

Review

THE GOLDEN JUBILEE OF THE COULSON–RUSHBROOKE
PAIRING THEOREM

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Abstract

The year 1990 marks the fiftieth anniversary of the much celebrated Pairing Theorem of Coulson and Rushbrooke. In its original form, the Theorem stated that for any alternant hydrocarbon: (1) the π -electron energy levels are symmetrically distributed about the zero energy level; (2) the LCAO-MO associated with the energy level ϵ_i is the same as that belonging to the energy level $-\epsilon_i$ except for a difference of sign (only) in every other atomic orbital coefficient; (3) the total π -electron charge density at any carbon atom in the molecule equals unity. Here, we trace the origins of this Theorem, describe its subsequent development, and outline some of its more significant uses. We conclude by discussing recent applications of the Theorem to positive and negative hydrocarbon ions, Möbius systems, and high-spin hydrocarbon species.

1. Introduction

The year 1990 signals the fiftieth anniversary of the well-known and much celebrated Pairing Theorem of C.A. Coulson and G.S. Rushbrooke [1]. The Theorem was originally published as a short communication in the *Proceedings of the Cambridge Philosophical Society* under the heading "Note on the Method of Molecular Orbitals" [1]. In spite of this unprepossessing title, the Theorem was an immediate success in that it found widespread application in the chemical context [2–5]. Even today, it is still of considerable importance and, over the last decade, has been the inspiration for much research work in mathematical chemistry [6–11]. In this review, we shall endeavor to trace the origins of the Theorem, follow the developments made down to the present time, and describe in some detail several of its more important uses. We shall conclude by briefly examining recent elaborations of the Theorem to chemical systems as varied as positive and negative hydrocarbons [11], Möbius structures [12,13], and high-spin hydrocarbon species [8].

The significance of the Pairing Theorem is that it represents a very important generalizing principle that can be applied to major areas of chemistry and physics. However, in its original formulation, the Theorem pertained only to conjugated hydrocarbons and, in particular, to a class of these hydrocarbons known today as *alternants*. Alternant hydrocarbons are conjugated systems in which the constituent carbon atoms can be partitioned into two mutually exclusive subsets. The partitioning process is carried out by alternately placing a star by every other carbon atom in the structural formula of the conjugated molecule in such a way that no two "starred" atoms are

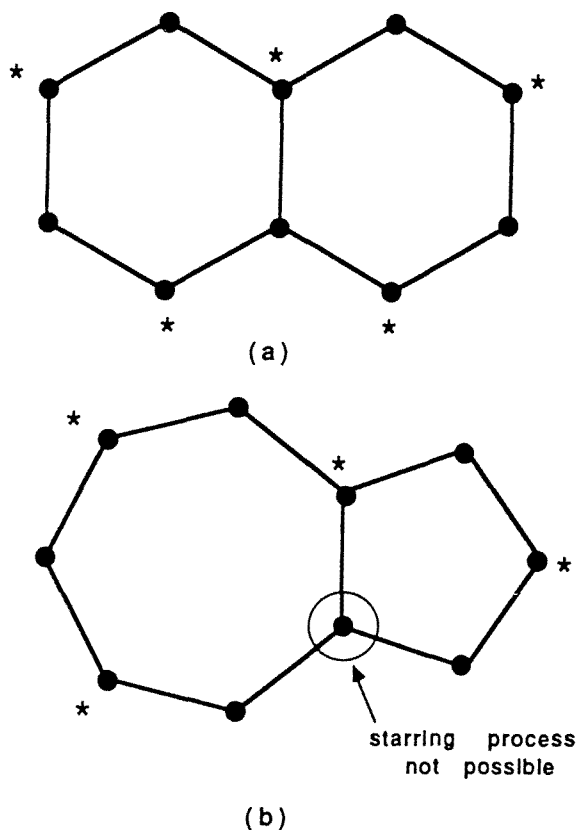


Fig. 1. The Coulson–Rushbrooke "starring process" for alternant and nonalternant isomers of the bicyclic hydrocarbon $C_{10}H_8$. (a) Shows the alternant isomer (naphthalene); (b) shows the nonalternant isomer (azulene). Note that the latter cannot be consistently "starred".

directly bonded together with a covalent bond. In other words, starred carbon atoms are linked only to unstarred carbon atoms, and vice versa. By way of illustration, the carbon atoms in the naphthalene molecule can be consistently "starred" in this way, as shown in fig. 1(a), whereas those in its isomer, azulene, cannot, as may be seen from fig. 1(b).

Naphthalene is therefore an example of an alternant species, while azulene is referred to as a nonalternant species. It is easily seen that any conjugated system containing an odd-membered ring of carbon atoms must be a nonalternant species. Indeed, the absence of an odd-membered ring is evidently the necessary and sufficient condition for any conjugated hydrocarbon to be alternant.

The Pairing Theorem was first put forward within the framework of simple Hückel molecular orbital (HMO) theory. This theory had been introduced a decade or so before the publication of the Pairing Theorem. In a pioneering series of papers on the subject, Hückel [14–17] devised the theory which now bears his name in an attempt to solve the Schrödinger equation for hydrocarbon molecules as large as benzene. The molecular orbital (MO) approach was subsequently greatly elaborated in the work of Coulson and Longuet-Higgins [18–22]. It was Hückel, however, who initially envisaged empirically an embryonic version of the Pairing Theorem in a physicochemical context, in his papers of the early 1930s [14–17]. He pointed out that a pairing of the energy levels was observed whenever HMO calculations were performed on the type of polycyclic aromatic hydrocarbon species that he was studying. Moreover, in 1937, Lennard-Jones [23], in discussing the nature of certain secular determinants that arose from HMO treatments of particular hydrocarbons, mentioned that the determinants of even degree would be possessed of roots that occurred "in pairs" and would, therefore, differ only in their sign. Thus, towards the end of the 1930s, the scene had been set for a formal proof of the Pairing Theorem.

