definition of the topological formula for total π-electron energy (E) is given and its necessary analytical from is shown to be a linear combination of graph invariants. It is demonstrated that no exact topological formula for E can exist, i.e. that E cannot be expressed as a function of graph invariants. The proof of the nonexistence of the topological formula is based on Ulam's conjecture.

Key words: Graph theory – Ulam's conjecture

Total π-electron energy (E) and a concept closely related to it – the resonance energy – play a central role in the theory of unsaturated organic compounds. From a chemist's point of view, the problem of how molecular structure determines a molecular property is of prime interest. Numerous authors [1] investigated the dependence of these two quantities on particular structural features of the molecule, especially in the framework of the Hückel molecular-orbital theory, where a relatively simple and straightforward correspondence exists between molecular structure and the numerical results [2].

There is a common endeavour in practically all papers listed in Ref. [1] to find a formula which would enable the enumeration of E when some details of the molecular topology (e.g. number of atoms, number of bonds, number of 4-, 6-, etc. -membered rings, etc.) are given. Since all this information is necessarily contained in the molecular graph [2, 3], it is justifiable to use the term *topological formula.* The possibility of deriving such a formula was always tacitly assumed, although no one of the numerous efforts gave more than an approximate expression. Satisfactory numerical results could be obtained only for restricted classes of compounds.

In the present work a satisfactorily rigorous definition of topological formula will be given which enables the specification of its analytical form. Further, it will be demonstrated that a topological formula for E having the desired properties cannot exist at all.

Definition of the Topological Formula

A graph G is an ordered pair of a (finite) set $\boldsymbol{V} = \{v_1, v_2, \ldots, v_N\}$ having N elements (vertices) and a binary relation $\boldsymbol{E}$ defined on $\boldsymbol{V}$ (that is, $\boldsymbol{E} \subseteq \boldsymbol{V} \times \boldsymbol{V}$) [4]. Symbolically

$$G = (\boldsymbol{V}, \boldsymbol{E}) . \tag{1}$$

Two graphs $G_1=(V_1, E_1)$ and $G_2=(V_2, E_2)$ are isomorphic ($G_1 \cong G_2$) if there exists a one-to-one mapping f

$$fV_1 = V_2 \tag{2}$$

such that $(fv_1, fv_2) \in E_2$ if, and only if, $(v_1, v_2) \in E_1$.

Let $\mathscr{T}_N = \{t_1, t_2, \ldots, t_{T_N}\}$ be the set of all mutually nonisomorphic graphs having not more than N vertices. Obviously, $\mathscr{T}_{N-1} \subset \mathscr{T}_N$.

If $V_1 \subseteq V$, $E_1 \subseteq E$ and $E_1 \subseteq V_1 \times V_1$, the graph $G_1=(V_1, E_1)$ is called a subgraph of the graph G. The set of all subgraphs of G will be denoted by $\mathscr{P}(G)$. Now, every element t of $\mathscr{T}_N$ is isomorphic to $J_G(t)$ elements of $\mathscr{P}(G)$. Hence, $J_G(t)=0, 1, 2, \ldots$. We say also that the subgraph t is contained $J_G(t)$ times in the graph G. It is easy to see that the J_G's are graph invariants, that is

$$G_1 \cong G_2 \Rightarrow J_{G_1}(t) = J_{G_2}(t) \tag{3}$$

for all $t \in \mathscr{T}$. Note that the number of atoms, number of bonds, etc. are graph invariants defined in the above sense. Thus, for instance, for the graphs t_1, t_2 and t_3

t_1 t_2 t_3

$J_G(t_1)=N=$ number of atoms, $J_G(t_2)=N(N-1)/2$ and $J_G(t_3)=$ number of bonds for an arbitrary molecular graph G.

Hence, every topological formula for E can be written as some function F of graph invariants of the corresponding molecular graph G:

$$E(G) = F(J_G(t_1), J_G(t_2), \ldots, J_G(t_{T_N})) \tag{4}$$

or in shorter notation

$$E(G) = F(\boldsymbol{J}_G^{(N)}) \tag{5}$$

where

$$\boldsymbol{J}_G^{(N)} = (J_G(t_1), J_G(t_2), \ldots, J_G(t_{T_N})) \,. \tag{6}$$

As an essential point in our discussion we use the well known Ulam's conjecture [5],[1] namely that the set $\{J_G(t) | t \in \mathscr{T}_{N-1}\}$ completely characterizes a graph G (for $N \geqq 3$). Therefore, the topological formula for E is necessarily of the form

$$E(G) = F(\boldsymbol{J}_G^{(N-1)}) \,. \tag{7}$$

The Nonexistence of the Topological Formula

Let $G_1=(V_1, E_1)$ and $G_2=(V_2, E_2)$ be two arbitrary graphs and let the sets V_1 and V_2 be disjoint (that is, $V_1 \cap V_2 = \emptyset$). Then the graph

$$G_1 \cup G_2 = (V_1 \cup V_2, E_1 \cup E_2) \tag{8}$$

is simply the composition [6] of two disjoint graphs G_1 and G_2. Therefore

$$J_{G_1 \cup G_2}(t) = J_{G_1}(t) + J_{G_2}(t) \tag{9}$$

[1] The validity of the conclusions to be drawn depend explicitly on Ulam's conjecture. Although this conjecture is not yet completely proved in graph theory, its validity is, nowadays, commonly accepted [6].

