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Topological Ring-Currents in Conjugated Systems[1]

T. K. Dickens[2], R. B. Mallion[3]

[2]*University Chemical Laboratory, University of Cambridge, Lensfield Road,*
Cambridge CB2 1EW, England, United Kingdom

[3]*School of Physical Sciences, University of Kent,*
Canterbury CT2 7NH, England, United Kingdom

tkd25@cam.ac.uk, R.B.Mallion@kent.ac.uk

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Abstract

The Review traces the detailed development of the graph-theoretical, topological approach to the concept of π-electron ring-currents and bond-currents in conjugated systems and covers the period from its original proposal in the 1930s up to the present day. Semi-quantitative and quantitative comparisons are made between numerical predictions based on the concept of topological ring-currents and the results of several sets of *ab initio* calculations that have become available only over the course of the last five years. This process reveals the remarkable ability of the topological approach to reproduce complex patterns of current in large polycyclic hydrocarbons and the surprising extent to which Hückel-based models can capture the essential features of the magnetic properties of delocalised systems. *Ab initio* procedures for the calculation of the magnetic properties of conjugated systems frequently depend first on the application of elaborate software in order to optimise starting geometries and then on the choice of wave-function basis-set employed; despite the appellation '*ab initio*', such approaches thus still require prescriptions for specific wave-functions and possibly other assumptions. It is, accordingly, claimed that, even with the present-day routine availability of *ab initio* calculations, the simple topological Hückel–London–Pople–McWeeny approach, dating back to the very early days of molecular-orbital theory, still has intuitive and even quantitative contributions to make to our understanding of the magnetic properties of conjugated systems. Application of this approach depends on knowledge only (a) of the molecular graph of the conjugated system in question (in the form of a vertex-adjacency matrix that describes its connectivity) and (b) of the areas of its constituent rings — and on no other parameters or procedures whatsoever.

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[1] RBM would like to dedicate this Review to his mentor in this field, Mr. C. W. Haigh, on the fiftieth anniversary of their initial collaboration in 1966 and in anticipation of CWH's ninetieth birthday (on April 2nd, 2017).

1. Introduction and Scope

In this contribution, we review the concept of *topological ring-currents* in conjugated systems and outline the historical development of ideas about them. We emphasise from the outset that the somewhat unfortunate use of the adjective 'topological' in this context is confined to its effectively being nothing more than a synonym for the description 'graph-theoretical'; accordingly, the term 'topological', as applied here, carries none of the connotations usually associated with algebraic topology *per se* (*e.g.*, ref. [1]). The appellation 'topological' is also liable to create even more ambiguity in the present context of magnetic properties in view of Gomes's seminal and complete description [2] of the electronic probability current-density field in molecules under the influence of an external homogeneous magnetic field. Nevertheless, we do, however, continue the practice of using the description 'topological' in this review, in deference to what has become common usage (*e.g.*, refs. [3–12]) — it was initially invoked more than sixty years ago [3] and is now well established — even though, if the terminology were being devised anew in the modern era, we should prefer to call the subject of our review 'graph-theoretical ring-currents'.

That said, however, one area [13–20] of what might properly be called 'graph-theoretical ring-currents' is expressly excluded from our consideration here: this is the approach based on the concept of what Randić [13, 17, 18] calls 'conjugated circuits' and what Gomes and one of the present authors (RBM) [14, 15] independently named 'circuits of conjugation'. We shall instead be concentrating solely on the quantum-mechanical Hückel [9]–London [21–23] formalism (1937) of π-electron ring-currents, and on subsequent versions of it up to the present day. In its own right, the Hückel–London method [21–23] has previously featured prominently in numerous extensive reviews (see, for example, refs. [24–31]). We begin by setting the historical scene for the appearance of the Hückel–London approach [9, 21–23].

2. Before Hückel–London

During the 1920s and 1930s a large body of experimental evidence accumulated for the belief that there existed a pronounced anisotropy in the diamagnetic susceptibility of benzene and other (geometrically) planar, conjugated hydrocarbons [28]. The component of this susceptibility perpendicular to the molecular plane was observed to be appreciably larger than that measured along each of two mutually perpendicular axes situated in the molecular plane itself, when the conjugated system in question is subjected to an external magnetic field with a component perpendicular to the plane containing the carbon atoms [28].

In the mid-1930s Linus Pauling [32], working at the California Institute of Technology, and Dame Kathleen Lonsdale [33], at the Royal Institution, London, independently, and almost simultaneously, presented formal calculations based on similar models that purported to account quantitatively for this phenomenon. They both proposed that this manifest anisotropy in the diamagnetic susceptibility of such molecules might be explained by a model in which inter-atomic currents arise, as Pauling [32] put it, from the ability of the π-electrons in benzene to pass ' . . . almost imperceptibly from the field of one carbon atom to that of the next . . .', in a preferred sense around the ring. Dame Kathleen [33] argued that the excess diamagnetism at right angles to the molecular plane in benzene '. . . is due solely to, and is the entire contribution of, the precession of the π-electron orbits . . .' and she further observed that such electronic movement '. . . is implicit in the theory of molecular orbitals, as applied by Hückel [34] to aromatic and unsaturated molecules.' Moreover, Pauling [32] classically invoked Maxwell's Rules and Kirchhoff's Conservation Law [19, 35] and treated a general conjugated system in the presence of an external magnetic field as if it were a microscopic version of a macroscopic Kirchhoff network with a fall of electrical potential applied across it (*cf.* ref. [29]). The work of these two eminent scientists demonstrates a classic 'priority issue': Lonsdale [33] published in the *Proceedings of the Royal Society of London* and Pauling [32] published in the (then) recently established *Journal of Chemical Physics* which, in those days, had a shorter publication time [29, 30]. Lonsdale wrote, in her Introduction to ref. [33]: 'This work was begun and completed and the following paper written, in ignorance that Pauling was making the calculations described in his recent paper, and it therefore adds independent evidence in favour of the essential principle.' Pauling's paper was received by the American Institute of Physics on July 11th, 1936, and published in the October issue of the *Journal of Chemical Physics*; Dame Kathleen's contribution was received by the Royal Society, in London, on October 21st, 1936, but was not published until March 2nd, 1937. Many more authors, therefore, over the years, have acknowledged only Pauling than have recognised the two proponents of this model. This dichotomy continues even to the present day — witness Kutzelnigg's otherwise impeccable recent essay entitled 'What I like about Hückel Theory' [36].