Before discussing the history of this proof, we give first a formal statement of the Coulson–Rushbrooke Theorem expressed in the language of molecular orbital theory. We do this because, as we have already pointed out, the Theorem was first formulated within the context of HMO theory [1], though we demonstrate later in our exposition that it is by no means necessary to use such language to express the mathematical content of the Theorem. In this terminology, therefore, the Coulson–Rushbrooke Theorem encompasses the following three statements:

- (1) The π -electron energy levels of an alternant hydrocarbon are symmetrically disposed about an appropriate zero energy level. (This is the "pairing" part of the Theorem.)
- (2) The molecular orbital constituted from a linear combination of atomic orbitals (LCAO-MO) that is associated with the energy level $\epsilon_i = \alpha + x_i \beta$ is the same as that belonging to the "conjugate" or "paired" energy level, $\alpha - x_i \beta$, except, simply, that the coefficients weighting the basis atomic orbitals centered on the unstarred atoms in the MO of energy $\alpha + x_i \beta$, differ from the corresponding coefficients in the LCAO-MO associated with the conjugate orbital (of energy $\alpha - x_i \beta$), but only in *sign*, not in magnitude.
- (3) The total π -electron charge densities at each of the constituent carbon atoms in an alternant hydrocarbon are all identically unity.

In the above MO theory formulation of the Coulson–Rushbrooke Theorem, the energy levels are stated in terms of Coulomb integrals α and resonance integrals β . For the Theorem to hold, the Coulomb integrals of all carbon atoms in the conjugated system must be identical, but the resonance integrals may be allowed to vary from one bond to another, and the Theorem will still be true [4a,b]. It should also be pointed out here that which of the two sets of carbon atoms is designated "starred" and which "unstarred" is purely arbitrary. In an alternant hydrocarbon with an odd number of carbon atoms participating in the conjugated system (for example, the benzyl radical), the larger set is conventionally taken to be the starred set [2].

In this review, we wish to draw attention to the basic topological [24–27] nature of the Coulson–Rushbrooke Theorem and, in particular, to the graph-theoretical ideas which underlie it; for, as will be seen presently, when removed from the context of HMO theory, the Theorem is revealed as a purely abstract mathematical theorem in linear algebra, having particular relevance to the theory of matrices and simple, connected graphs. However, we would further emphasize that the Coulson–Rushbrooke Theorem affords an example of what appears to be a rare phenomenon – namely, the proposition, and proof, *initially* in a *chemical* context, of what subsequently was realized to be a fundamental theorem in a branch of pure mathematics, the Theorem itself only later, it seems, being discovered (apparently independently) by mathematicians per se [28]. It is for this reason that we regard the Theorem as a "case study" for the interplay between mathematical and chemical ideas. As we shall show, the Pairing Theorem provides an interesting example of the interaction between mathematics and chemistry but, more significantly, it also illustrates what one might consider to be a regrettable lack of cooperation and awareness of each other's work, between the exponents of these two disciplines.

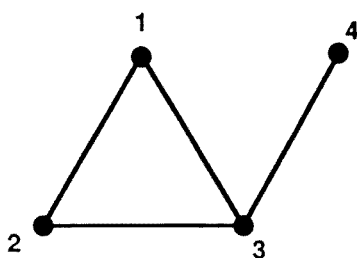
2. Graph theory and simple molecular orbital theory

2.1. GRAPH-THEORETICAL DEFINITIONS

To illustrate the relation between simple HMO theory and mathematical graph theory, we give the following definitions of graph-theoretical concepts [24,26] that will be required for the subsequent discussion.

2.1.1. Graph

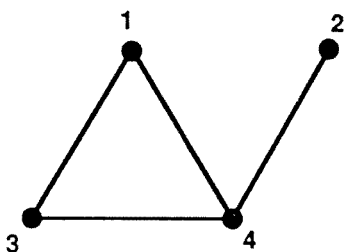
The types of graph G that we shall be considering may be defined as a pair $(V(G), E(G))$, where $V(G)$ is a non-empty set of elements called *vertices*, and $E(G)$ is a finite set of unordered pairs of distinct elements of $V(G)$ called *edges*. We therefore represent a graph as a set of labeled points (vertices), some of which are connected by lines (edges). By the latter, we mean that vertex i of G is "connected" to vertex j of G if the element (i, j) is contained in $E(G)$. Such a diagrammatic representation of a specific graph is shown in fig. 2(a). It is evident, therefore, that graphs in which there is never more than one edge connecting a given pair of vertices, and every vertex is connected to



(a)

$$A = \begin{bmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

(b)



(c)

$$A = \begin{bmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{bmatrix}$$

(d)

Fig. 2. Two differently labeled isomorphic graphs and their corresponding adjacency matrices.

at least one other, may represent the sigma bond framework of a general conjugated system of the type to which HMO theory is conventionally applied. In this representation, the vertices correspond to atoms, and the edges correspond to the sigma bonds of the carbon atom skeleton.

2.1.2. Vertex adjacency matrix

If G is a graph, as defined above, with previously labeled vertex set $\{V_1, V_2, \dots, V_n\}$, the adjacency matrix $A(G)$ of G is defined to be the $n \times n$ matrix $[a_{ij}]$ in which

$$a_{ij} = \begin{cases} 0, & \text{if } i = j; \\ 1, & \text{if } i \neq j, \text{ and there is an edge connecting vertices } i \text{ and } j; \\ 0, & \text{if } i \neq j, \text{ and there is no edge connecting vertices } i \text{ and } j. \end{cases} \quad (1)$$

The matrix shown in fig. 2(b) is, for example, the vertex adjacency matrix of the graph depicted in fig. 2(a), with vertices labeled as shown.