for all $t \in \mathscr{T}$. Besides:[2]

$$E(G_1 \cup G_2) = E(G_1) + E(G_2)\,. \tag{10}$$

Substituting Eqs. (9) and (10) back into (7) one obtains

$$F(\boldsymbol{J}_{G_1} + \boldsymbol{J}_{G_2}) = F(\boldsymbol{J}_{G_1}) + F(\boldsymbol{J}_{G_2}) \tag{11}$$

which is a Cauchy type functional equation, the general solution of which is

$$F = \sum_{j=1}^{T_{N-1}} c_j J(t_j) \tag{12}$$

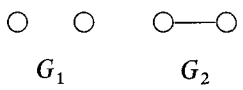
where c_j are arbitrary constants. Hence, the only correct form of a topological formula for E is a linear combination of graph invariants

$$E(G) = \sum_j c_j J_G(t_j)\,. \tag{13}$$

Gordon and Kennedy [8] recently used the same topological expression in a graph-theoretical study of saturated hydrocarbons, where c_j have been determined by a least squares method. The convergence of Eq. (13) in the case of saturated systems is excellent – the c_j's turn out to be negligibly small for large t_j's (that is for t_j's having a large number of vertices and edges). Of course, an analogous empirical treatment should be possible for π-electron energy also, but convergence is poor [9] and therefore many hundreds of terms would have to be taken into account.

Moreover, we demonstrate now that an *exact* topological formula cannot be of the form (13).

Let us consider first the graphs G_1 and G_2



G_1 $\qquad$ G_2

These are the only two nonisomorphic graphs having $N = 2$ vertices. The corresponding energies are 0 and 2, respectively. Besides $\mathscr{T}_1 = \{t_1\}$ and $J_{G_1}(t_1) = J_{G_2}(t_2) = 2$. Substituting this back into Eq. (13) one obtains

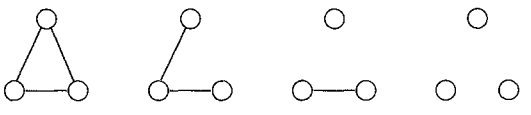
$$\begin{aligned} &\text{for } G_1 \quad 2c_1 = 0 \\ &\text{for } G_2 \quad 2c_1 = 2 \end{aligned} \tag{14}$$

which is a contradiction. The use of Hückel values for energy (in β units) is, of course, of no relevance for our conclusions.

There is an obvious objection to the above conclusion, namely Ulam's conjecture holds for $N \geqq 3$ and graphs G_1 and G_2 are the only two graphs for which

[2] Except for the case when G_1 corresponds to an electron excessive and G_2 to an electron deficient molecule [7]. These exceptions, however, do not alter the generality of the argument.

the conjecture is not valid. Therefore we will repeat the same consideration for the graphs $G_3 - G_6$, which are the only four nonisomorphic graphs



G_3 G_4 G_5 G_6

with $N = 3$ vertices. The corresponding energies are 3, $2\sqrt{2}$, 2 and 0, respectively. Of course $\mathscr{T}_2 = \{t_1, t_2, t_3\}$ and $\boldsymbol{J}^{(2)}_{G_3} = (3, 3, 3)$, $\boldsymbol{J}^{(2)}_{G_4} = (3, 3, 2)$, $\boldsymbol{J}^{(2)}_{G_5} = (3, 3, 1)$, and $\boldsymbol{J}^{(2)}_{G_6} = (3, 3, 0)$. From Eq. (13) it follows that

$$\begin{aligned} &\text{for } G_3 \quad 3c_1 + 3c_2 + 3c_3 = 3 \\ &\text{for } G_4 \quad 3c_1 + 3c_2 + 2c_3 = 2\sqrt{2} \\ &\text{for } G_5 \quad 3c_1 + 3c_2 + c_3 = 2 \\ &\text{for } G_6 \quad 3c_1 + 3c_2 = 0 . \end{aligned} \tag{15}$$

Similar contradictions can be obtained if graphs with four, five, etc. vertices are analysed in the analogous manner.

Therefore, we have proved the amusing conclusion that *the total π-electron energy cannot be expressed as a finite function of molecular topology*. This means that any general algorithm for the enumeration of E necessarily should contain a step which requires numerical solution of some algebraic equation or an equivalent procedure (e.g. matrix diagonalization). We mention however that the theorem holds for molecular graphs without any restrictions. For restricted classes of graphs, general formulae for E can be (and are in many cases) obtained. Moreover, if one considers connected graphs only, Eqs. (8)–(11) are meaningless.

Finally, hope can be expressed that the presented theorem will influence further work on topological properties of E.

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