It should, however, be emphasised that, although Pauling [32] and (less so, as noted) Lonsdale [33] are traditionally credited with the concept of 'inter-atomic currents' in these situations, such suggestions did not just suddenly appear from nowhere, in their work: precursors of such ideas had in fact previously been mooted by others [28]. Some three or four years earlier Ubbelohde [37] had explicitly stated that what are now known as the π-electrons in certain three-ring and four-ring condensed benzenoid hydrocarbons that had then just been shown (by Iball and Robertson [38]) to be geometrically planar '. . . have a certain possibility of movement to other nuclei within the same molecule. . .' and that this would lead to an expected anisotropy in magnetic susceptibility. Ubbelohde [37] also made comparisons with the theory of metallic bonding, delocalisation effects in which were then being examined by Peierls [39]. These hypotheses and suggestions had certain parallels with analogous, and even earlier, ideas of Ehrenfest [40] and of Raman [41]. Accordingly, although Linus Pauling [32] and Dame Kathleen Lonsdale [33] are usually credited with what is now known as the 'ring-current' model — though they emphatically did not use that term, which arose [in English] only 15–20 years later [42, 43], and in French (‘*courant annulaire*’) within a year [22] — it should be borne in mind that even they (like, apocryphally, Sir Isaac Newton himself) ‘. . . stood on the shoulders of giants’.

Furthermore, despite the appearance, five years earlier, of Hückel’s revolutionary ideas [34, 9] on unsaturated hydrocarbons, and the (then) recent availability of Van Vleck’s celebrated quantum-mechanical treatise on magnetism [44], the theoretical treatments offered by Pauling [32] and by Lonsdale [33] were both ‘avowedly classical’ [28–30] in nature, relying, as they did, on the phenomenon of Larmor precession and on formulae derived from the classical Langevin scheme [28]. It was London [21–23], in 1937, who successfully coalesced the quantitative classical ideas of Pauling [32] and Lonsdale [33] — and the qualitative deliberations of their predecessors [37–41] — with Hückel’s contemporary theory [34] of molecular orbitals, finally to give an elegant quantum-mechanical rationalisation of the observed anisotropy in the magnetic susceptibility of conjugated systems. London’s main account was a substantial publication [21] in the 7th series of *Journal de Physique et le Radium* but, in addition, he heralded this with two shorter communications — presumably for the purposes of wider dissemination of his message — aimed, respectively, at European, and at American, readers: a contribution to the 1937 *Comptes Rendus* (*Paris*) (in French) [22] and a note in the *Journal of Chemical Physics* (in English) [23]. It is to the London approach [21–23] that we now turn attention for much of the rest of this review.

3. The Hückel–London Approach

In this section we give just the bare bones of the London method that are going to be needed in the subsequent discussion: readers requiring further details are referred to London’s own papers [21–23] and to numerous reviews that have become available over the course of many years (*e.g.*, refs. [24–31] and [45] & [46]). For the world-historical context of this work in the form of a detailed account of London’s life and times a detailed biography by Gavroglu may be consulted [47], while Hückel’s circumstances and career during the turbulent decade of the 1930s are well documented in the book by Berson [48].

The essence of London’s approach was to show that, when a planar conjugated system is in the presence of an external magnetic field with a component at right angles to the molecular plane, the non-zero off-diagonal elements, β_{pq}, $p \neq q$, of the Hückel secular determinant [9, 34] are modified from the corresponding field-free values, $\beta_{pq}^{(0)}$, by imaginary exponential phase-factors that depend on the external magnetic field and on certain geometrical areas. Thus (*e.g.*, ref. [49]):

$$\beta_{pq} = \beta_{pq}^{(0)} \mathrm{e}^{2\pi \mathrm{i} f_{pq}} \qquad (1),$$

where

$$f_{pq} = \frac{eB_0}{hc} S_{pq} \qquad (2),$$

in which B_0 is the magnitude of the component of the external magnetic field perpendicular to the molecular plane and S_{pq} is the area of the triangle formed by the (arbitrarily selected) origin, *in* the molecular plane [50], and the vertices (carbon atoms) p and q of the conjugated system being considered; (e, h, and c are the usual constants with these symbols and $\mathrm{i} = \sqrt{-1}$). It is important to note that S_{pq} is an *algebraical* area — that is, $S_{qp} = -S_{pq}$. It can then be shown [21–31] that (in modern units and symbolism, consistent with the *Système International*) the molecular diamagnetic susceptibility, χ^{π}, arising from the inter-atomic π-electron currents — what might be called 'the London contribution to magnetic susceptibility' — is given by

$$\chi^{\pi} = -\mu_0 \left(\frac{\partial^2 E^{\pi}}{\partial B_0^2} \right)_{B_0=0} \qquad (3),$$

where μ_0 is the permeability of a vacuum, and E^{π} is the total magnetic energy, itself defined by

$$E^{\pi} = \sum_K \nu_K E_K \qquad (4),$$

in which ν_K is the electron occupation number of the orbital with energy E_K when the *Aufbau* process has been applied [10, 12, 51–53].