$A(G)$ is thus a real, symmetric matrix with (nonnegative) integer entries, in which every diagonal element is zero and in which the sum of the entries in any row or column is equal to the number of edges incident upon (i.e. the *degree* of) the corresponding vertex. We note that a real symmetric matrix is merely a special case of an Hermitian matrix and that the eigenvalues $\{\lambda_i\}$, $i=1, 2, \dots, n$, of $A(G)$ will, therefore, be purely real. Furthermore,

$$\sum_{i=1}^n \lambda_i = \text{Tr}(A(G)) = 0. \quad (2)$$

The *eigenvalues* of a graph G , i.e. the eigenvalues of its adjacency matrix, are very useful characteristics of G [4,5,12,24,25,29–38] since they represent a property of G that remains invariant under permutation of the rows and simultaneous permutation of the columns of $A(G)$. This process is tantamount to relabeling the vertices of G . For example, the graph shown in fig. 2(c) is *isomorphic* with that in fig. 2(a), and the adjacency matrix of the graph in fig. 2(c) is shown in fig. 2(d). The list of eigenvalues of G is known as the *spectrum* of G ; the polynomial which has the spectrum of G as its roots is called the *characteristic polynomial* of G [4,5,12,24,25,29–42]. Since the eigenvalues are the zeros of the equation

$$(-1)^n |A(G) - \lambda \mathbf{1}_{n \times n}| = 0, \quad (3)$$

the characteristic polynomial is the expansion (multiplied by $(-1)^n$) of the determinant on the left-hand side of the above equation. As already mentioned, the graph spectrum (and hence the characteristic polynomial) is invariant to a relabeling of the vertices of G , and so the adjacency matrices in figs. 2(b) and 2(d) (and others corresponding to any other arbitrary relabeling of the vertices of the graph these represent) give rise to the same characteristic polynomial, as follows:

$$\begin{aligned} (-1)^4 \begin{vmatrix} -\lambda & 1 & 1 & 0 \\ 1 & -\lambda & 1 & 0 \\ 1 & 1 & -\lambda & 1 \\ 0 & 0 & 1 & -\lambda \end{vmatrix} &= (-1)^4 \begin{vmatrix} -\lambda & 0 & 1 & 1 \\ 0 & -\lambda & 0 & 1 \\ 1 & 0 & -\lambda & 1 \\ 1 & 1 & 1 & -\lambda \end{vmatrix} \\ &= \lambda^4 - 4\lambda^2 - 2\lambda + 1. \end{aligned} \quad (4)$$

2.1.3. *Bipartite and nonbipartite graphs*

We first define a process of *coloring* in which a certain color is assigned to each vertex in G . A graph (without loops) is said to be *k-colorable* if, to each of its vertices, one of k colors can be assigned in such a way that no two vertices having been allotted the same color are connected by an edge. If $k=2$, the graph G is *bipartite*; graphs which

cannot be so colored with only two colors are *nonbipartite*. A bipartite graph is occasionally, for short, referred to as a "bigraph".

From the above definition, it is immediately evident that the Coulson–Rushbrooke "starring" procedure is equivalent, graph-theoretically, to a coloring process. The graphs representing the sigma bond connectivities of the carbon atoms in an alternant hydrocarbon are thus bipartite, while those similarly representing nonalternant hydrocarbons are nonbipartite. Other quantities familiar in HMO theory also have exact counterparts in pure graph theory – correspondences that are conveniently summarized in table 1.

Table 1
Equivalence of graph-theoretical and HMO quantities

Graph-theoretical quantity	Corresponding HMO quantity
Vertex	Carbon atom in a conjugated system
Edge	Carbon-carbon sigma bond
Bipartite } graph (G) Nonbipartite }	Alternant } hydrocarbon Nonalternant }
$(-1)^n A(G) - \lambda \mathbf{1}_{n \times n} $	Simple Hückel secular determinant
Characteristic polynomial of G (expansion of the above determinant)	Polynomial in x obtained by expansion of the Hückel secular determinant
λ_i , i th eigenvalue of G (i.e. of $A(G)$)	$x_i (= (\varepsilon_i - \alpha)/\beta)$, where ε_i is the i th HMO energy level
$\{c_{ij}\}_{j=1,2,\dots,n}^T$ eigenvector of G belonging to the i th eigenvalue	$\{c_{ij}\}_{j=1,2,\dots,n}$ MO corresponding to the i th energy level

2.2. RELATION BETWEEN GRAPH-THEORETICAL AND HMO QUANTITIES

We shall illustrate the equivalence just referred to by use of a specific example; for a deeper and more formal demonstration of this relationship, the reader is referred to refs. [4,5,12,24,29,38]. We consider a simple HMO calculation on the planar, π -electron system represented by the graph in fig. 2 (with vertex numbering as in fig. 2(a)). The Hückel secular determinant with all α 's equal and all β 's the same is:

$$\begin{vmatrix} \alpha - \varepsilon & \beta & \beta & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ \beta & \beta & \alpha - \varepsilon & \beta \\ 0 & 0 & \beta & \alpha - \varepsilon \end{vmatrix}.$$

Dividing the above determinants by β , and making the conventional substitution $x = (\varepsilon - \alpha)/\beta$, we obtain:

$$\begin{vmatrix} -x & 1 & 1 & 0 \\ 1 & -x & 1 & 0 \\ 1 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{vmatrix}$$

– exactly the same as $|\mathbf{A}(G) - \lambda \mathbf{1}_{n \times n}|$ encountered earlier, with the symbol " λ " now replaced by " x ". Thus, requiring that the above determinant be zero gives:

$$x^4 - 4x^2 - 2x + 1 = 0, \quad (5)$$

the left-hand side being an expression analogous to the characteristic polynomial of the graph depicted in fig. 2. However, the roots of the above equation $\{x_i\}_{i=1,2,3,4}$ are the Hückel energy levels (where $x_i = (\varepsilon_i - \alpha)/\beta$) and so the Hückel quantities $\{x_i\}$ are the exact counterpart of $\{\lambda_i\}$. In other words, the problem of finding a Hückel energy level, on the assumption of all α 's equal and all β 's the same, is analogous to the abstract mathematical problem of finding the eigenvalues of an adjacency matrix of the graph representing the sigma bond connectivity of the atoms comprising the conjugated system [4,5,12,24,25,29,38].

3. The Perron–Frobenius Theorem as a historical forerunner of the Coulson–Rushbrooke Theorem

In the period 1907–1912, Perron and Frobenius [43–48,34] produced their famous theorem on irreducible, nonnegative matrices [29,34,47], stated as follows:

- (1) An irreducible, nonnegative matrix, A , always has a real and positive eigenvalue, r ; the moduli of all the other eigenvalues do not exceed r .
- (2) This real, maximal eigenvalue, r , belongs to an eigenvector having components that are all of the same sign.
- (3) Furthermore, if A has h eigenvalues, $\lambda_0 (= r)$, $\lambda_1, \lambda_2, \dots, \lambda_{h-1}$, of modulus r , these are all distinct roots of the equation

$$\lambda^h - r^h = 0. \quad (6)$$

- (4) More generally, the whole spectrum, $\lambda_0, \lambda_1, \lambda_2, \dots, \lambda_{n-1}$, regarded as a system of points in the Argand λ -plane, maps onto itself under a rotation by $2\pi/h$.

The last part of the Perron–Frobenius Theorem is the key to the Coulson–Rushbrooke Theorem. Since the adjacency matrix of a graph (or the Hückel matrix of a molecule) is a real, symmetric matrix, all its eigenvalues are real. Because of this, there can be at most two distinct eigenvalues with the maximum modulus, namely r and $-r$; then h , referred to in the statement of the Perron–Frobenius Theorem just given, is equal to 2. Hence, the whole spectrum of eigenvalues, regarded as a system of points in the complex plane, maps onto itself under a rotation of the plane by $2\pi/2 = \pi$. In other words, if the highest (real) eigenvalue, r , of a nonnegative, real, symmetric matrix A is paired with an eigenvalue of $-r$, all the remaining $(n - 2)$ real eigenvalues (with the exception of *one* zero, if there is an odd number of zero eigenvalues in the spectrum of A) will also be paired. A specific theorem to this effect was published by Wielandt in 1950 [49]; Hoffman [50], in 1963, proved a theorem concerning pairing of the highest and lowest eigenvalues of a *regular* graph (i.e. one in which all the vertices are of the same degree) if and only if the graph is bipartite. The Perron–Frobenius Theorem continues to stimulate current mathematical interest (for a recent instance, see, for example, ref. [51]). Although, as we have claimed above, the latter part of the Perron–Frobenius Theorem is the crux of the Coulson–Rushbrooke Theorem, it is necessary, before the Coulson–Rushbrooke Theorem can be secured from the Perron–Frobenius Theorem, to make the connecting observation that the adjacency matrix of a bipartite graph is an irreducible matrix of the Perron–Frobenius type with $h = 2$, while the adjacency matrix of a nonbipartite graph is such a matrix with $h = 1$. This sequitor was not, however, made until much later. If this connection *had* been made contemporaneously, the mathematical analog of the Coulson–Rushbrooke Theorem of 1940 could well have been proved in 1912!

4. Early evolution of the Coulson–Rushbrooke Theorem

The Pairing Theorem was finally proved by Coulson and Rushbrooke in their classic paper published from the University of Dundee in 1940. Our investigations among the Coulson Papers in the Contemporary Scientific Archives Collection at the Bodleian Library, University of Oxford [52], and subsequent personal correspondence [53,54], reveal documentary evidence that the actual *proof* of the Theorem was in fact due to Rushbrooke alone. In a letter to the late Dr. E.J. Bowen, FRS, of March 26th 1974 [52], Professor G.S. Rushbrooke, FRS, wrote:

“The day I arrived [in Dundee], in October 1939, Charles [Coulson] said he was faced with a mathematical problem, which he explained to me. It was how to prove the key theorem in his paper on Alternant Hydrocarbons (A Note on the Method of Molecular Orbitals [1]), the truth of which he had discovered empirically. Happily, I recognized this as a geometrical theorem that I knew about (and wrote out a proof the next morning).”

(As noted in our introduction, however, Hückel [14–17] had already observed the energy level "pairing" empirically and, in a more restricted way, so had Lennard-Jones [23].)

Intrigued by this reference to an apparently familiar "geometrical theorem", one of the present authors (R.B.M.) wrote (on August 21st 1977) to ask Professor Rushbrooke personally whether by "geometrical" he had perhaps meant "topological" or "graph-theoretical" or whether, possibly, he had recognized Coulson's problem as being soluble as a very special case of the Perron–Frobenius Theorem on nonnegative matrices. Professor Rushbrooke's reply (of August 25th 1977 [53]) is worth quoting in full, both for the historical record and for the way in which it ties down precisely how his mind, and that of Coulson, were working as the Theorem developed:

“... perhaps I should be a bit more explicit about what part I actually played in establishing the "Pairing" theorem.

What Coulson could not prove was equation (6) of the "Note on the Method of Molecular Orbitals" [1]; and what I supplied was essentially the text between equations (2) and (6) respectively. I had learned this kind of mathematics from F.P. White's course on "geometry" at Cambridge: though it's really concerned with quadratic forms (and I suspect I was previously aware of it only in 3 dimensions). But it's the text between equations (2) and (6) that I wrote out for Coulson (essentially as it stands). The alternate "crossing" part of the theorem, if I remember rightly, Coulson knew how to do if he could prove (6). Incidentally, I was not aware of the work of Frobenius, or any graph theory, at that time.”

As regards authorship of this classic paper, Professor Rushbrooke explains [52]:

“Charles reciprocated by asking what I intended to work on, and I expressed an interest in incorporating temperature-dependent energy levels within the framework of statistical mechanics. I knew I needed to start by exploring the thermodynamic consequences of temperature-dependent energies (such as heats of adsorption) but was at a loss as to how to begin. Charles said “take the system round a Carnot cycle and let it shrink to zero: you can get everything that way”. So I did so, and something came out of it. (The Thermodynamic Derivation of Langmuir's Isotherm [55]). He then raised the question whether we should just thank each other, or publish these two papers jointly. And we decided joint authorship would be appropriate in both cases.”