In the light of all the experimental activity reviewed in the preceding section London [21–23] was of course entirely concerned solely with the overall magnetic susceptibilities of the conjugated systems that he studied, applying his method to calculate the π-electron contribution (the 'London contribution') to the diamagnetic anisotropies of benzene, diphenyl, naphthalene, phenanthrene and pyrene. He did not feel the need to compute individual ring-current intensities in the several rings of such systems: the impetus for that activity did not arise until the advent of ^{1}H-nuclear-magnetic-resonance (NMR) spectroscopy, some twenty years later, in the early 1950s [54]. Subsequent work [25–31] did, however, show that, in the London method [21–23], the individual ring-current intensity, J_i, in the i^{th} ring may be represented by

$$J_i = -\frac{e}{h} \left(\frac{\partial E^{\pi}}{\partial f_i} \right) \qquad (5),$$

where

$$f_i = \frac{eB_0}{hc} S_i \tag{6}$$

and S_i is the signed area of the i^{th} *ring* of the conjugated system; in the case of a closed-shell system, by combining equations (4) and (5) we may write the latter thus [20, 29]:

$$J_i = -\frac{2e}{h} \sum_{K=1}^{\text{occ}} \left(\frac{\partial E_K}{\partial f_i} \right) \tag{7}$$

Furthermore, for a system comprising *r* rings, the quantity χ^{π} in equation (3) — the quantities that London was primarily interested in — may be cast in terms of the individual ring-currents, $\{J_i\}$, as [29]:

$$\chi^{\pi} = \frac{\mu_0}{B_0} \left(\sum_{\substack{\text{(rings)} \\ i\,=\,1}}^{r} S_i J_i \right) \tag{8}$$

Finally, as Gomes and one of the present authors (RBM) have emphasised [29], if $\chi^{\pi}_{\text{benzene}}$ stands for the 'London' contribution to the diamagnetic susceptibility of benzene, perpendicular to its molecular plane (calculated from equation (8)), whilst S_{benzene} represents the area of a standard benzene hexagon and J_{benzene} is the ring-current intensity calculated, by the same method, for benzene, then the following pleasingly simple result [29] is obtained:

$$\left(\frac{\chi^{\pi}}{\chi^{\pi}_{\text{benzene}}} \right) = \sum_{\substack{\text{(rings)} \\ i\,=\,1}}^{r} \left(\frac{S_i}{S_{\text{benzene}}} \right) \left(\frac{J_i}{J_{\text{benzene}}} \right) \tag{9}$$

The equivalent of equations (3), (7) and (9) was applied by London [21–23] to the several condensed, benzenoid hydrocarbons mentioned above, thereby providing the first quantum-mechanical account of the diamagnetic anisotropies in these fundamental conjugated structures.

Two years later, however, World War II intervened — an event that had considerable effect on London's personal life [47] — and, pre-1941, there was one application by Squire [55], in 1938, (which studied coronene by London's method), two by Brooks [56, 57] (investigating the relevance of overlap integrals in the context of London's method), and the introduction of the free-electron ('box' ['*Kasten*']) model [58], by Schmidt (*e.g.*, ref. [59]). After that, little more was done on the subject until the late 1940s and early 1950s. When activities did resume, a decade after London's original papers [21–23], this was largely in France (where London had taken refuge [47] at the time when he wrote his 1937 papers [21–23]) and in the United Kingdom. The French work [24, 60–66] was largely by Berthier, Mayot, Bergmann, Bernard Pullman, Alberte Pullman, Hoarau, and Pacault, and the British contribution was almost exclusively due to McWeeny [42, 67–70]. Rogers [71], and Evans, De Heer & Gergely [72] and Pauncz & Berencz [73, 74] also applied or discussed the London method during this immediate post-war period. Some of this concerned the minutiae of the pre-war work: for example, Rogers [71] claimed that there were errors in Squire's results [55] on coronene, and McWeeny [42] later expressed satisfaction that this discrepancy had eventually been resolved. It may be noted in passing that the value (9.796) quoted by McWeeny [42] 65 years ago in 1951 for the diamagnetic anisotropy of coronene, expressed as a ratio to the benzene value, is consistent (to within four digits in the third decimal-place) with the most-recent [31] topological ring-current values for coronene (1.038 for the inner ring, 1.459 for the six outer rings). These are the result of a modern, double-precision computer calculation reported by the present authors in ref. [31]; (this agreement arises because, on applying equation (9), above, we see that $(1\times1.038) + (6\times1.459) = 9.792$ — to be compared with McWeeny's value [42] of 9.796). This is also consistent with another modern (and independent) calculation, by Aihara [75].

4. The 1950s — Pople & McWeeny

As has been observed by Haigh and one of the present authors (RBM) [28], there are two distinct processes for calculating the 'London' magnetic susceptibility [21–23] of a conjugated system: either directly, from the eigenvalues and eigenvectors of the modified secular determinant [9, 34] (*via* equation (3)) and knowledge of an assumed molecular geometry — this was the approach adopted by London himself [21–23] — *or* χ^{π} can be computed, by means of equation (9), *via* an intermediate calculation of the π-electron ring-currents associated with each individual ring of the conjugated system in question (together with, once again, knowledge of an assumed molecular geometry).