When lecturing to undergraduates on this subject, Coulson adopted a different proof of his Theorem with Rushbrooke from the one presented in their 1940 paper [1]. The proof in question (which, Coulson claimed [4a], though not the most obvious or straightforward one available, does have “... a certain aesthetic charm about it” [4a]) depends on the properties of determinants, and is given in detail in section 6.3 (pp. 91–96) of ref. [4a]. (It should be noted in passing that the matrix proof of the

Coulson–Rushbrooke Theorem presented in appendix D [4b] of ref. [4] is *not* due to Coulson; this appendix was prepared by Professor Brian O’Leary and one of the present authors (RBM) after Professor Coulson’s death in 1974. Appendix D [4b] was thus contributed to ref. [4] by the surviving authors and, although Coulson was aware of it, the proof given in that appendix is actually based on similar, yet independent, proofs of Ruedenberg [56], Cvetković [57], and the other of the present authors (DHR) [58].)

5. Chemical and mathematical developments in the 1950s and 1960s

The 1950s and 1960s was a time of considerable activity on the part of chemists as far as the properties of alternant hydrocarbon molecules were concerned. This activity was largely devoted to improving upon the sophistication of the simple Hückel method and ascertaining how many of the well-known properties of this class of molecules carried over into these less-approximate theories. In particular, theorems analogous to the Coulson–Rushbrooke Theorem were found [59] with the LCAO self-consistent field (SCF) method via approximations of the Pariser–Parr–Pople (PPP) type [59–63] and with the unrestricted LCAO-SCF method by use of the same approximations [64–66]. Using "standard equivalent orbitals" [67], Hall and collaborators [68,69] made a thorough study of the properties of alternant hydrocarbons. The Pairing Theorem was also proved for the multi-electron solution of the eigenvalue problem of alternant hydrocarbons [62,63]. Finally, Koutecký [70] gave the definition of an alternant system in terms of commutation and anticommutation relations of the Hamiltonian with certain operators, and showed that pairing properties follow as a consequence of this definition; these were summarized in general equations for the matrix elements of an arbitrary operator [70].

Meanwhile, at the simple Hückel level, a number of groups were beginning to realize the essentially graph-theoretical nature of the method, as discussed in the introduction to this review. There were some forerunners of this in the late 1940s and early 1950s [71–73]. Then, in the United States, the pioneering work of Ruedenberg, Ham and collaborators (e.g. [74–78,56]) slowly appeared throughout the mid-to-late 1950s (sometimes being published years after its original submission). Simultaneously, in Switzerland, Günthard and Primas [79] and, later, Schmidtke [80] were independently pointing out the "topological" (i.e. graph-theoretical) nature of simple HMO theory. In his initial papers [74,75], Ruedenberg introduced the "topological matrix" (defined above as the adjacency matrix) of a molecular graph. In one of his 1958 papers [76], Ham partitioned this matrix in a way that set it up for a proof of the Pairing Theorem, although he did not actually prove the Theorem itself. It was, appropriately, left to Ruedenberg, in another 1958 paper [56], to give the first entirely graph-theoretical proof of the eigenvalue-pairing part of the Coulson–Rushbrooke Theorem.

In the meantime, the mathematical literature was, at this stage, devoid of such a proof. The only relevant reference dating from the mid-1950s is the 1957 work of Collatz and Sinogowitz [33]. (However, this paper must have been written – at least in

part – much earlier than its 1957 date would indicate, for a footnote in it records that one of the authors (U.S.) had been killed during an air raid in September 1944.) It was not until over a decade later, in 1969, that proofs of the Pairing Theorem appeared in the mathematical literature as such. Surprisingly, that year brought *two* of them. Cvetković [57] offered a proof by extending the Perron–Frobenius Theorem and partitioning the adjacency matrix of a bipartite graph in a way similar to that in Ruedenberg's proof [56], while Marimont [81] provided a proof that depended on showing that in the characteristic polynomial of a bipartite graph with an even number of vertices “. . . only even powers of λ will have non-zero coefficients . . .”; the result of this is that the characteristic equation “. . . will be a function of λ^2 , so that if $+\lambda$ is a root, so is $-\lambda$ ”. One of the present authors (DHR) also formulated a proof at about this time [58,24,4b]; it depended on partitioning the adjacency matrix in the way that Ruedenberg [56] and Cvetković [57] had done. He also tried to extend the results to tripartite graphs [82], but was unable to find any corresponding theorem.

6. The era initiated by the Zagreb Group

The initial stimulus for the modern application of graph-theoretical ideas to the interpretation of HMO theory was the now-classic paper of Graovac et al. in 1972 [38], in which Sachs' theorem [37,83] was used to obtain characteristic polynomials of molecular graphs (see also ref. [84]). They gave a proof of the "pairing" part of the Coulson–Rushbrooke Theorem (for, specifically, *even* alternant hydrocarbons) which, in its logic, was similar to that of Marimont [81]. Like Marimont, they showed that the characteristic polynomial of such a system contains only even powers of the argument, and hence possesses roots that are symmetrically disposed around zero – but in ref. [38], Graovac et al. proved this by appeal to Sachs' theorem [37,83].