The motivation for considering intermediate ring-currents arose only when the phenomenon of NMR spectroscopy more widely presented itself in the early 1950s [28, 43, 54]. This caused Sir John Pople [76], in 1956, to resurrect the Pauling–Lonsdale model [32, 33] of 1936/1937 and extend it so that, in addition to explaining diamagnetic anisotropy, it was also able to account for the ^{1}H-NMR downfield-shifts of in-planar protons in conjugated molecules such as benzene [76] and in polycyclic conjugated systems [43]. Pople's first contribution [76] was unashamedly classical, along the lines of Pauling's [32] and Lonsdale's [33] formulations on benzene, and, with Bernstein and Schneider [43], he extended these investigations to polycyclic systems. One of the present authors (RBM) has claimed that the latter study was the first explicitly to use the term 'ring current' (in English), in this context [30]. This assertion is in fact not correct, as we now find that the term was used at least five years earlier — by McWeeny, during the course of his classic work reported in ref. [42] and discussed above. In addition, it may be noted that London had already used the French equivalent of the term 'ring current' — '*courant annulaire*' — in one [22] of his classic papers from 1937.

Very soon afterwards, however, in 1958, Pople did offer a quantum-mechanical model of π-electron ring-currents, based on the Hückel–London approach [21–23], in a seminal paper entitled [77] 'Molecular Orbital Theory of Aromatic Ring Currents' published in Volume 1 of *Molecular Physics.* Independently, in an article in the same volume of the same journal entitled 'Ring Currents and Proton Magnetic Resonance in Aromatic Molecules', McWeeny published an alternative (but equivalent) approach [78] to the calculation of relative ring-current intensities — also based on the Hückel–London formalism [21–23] — that was expressly tailor-made for application to the (then) recently established phenomenon of ^{1}H-NMR (*e.g.*, refs. [28, 43 & 54]).

Before discussing these classic contributions to the field, we just make mention of an advance that should chronologically be placed in the early 1950s (May 16th, 1953, to be precise) but which was not known to a wider public for some 35 years. In a hand-written manuscript bearing the said date [79], a mentor of one of the present authors (RBM), the late Professor C. A. Coulson, FRS, cast the London theory [21–23] in terms of his own contour-integral formulation [80] of the Hückel model [9, 34]. In 1953, Coulson was presumably inspired by the contemporary work going on in France [24, 60–66] and in England [42, 67–70], already mentioned: he does indeed make reference to some of these papers in the document in question [79]. Especially connected with it is McWeeny's [42] pioneering work of two years earlier, which also invoked a Coulson contour-integral approach [80]. As Haigh and one of the present authors (RBM) have pointed out [28], Coulson's 1953 contour-integral formulation [79] of the Hückel–London formalism [21–23], being based, as it is, on bond-bond polarisabilities (discussed later), '. . . provides an interesting parallel to certain aspects of the McWeeny polarisability method [78]. . .', which was to emerge five years later, although the former '. . . does not provide for the explicit computation of individual "ring current" intensities nor . . . (since it preceded the experimental observation [43, 54]) for direct calculation of "ring current" secondary fields (and hence ^{1}H-NMR chemical shifts).' Coulson's contribution [79] of May 16th, 1953 did, however, remain unpublished and it came to light only when, more than twenty years later, one of us (RBM) was helping Mrs. Coulson to sort and catalogue her late husband's papers after the latter's death (which occurred on January 7th, 1974). Even then, Coulson's hand-written manuscript was not at the time explicitly made public, it being simply deposited with the rest of his papers in the Coulson Collection held by the Department of Western Manuscripts at the Bodleian Library, University of Oxford [79]. Some fifteen years after Professor Coulson's demise — and more than 35 years after he had assembled his original notes — Mizoguchi [81] independently published a further elegant exposition of the London method [21–23] in terms of the Coulson contour-integral formalism [80]; it was therefore decided (with Mrs. Coulson's permission) to write up and publish Coulson's contribution which, up till then, had been 'private'. This project was achieved in collaboration with Professor Brian O'Leary, another former member of Professor Coulson's group, and the result was published (as what was designated as a 'Special Paper') in the 1989 *Journal of Mathematical Chemistry* [49].

What Pople [77] and McWeeny [78] did in their respective 1958 modifications of the original Hückel [9, 34]–London [21–23] formalism had slightly different emphases: Pople [77] was concerned with calculating individual ring-current intensities and, in order to effect this, he offered an expression (equations (2.23), (2.24) and (3.4) of ref. [77], which amount to equation (82) of ref. [28]) that — at least, implicitly — is equivalent to our equation (7), above. McWeeny [78], by contrast, was more interested in accounting for ^{1}H-NMR chemical shifts by a direct quantum-mechanical calculation of the total secondary magnetic field at a given peripheral proton in a conjugated molecule, due cumulatively to the influence of the ring currents in each and every one of the several rings within such a polycyclic system. McWeeny did this by introducing a 'test dipole' [78, 82–84] and he presented essentially three (numerically equivalent) versions of his theory [78];

(i) one (represented by equations (4.4) and (4.5) of ref. [78]) in which the secondary magnetic field at a peripheral proton is estimated as a sum of contributions due to the *bond* currents in each of the individual carbon–carbon bonds in the conjugated system under study, and

(ii) one (embodied in equations (4.4) and (5.4) of ref. [78]) that involves a summation over a certain set of *r cycles* within the *r*-ring system (the so-called Fundamental System of Cycles, to be discussed later), and

(iii) one (equation (6.1) of ref. [78]) in which a sum is effected, over the *r rings* possessed by the structure, of all the contributions due to the *ring* currents in each of its individual *rings* — though without necessarily invoking any intermediate explicit calculation of actual numerical ring-current intensities *per se*.