The following ten years saw extensions [85–88] of parts of the Coulson–Rushbrooke Theorem to molecular graphs representing certain types of hetero-conjugated molecules [89], and even to such molecules in the presence of an external magnetic field [90]. Schwenk, Trinajstić and one of the present authors (RBM) [85] showed that an analogy of the Pairing Theorem could apply to alternant conjugated systems having the same number of "starred" and "unstarred" atoms, the atoms of one set all being, say, carbon, with Coulomb integral α , and those of the other set all being the same type of heteroatom (nitrogen, say) with Coulomb integral $\alpha + h\beta$. An example of a molecule like this is *s*-triazine (fig. 3). In a graph-theoretical interpretation, such a molecule may be represented by a bipartite graph on n vertices in which the vertices of one set in the bigraph are unweighted, and those in the other set are all weighted with a unique value h . Schwenk et al. [85] showed that the eigenvalues of such a graph are paired around h – or, as they put it,

$$\lambda_i + \lambda_{n-1+i} = h, \quad \text{for } 1 \leq i \leq n. \quad (7)$$

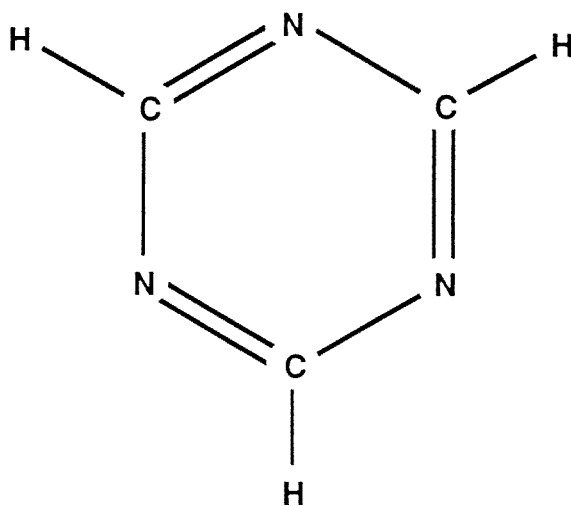


Fig. 3. The structural formula for the heterocyclic conjugated molecule *s*-triazine, an example of a so-called [91,92] "truly alternant system".

Later, with Rigby [86], one of the present authors (RBM) further generalized the established, spectral characterization of bipartite graphs (which they called *homogeneous* graphs) to a type of bipartite graph which they called *heterogeneous*. In these latter graphs, the vertices in one set are weighted h_1 and each of those in the other set of the bigraph is weighted h_2 , the number of atoms in the two sets now no longer necessarily being equal. They then showed that while, in accord with the Coulson–Rushbrooke Theorem, all the eigenvalues of a homogeneous, bipartite graph occur in pairs around zero, some of the eigenvalues of an arbitrary, heterogeneous, bipartite graph are paired around $(1/2)(h_1 + h_2)$, the remainder having the value h_2 (or h_1). These same authors also extended [86] the documented, explicit relations between the eigenvectors belonging to "paired" eigenvalues of a homogeneous, bipartite graph (which are the subject of part (2) of the Coulson–Rushbrooke Theorem (section 1)) to relate the components of the eigenvectors associated with each couple of "paired" eigenvectors of the corresponding heterogeneous, bipartite graph. They were led to these generalizations by a detailed study of the pioneering work of Bochvar, Stankevich and Chistyakov [91,92] on what these latter authors termed "truly alternant systems" and by the very early ideas of Longuet-Higgins [93] on "predictable" and "supernumerary" zero eigenvalues. A rather more chemically artificial, but nevertheless mathematically interesting, extension to the Coulson–Rushbrooke Theorem was made by Gutman [88]. He pointed out that the Pairing Theorem is a consequence of the fact that the characteristic polynomial of a bipartite graph is either an odd or an even function – summarized by

$$\Phi(G, -x) = (-1)^n \Phi(G, x), \quad (8)$$

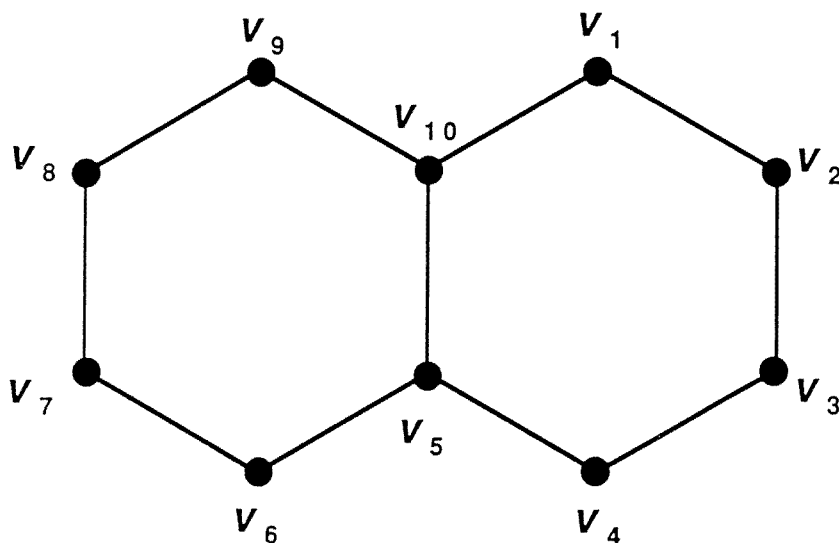


Fig. 4. The molecular graph of naphthalene, with vertices labeled ready for the discussion given by Gutman in ref. [88]. (Redrawn from ref. [88]).

and went on to show [88] that the presence of heteroatoms usually destroys this pattern and that, consequently, in the general case, the Pairing Theorem does not hold for heteroconjugated molecules, irrespective of the number of heteroatoms they comprise; (see also [4b] for a different demonstration of this point). Gutman circumvents this difficulty by defining the "equivalence" of pairs of vertices. Two vertices v_i and v_j are *equivalent* if there is a symmetry operation (or, more precisely, an element of the automorphism group of the graph) which maps v_i onto v_j and vice versa. In fig. 4, of the naphthalene molecule, v_1 and v_6 are equivalent, so are v_1 and v_4 , v_2 and v_8 , etc. In general, let v_1, v_2, \dots, v_{2k} be some vertices of the graph G . Then $v_1, v_3, \dots, v_{2k-1}$ are said to be equivalent to the vertices v_2, v_4, \dots, v_{2k} if there is a symmetry operation that maps v_{2j-1} onto v_{2j} , $j = 1, 2, \dots, k$. Let H be the molecular graph of an alternant hydrocarbon and let v_1, v_2, \dots, v_k and w_1, w_2, \dots, w_k be its equivalent vertices (all with vertex weightings of zero). Gutman then proved the following theorem: if the molecular graph H_h of a heteroconjugated molecule is formed from H by assigning weights h_r on the vertices v_r and weights of $-h_r$ on the vertices w_r , $r = 1, 2, \dots, k$ (by the device of adding appropriately weighted self-loops to the vertices in question), then its eigenvalues, $\{\lambda_i\}$, still conform to the Coulson–Rushbrooke Pairing Theorem:

$$\lambda_i + \lambda_{n+1-i} = 0, \quad i = 1, 2, \dots, n. \quad (9)$$

For example, the Pairing Theorem holds for the two molecular graphs related to the naphthalene molecular graph shown in fig. 5; h_1, h_2, h_3 may be any real numbers.

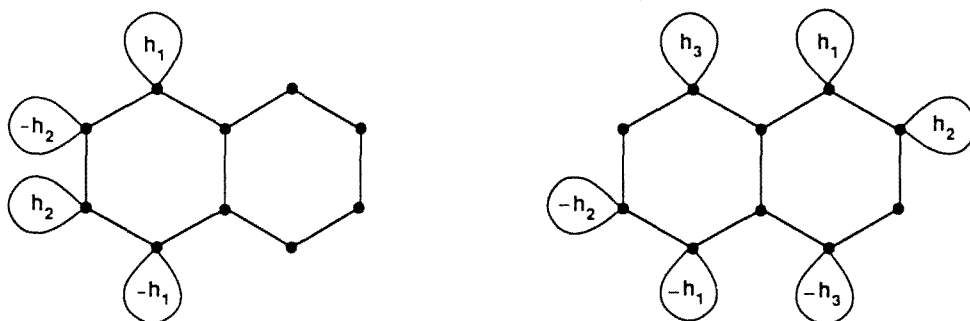


Fig. 5. Two molecular graphs, derived from the naphthalene molecular graph, for which Gutman's pairing theorem [88] holds. The vertex weightings h_1 , h_2 and h_3 may be any real numbers. (Redrawn from ref. [88]).

In another interesting development, Maouche and Gayoso [90] have applied London's gauge-invariant LCAO version of HMO theory (see, for example, [94]) to show that even when an alternant hydrocarbon is immersed in an applied, external magnetic field, the eigenvalue-pairing part of the Coulson–Rushbrooke Theorem remains valid. This is so despite the fact that the eigenvalues themselves are an explicit function of the external magnetic field. They also considered [90] what Bocharov et al. [91,92] called "truly alternant systems" and what in ref. [86] were dubbed "heterogeneous" molecular graphs – that is, more general alternant conjugated systems formed by replacing the starred atoms of an alternant hydrocarbon by an atom A and unstarred ones by an atom B , A and B both being sp^2 -hybridized. They then showed that the eigenvalue spectrum of such a system may be established starting from the eigenvalue spectrum of the corresponding ("isotopological" [90]) conjugated hydrocarbon in the presence or absence of an external magnetic field. When the value of this external magnetic field is set at zero, the resulting relations constitute a generalization of the Coulson–Rushbrooke Theorem to alternant compounds of the type A - B [90].

There has recently been a considerable resurgence of interest in the eigenvalue spectra [95] of Möbius systems [6, 12a–d, 13, 25, 96–100]. The adjacency matrices of Möbius molecules contain *negative* elements [6, 12a–d, 13, 25, 96–100] and they are not, therefore, the "*Matrizen aus nicht-negativen Elementen*" envisaged in Frobenius' extension [46] of Perron's original theorem [43]. Parts (1), (3) and (4) of the Perron–Frobenius Theorem (section 3) may, however, properly be applied to the adjacency matrices of Möbius hydrocarbons, despite the fact that they are *not* nonnegative matrices. However, the fact that such adjacency matrices are not nonnegative ones does invalidate the applicability of part (2) of the Perron–Frobenius Theorem (which provides for the real, maximal eigenvalue mentioned in part (1) of the theorem to have belonging to it an eigenvector in which all the components are of the same sign). As has been observed [13], the consequence of this in a molecular orbital context is that the lowest-

energy bonding molecular orbital of a Möbius alternant hydrocarbon does not necessarily have to be nodeless [13].

All three parts of the Coulson–Rushbrooke Theorem (section 1) do, however, still apply to the adjacency matrices of Möbius alternant hydrocarbons for, as is shown in ref. [4b], the validity of the Theorem does not depend in any way on the *off-diagonal* elements of the adjacency matrix in question, but merely on (a) its capability of being partitioned, by a judicious labeling of the carbon atoms, into the requisite blocked form, and on (b) the values of its *diagonal* elements having an appropriate pattern. (Details of the exact conditions required for the Coulson–Rushbrooke Theorem to hold are given in [4b].) The claim [13, 12c] that the Coulson–Rushbrooke Theorem still applies to Möbius alternant hydrocarbons is consistent (at least as far as the "pairing" part of it is concerned) with, for example, the fact that eigenvalue "pairs" may be discerned in the published, eigenvalue spectrum of Möbius cyclobutadiene [12c, 97, 101–103], and of Möbius benzene [12b], but *not* in the eigenvalue list of (nonalternant) Möbius cyclopropenyl [12b] or of the likewise nonalternant Möbius cyclopentadienyl [12c].