The latter two versions were achieved by devising and applying a clever unitary transformation on the basis orbitals in such a way that all the perturbation brought about by the presence of the external magnetic field with a component normal to the molecular plane is concentrated into just *one bond* in *each ring* of the conjugated system under study — the so-called 'circuit/cycle-completing' bonds (*e.g.*, refs. [29–31 & 78]), discussed later. This transformation not only simplified the calculation but demonstrated that the presence of what McWeeny called 'closed circuits' of carbon atoms in the conjugated system under study is a necessary requirement for ring currents to arise at all, and that, ' . . without such circuits, the [external] field has no effect . . .' in exciting ring currents [78]. Pople [77] had also explicitly demonstrated a similar result, in a different (but equivalent) way, and he concluded that '. . . if there are no closed cycles of bonds (as in linear polyenes for example), all solutions . . . will be independent of the magnetic field, corresponding physically to the absence of ring currents'. Many years earlier, London himself [22] had further pointed out that the electrons in a cyclic, but saturated, system (such as cyclohexane) '. . *au contraire . . . ne donnent donc, dans un champ magnétique*, *naissance à aucun courant annulaire résultant.*' This translates as '. . . so [*such electrons*], on the contrary, in a magnetic field, give rise to no resultant ring-current'. Note incidentally that this quotation also clinches the first use of (the French equivalent) of the term 'ring current'.

As already remarked, although an expression for ring-current intensity is implicit in equation (6.1) of ref. [78], McWeeny [78] did not explicitly formulate calculation of individual ring-current intensities by his method. However, a straightforward extension by one of the present authors (RBM) provided for this. Two versions were given: one [84] a generalised expression that can be used if variable Hückel Coulomb and resonance integrals [9, 34] are to be invoked, and another [85], which is a simplified special case of the first, that is appropriate if all Coulomb and resonance integrals, in whatever conjugated structure be considered, are set at the respective standard values for benzene. In view of the 'topological'/'graph-theoretical' approaches almost exclusively being reviewed here, this second, simplified, version is the one presented in equation (10), for the moment. (The full version will, however, arise later, as equation (12), when extensions to this method are considered.)

$$\left(\frac{J_i}{J_{\text{benzene}}}\right) = 9\left\{\sum_{(\mu)}[P_{(\mu)} + \beta\overline{\pi}_{(\mu)(\mu)}]S_{(\mu)}\,C^i_{(\mu)} + \sum_{(\mu<\nu)}\sum_{(\nu)}\beta\overline{\pi}_{(\mu)(\nu)}[S_{(\mu)}C^i_{(\nu)} + C^i_{(\mu)}S_{(\nu)}]\right\} \tag{10.}$$

The $\{P_{(\mu)}\}$ are the standard Coulson bond-orders [9] of the individual circuit/cycle-completing bonds [31] and the $\{\overline{\pi}_{(\mu)(\mu)}\}$ and $\{\overline{\pi}_{(\mu)(\nu)}\}$ (which are self- and mutual imaginary bond-bond polarisabilities [78, 85], respectively, of such bonds) are all quantities that are calculable (a) from the (field-free) Hückel energy-levels and LCAO-MO coefficients and (b) from knowledge of an electronic ground-state for the structure, as constructed from the *Aufbau* process [10, 12, 51–53], and as described in detail in, for example, refs. [78, 84 & 85] (especially Appendix A of that latter reference), and refs. [29–31], and also as prescribed in the equations below. For the bonds between carbon atoms *r* and *s* and between carbon atoms *t* and *u*:

$$P_{(rs)} = \sum_{J=1}^{N} \nu_J\, c_{Jr}\, c_{Js} \tag{11}$$

and

$$\overline{\pi}_{(rs)(tu)} = \pi_{rs,tu} - \pi_{rs,ut} + \pi_{sr,ut} - \pi_{sr,tu} \tag{12),}$$

where

$$\pi_{rs,tu} = \frac{2}{\beta}\sum_{I=1}^{M}\sum_{J=M+1}^{N}\frac{c_{Ir}\,c_{Js}\,c_{Jt}\,c_{Iu}}{E_I - E_J} \tag{13),}$$

where the orbitals 1 to *M* are (doubly) occupied and *N* is the total number of orbitals. In equations (11) and (13), $\{\mathbf{c}_J\}_{J=1,2,\ldots,N}$ $(=\{(c_{J1}\, c_{J2}\ldots, c_{JN})^T\}_{J=1,2,\ldots,N})$ is the set of eigenvectors of the vertex-adjacency matrix [86] of the (*N*-vertex) molecular graph [11] (*i.e.*, the standard, field-free LCAO-MO Hückel coefficients [9]), $\{E_J\}_{J=1,2,\ldots,N}$, is the family of eigenvalues of that molecular graph (that is, the Hückel energy levels, when expressed in the conventional [9] form $\varepsilon_J = \alpha + E_J\beta$), and $\{\nu_J\}_{J=1,2\ldots,N}$ are the energy-level/eigenvalue occupation numbers, obtained by an application of the *Aufbau* Principle [10, 12, 51–53].

The meaning of the term ‘circuit/cycle-completing bond’ will become clear in the course of studying the example that follows. Also in equation (10), it is important to note that the $\{C^i_{(\mu)}\}$ are purely topological in nature (and will also be discussed later) but that the quantities $\{S_{(\mu)}\}$ are, by contrast, *geometrical*, because they depend on the *areas* of the several individual rings comprising the polycyclic conjugated system in question.

5. Worked Example of Application of the McWeeny Method

In a recent account [31], the present authors gave an extended example of equation (10)’s application to a seven-ring system (coronene); earlier, Gomes and one of us (RBM) illustrated an application of the method to the four-ring benzenoid hydrocarbon pyrene [29, 30] (originally presented in ref. [45]) while a later work [87] illustrated the method as applied to the carcinogen 3,4 benzopyrene. We present a simpler example here, which should make McWeeny’s methodology [78] even more clear because — as in the case of McWeeny’s original example (naphthalene) [78] — the molecule in question has a small enough number of rings (just two) that, once the required molecular-orbital quantities have been computed, the ‘master’ equation ((10)) can be applied to it ‘by hand’, ‘on the back of an envelope’, as-it-were, without having to invoke extensive arithmetical electronic computation. The detailed steps of the calculation should, accordingly, be easier for the reader to follow. We therefore now perform a calculation by the McWeeny method [78] on the paradigm non-alternant two-ring system azulene, with its carbon-atoms and its rings numbered as in Figure 1. (This structure was, incidentally, the one used by Pople, in his original paper of 1958 [77], in order to demonstrate application of his own method [77], computationally numerically equivalent to McWeeny’s [78], which appeared later that same year.) It is hoped that the example may serve to justify a previous claim [87] of one of the present authors (RBM) — who, like Kutzelnigg [36] has an unashamed attachment to the HMO method — that the McWeeny formalism is ‘. . . one of the most exquisite applications of Hückel Theory’ [87].

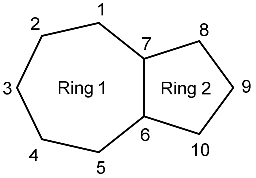


Figure 1. A (vertex-) labelled molecular graph [11] of azulene, with ring labellings added.

From here onwards it will be necessary to move more formally into the language of Graph Theory [11, 12, 86, 88, 89]. We shall therefore refer to Figure 1 — though without the added embellishments 'Ring 1' and 'Ring 2'— as the (arbitrarily) *labelled molecular graph of azulene.* A Chemist would say that azulene has two rings: a Graph-Theorist [88] would say that the molecular graph of azulene is of *circuit rank 2*. Accordingly, in order to apply the McWeeny method [78] it is first necessary to *delete* exactly *two* bonds (in the graph-theoretical language: *edges*) from the molecular graph in such a way as to leave a structure in which all the original carbon-atoms (in graph-theoretical language: the *vertices*) are still joined by *edges* (bonds) but the graph now no longer contains any closed circuits of vertices. Such an object (shown in Figure 2) is known as a *spanning tree* of the original molecular graph [31, 90–92]. In the case of azulene, there are 34 different ways [90–92] in which this could have been done and the way illustrated in Figure 2 has resulted in a path through the vertices that constitutes what McWeeny [78] called a '. . . chain which is continuous and open . . .' — that is, without branches. (In graph-theoretical language: we have chosen a semi-Hamiltonian path [31, 85, 93] through the original molecular graph of azulene.)

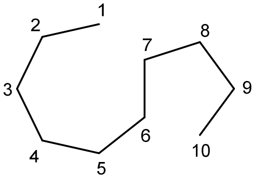


Figure 2. A continuous, unbranched spanning-tree of the azulene molecular graph depicted in Figure 1.

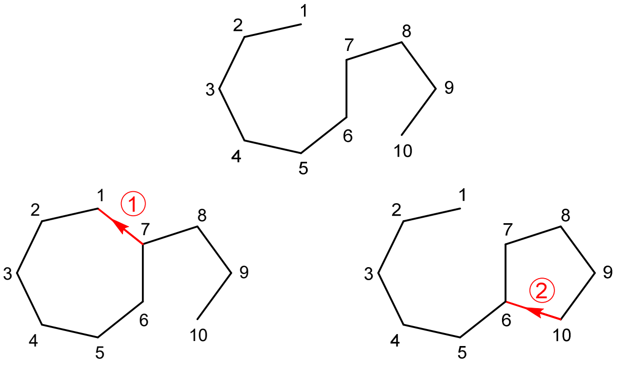


Figure 3. (*Above*): The continuous, unbranched spanning-tree (shown in Figure 2) of the labelled molecular graph of azulene depicted in Figure 1; (*Below*) the Fundamental System of Cycles [31, 88] associated with this spanning tree.

This was the procedure originally prescribed by McWeeny [78] when applying his unitary transformation on the basis orbitals. A later unitary transformation proposed by Gayoso and Boucekkine [94] enabled a branched spanning-tree to be chosen, if necessary (or, if not actually necessary, if desired). We shall give an example of the McWeeny [78] /Gayoso–Boucekkine [94] method, applied to such a spanning tree, a little later.