7. Generalization of alternant systems

The past decade has witnessed an increasingly sophisticated generalization of the concept of alternant systems, by workers such as Živković [11] and Karadakov [9]. These developments were founded on the idea that a symmetry in a quantum-mechanical system should be explicitly incorporated into the parameters and descriptors used in the characterization of that system [11]. In the case of conjugated alternant molecules and ions, alternancy symmetry arises naturally and such symmetry leads to many of the remarkable properties of alternant species that are not shared by their nonalternant counterparts [11, 104]. For instance, there is a close resemblance between the spectra of the positive and negative ions of a given alternant hydrocarbon, whereas no such resemblance exists for the ions of nonalternant isomers [62, 63]. Moreover, because polyenes are alternant hydrocarbons, they are known to possess certain surprisingly low-lying excited states which are accessible only by two-photon absorptions [105]. It has been observed earlier (section 5) that such alternancy symmetry properties hold also in approximations other than the simple Hückel one. Thus, these properties are known to apply in the cases of the PPP approximations, both at the SCF one-particle level and at the n -particle level in the Tamm–Dancoff approximation [106]. Moreover, McLachlan [62] has demonstrated that these still apply even when the complete configuration interaction (CI) space is considered in conjunction with the PPP Hamiltonian. In his approach to alternant hydrocarbons, McLachlan [62, 63] wrote the PPP Hamiltonian first in terms of particle creation and particle annihilation operators and then in terms of hole creation and hole annihilation operators. The two expressions he obtained differed only by a constant, and this formally accounts for all the pairing properties. Subsequently, a number of other workers made either implicit or explicit application of various forms of the particle-hole symmetry operators; examples of such

include Koutecký [70] who used this approach at the n -electron level, and Visscher and Falicov [107] who used these operators in their study of the benzene molecule. These and a variety of other procedures were united in one very general formulation [104] of the adaptation necessary for alternancy symmetry when PPP-type Hamiltonians are being employed. This work led ultimately to a resolution [11] of two major problems confronting researchers in this field, namely (1) the construction of general Hamiltonians that incorporate alternancy symmetry, and (2) the search for all of the properties characteristic of alternant systems. These two problems were tackled [11] by making use of the so-called splitting theorem [10,108], which states that the CI space, X_n , generated by n electrons located over $2n$ orthonormalized spin orbitals can be partitioned into two complementary subspaces, X_n^+ and X_n^- , such that each state $\psi^+ \in X_n^+$ and each state $\psi^- \in X_n^-$ is "alternant-like" in that it resembles the π -electron eigenstates of neutral, alternant molecules. This led to the formulation [10,108,109] of a completely general alternancy symmetry-adapted approach for the treatment of alternant species.

Among other systems which have been studied within the framework of this formulation, mention should be made of the Friedel oscillations in metals [110], the Heisenberg models of ions, functional groups, or molecules within a crystal [7], high-spin hydrocarbon species [8], and the ferromagnetic or antiferromagnetic ordering of exchange-coupled sites in magnetic media [111]. In his study of Heisenberg models, Klein [7] elaborated six theorems that specify conditions which the exact ground state for the model must satisfy. These conditions lead to prediction of a number of the physicochemical properties of these systems at a quantitative level. In the case of π -electron networks of hydrocarbons, the above conditions may be regarded as valence-bond analogs of some of the more well-known theorems for HMO descriptions of the hydrocarbons [8]. Klein and collaborators [8] also made use of alternant graphs in connection with the prediction of the existence of a class of very high-spin hydrocarbons. Such systems, which have been termed "organic ferromagnets", seem to have a high probability of physical existence, although they may be highly reactive and difficult to prepare [8]. It is possible that such networks may be stabilized by functional groups attached to the network. Further research along these lines will be necessary to determine whether the promise of these theoretical studies can become reality. What is certain, however, is that approaches of this type lead to a number of important predictions of the properties of an exciting range of materials and will perhaps one day eventually yield sufficient insights to make production of the materials themselves possible.

8. Conclusion

We conclude this review of the first fifty years of the Coulson–Rushbrooke Theorem by re-emphasizing a general, philosophical point that the present authors have stated elsewhere [4b,5,112–114]. We have shown that parts (1) and (2) of the Coulson–Rushbrooke Theorem “. . . have an underlying mathematical significance outside the context of, not merely the HMO model, but quantum chemistry and, indeed,

chemistry itself" [4b]. This is because, when the simplest HMO approximations are invoked, there is an exact isomorphism between HMO energy levels and LCAO-MOs on the one hand and, on the other, eigenvalues and the corresponding eigenvectors, respectively, of the associated molecular graph. Part (3) of the Coulson–Rushbrooke Theorem, with its reference to π -electron atomic charges, would appear less obviously to have a topological basis. As we have previously pointed out [4b,5], the concept of "charge", as defined in the HMO method [4], implicitly involves the *Aufbau* process, embracing the Pauli Exclusion Principle and Hund's Rules, for assigning π -electrons to the available orbitals. We have shown [112–114], however, that the *Aufbau* scheme may be simulated by a completely nonphysical algorithm to yield energy level occupation numbers which may be regarded as *entirely graph-theoretical quantities* since, once the algorithm [112,113] has been established, they are predetermined by the relative magnitudes of the *eigenvalues* of the molecular graph in question. Once these energy level ("eigenvalue") electron occupation numbers have been thus obtained, the π -electronic charge densities on the constituent carbon atoms of a conjugated hydrocarbon then depend only on the *eigenvectors* of the hydrocarbon's molecular graph [112]. Charge densities may, therefore, *also* be considered as purely topological quantities (at least for the case of neutral hydrocarbons). It is for this reason that the present authors have already proposed [112,113] that the concept of atomic charge might usefully be regarded as an abstract, nonphysical, graph-theoretical index which is a characteristic of the vertices of certain nonbipartite graphs, and have extended this by venturing to suggest [5] that graph theorists "... might do well to examine closely other molecular orbital indices (such as bond orders, polarizabilities, etc.) that chemists have devised in the course of their study of planar, conjugated systems" [5]. It can, therefore, be argued that all three parts of the Coulson–Rushbrooke Theorem of 1940, including the one concerned with uniformity of atomic charge, have an entirely topological basis in that, in the final analysis, their validity depends solely on the carbon atom connectivity of an alternant hydrocarbon.

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