The next stage is to re-insert the removed edges, singly and one at a time, and to consider the closed circuits that are, thereby, re-formed. We also agree to associate a *sense* with each 'circuit-completing bond' by defining its direction as being *from* the vertex of higher number *to* the vertex of lower number, in the bond. (The opposite, or no, convention could equally well have been used, however.) The lower part of Figure 3 then shows what is known in Graph Theory as a Fundamental System of Cycles [31, 88] for the spanning tree depicted in Figure 2 (and at the top of Figure 3) — a 'cycle' being taken to mean a 'circuit' that has a sense of direction — clockwise or anti-clockwise — associated with it [31, 95, 96]. (It may, incidentally, be noted in passing [31] that this is precisely the procedure adopted by Kirchhoff [19, 35] in his classic work on macroscopic electrical networks, more than 160 years ago.)

Referring back to equation (10) we are now in a position to define the quantities $\{S_{(\mu)}\}$ and $\{C^{i}_{(\mu)}\}$. $S_{(\mu)}$ is the area created when the μ^{th} cycle-completing bond (*only*) is inserted into the chosen spanning-tree and this area is counted as *positive* if the direction of the arrow on that cycle-completing bond points in the *anti-clockwise* sense around the cycle that it completes and *negative* if the direction of its arrow points in the *clockwise* sense around the cycle that it completes. Thus, from Figure 3, $S_{(1)}$ is the area of a standard seven-membered ring with side equal in length to the carbon–carbon bond-length in benzene — *i.e.*, $S_{(1)} = 1.398693552$ benzene-hexagon units — and $S_{(2)}$ is equal to (minus) the area of a regular pentagon of that same side-length; hence, $S_{(2)}$ = –0.662212060 benzene-hexagon units. The quantity $C^{i}_{(\mu)}$ in equation (10) is +1, −1 or 0, according to the following rules:

(a) $C^{i}_{(\mu)}$ = +1 if ring i is contained within the cycle completed when the μ^{th} cycle-completing bond (only) is inserted, and the arrow borne by that cycle-completing bond points in the *anti-clockwise* sense around the cycle that it completes;

(b) $C^{i}_{(\mu)}$ = −1 if ring i is contained within the cycle completed when the μ^{th} cycle-completing bond (only) is inserted, and the arrow borne by that cycle-completing bond points in the *clockwise* direction around the cycle that it completes;

(c) $C^{i}_{(\mu)}$ = 0 if ring i is *not* contained within the cycle completed when the μ^{th} cycle-completing bond (only) is inserted.

With these definitions, it can be seen from the Fundamental System of Cycles shown in Figure 3 that, in this case, $C^{1}_{(1)}$ = +1; $C^{2}_{(1)}$ = 0; $C^{1}_{(2)}$ = 0; and $C^{2}_{(2)}$ = −1. The two bond-orders required are $P_{(1)}$ = 0.5857956297 and $P_{(2)}$ = 0.5956317960 and the two imaginary, self-bond-bond polarisabilities needed are $\beta\overline{\pi}_{(1)(1)}$ = –0.5292672672 and $\beta\overline{\pi}_{(2)(2)}$ = –0.5292672667. The one mutual imaginary bond-bond polarisability wanted is $\beta\overline{\pi}_{(1)(2)}$ (= $\beta\overline{\pi}_{(2)(1)}$) = – 0.0599151042. The necessary bond-orders are calculated from equation (11) and the imaginary bond-bond polarisabilities required are evaluated by means of equations (12) and (13); both the bond orders and the polarisabilities are computed from the unperturbed, field-free Hückel energy-levels and the LCAO-MO coefficients [9, 34], as well as from a knowledge of the ground-state π-electronic configuration, determined by an application of the *Aufbau* process [9, 10, 12, 51–53].

Finally, in the case of the two-ring system (azulene) being dealt with here, the summations and multiple summations featuring in our 'master' equation (10) may be dropped, and explicit expressions for the ring-current intensities in Ring 1 and Ring 2 of azulene (expressed as a ratio the ring-current intensity in benzene — equal to $-\frac{1}{9}$, in these units [31, 78], hence the factor of 9 in equations (10) and (14) — may explicitly be written out in full, as follows:

$$\left(\frac{J_1}{J_{\text{benzene}}}\right) = 9\{[P_{(1)} + \beta\overline{\pi}_{(1)(1)}]S_{(1)}C^{1}_{(1)} + [P_{(2)} + \beta\overline{\pi}_{(2)(2)}]S_{(2)}C^{1}_{(2)} + \beta\overline{\pi}_{(1)(2)}[S_{(1)}C^{1}_{(2)} + C^{1}_{(1)}S_{(2)}]\}$$

$$\left(\frac{J_2}{J_{\text{benzene}}}\right) = 9\{[P_{(1)} + \beta\overline{\pi}_{(1)(1)}]S_{(1)}C^{2}_{(1)} + [P_{(2)} + \beta\overline{\pi}_{(2)(2)}]S_{(2)}C^{2}_{(2)} + \beta\overline{\pi}_{(1)(2)}[S_{(1)}C^{2}_{(2)} + C^{2}_{(1)}S_{(2)}]\} \tag{14}$$

When all the data provided above are inserted into equations (14), it is found that the relative ring-current intensity in the seven-membered ring, $\left(\frac{J_1}{J_{\text{benzene}}}\right)$, is 1.068706423 and that in the five-membered ring is calculated to be 1.149752354 — agreeing, when rounded to three decimal-places, with the values originally published by Pople [77] (though not actually calculated by the McWeeny [78] method but rather by an application of Pople's own method [77]) and also agreeing with values recently re-calculated (using the McWeeny approach [78]) in a double-precision calculation carried out by the present authors [97]. This again empirically illustrates that the Pople [77] and McWeeny [78] methods, though superficially different, are in fact entirely equivalent, numerically, when comparable Hückel conventions are adopted and the same assumptions are made about molecular geometry.

It may be noted that any one of the 34 spanning trees [31, 90–92] of the azulene molecular graph (Figure 1) could have been selected as the starting point: for example, another unbranched spanning-tree which, in fact, also represents a semi-Hamiltonian path [31, 85, 93] through the original molecular graph shown in Figure 1, is illustrated in Figure 4, along with the Fundamental System of Cycles [31, 88] that is associated with it.

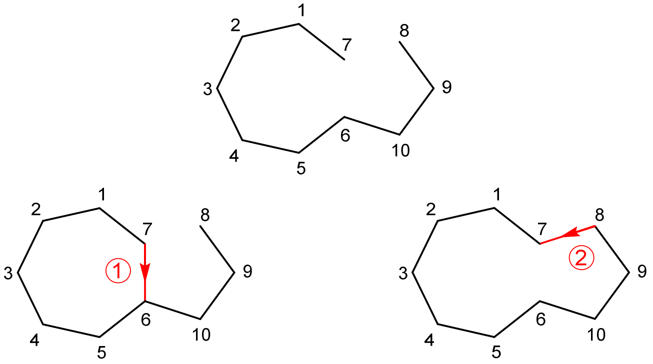


Figure 4. (*Above*): A second unbranched spanning-tree of the labelled molecular graph of azulene shown in Figure 1; this spanning tree is an alternative to the unbranched spanning-tree depicted in Figure 2. (*Below*) the Fundamental System of Cycles [31, 88] associated with the above spanning tree.

The relevant data needed here in order to apply equations (14) are now as follows:

$P_{(1)} = 0.4009446296$; $P_{(2)} = 0.5956317960$; $\beta\bar{\pi}_{(1)(1)} = -0.3978799460$; $\beta\bar{\pi}_{(2)(2)} = -0.5292672670$; $\beta\bar{\pi}_{(1)(2)} = 0.0064494251$; $S_{(1)} = -1.398693552$ benzene-hexagon units; $S_{(2)} = (0.662212060 + 1.398693552) = 2.060905612$ [the sum of the area, in benzene-hexagon units, of a regular five-membered ring and a regular seven-membered ring of the same side length]; $C^1_{(1)} = -1$; $C^2_{(1)} = 0$; $C^1_{(2)} = +1$; and $C^2_{(2)} = +1$. When these data are inserted into equations (14), the values 1.068706426 for the seven-membered ring, and 1.149752346 for the five-membered ring, are obtained. These agree with the results of previous calculations in the first seven or eight decimal-places and thus they certainly round to the same three-decimal-place values — traditionally reported for topological ring-currents [87] — as have previously, and independently, been obtained for azulene [77, 97].

For completeness, we conclude this illustrative example by carrying out the calculation one more time but, on this occasion, basing it on a *branched* spanning-tree which, therefore, does *not* represent a semi-Hamiltonian path [85, 93] through the azulene molecular graph [31, 85, 93]. This situation was not explicitly dealt with by McWeeny [78] but Gayoso and Boucekkine [94] showed how McWeeny's unitary transformation [78] can be generalised in order to encompass this case. The present authors have found from practical experience that, with persistence, a continuous ('non-branched') spanning-tree can be found through the molecular graphs of most conjugated systems commonly encountered, but not always [31, 85]: the Gayoso–Boucekkine transformation [94] therefore comes into its own in such cases — please see refs. [31 & 85] for discussion of this aspect. One practical repercussion is that the use of branched spanning-trees can frequently reduce the round-off error [31] in the calculation of topological ring-currents because, in general, each ring appears less frequently in the intermediate calculations than it does when the computation is based on a non-branched ('continuous') spanning-tree. Figure 5 shows a branched spanning-tree and the Fundamental System of Cycles [31, 85, 88] associated with it.

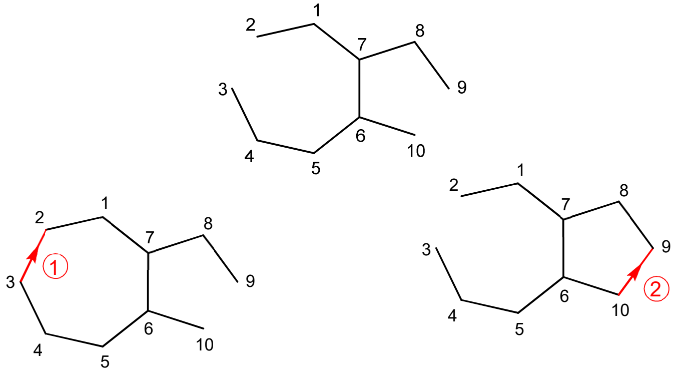


Figure 5. (*Above*): A branched spanning-tree of the labelled molecular graph of azulene shown in Figure 1. (*Below*): the Fundamental System of Cycles [31, 85, 88] associated with the above spanning tree.

The relevant data needed here in order to apply equations (14) are as follows: $P_{(1)}$ = 0.6388989804; $P_{(2)}$ = 0.6560392954; $\beta\overline{\pi}_{(1)(1)} = -0.5823686174$; $\beta\overline{\pi}_{(2)(2)} = -0.5896747660$; $\beta\overline{\pi}_{(1)(2)} = -0.0599151041$; $S_{(1)} = -1.398693552$ benzene-hexagon units; $S_{(2)}$ = 0.662212060 benzene-hexagon units; $C^{1}_{(1)} = -1$; $C^{2}_{(1)} = 0$; $C^{1}_{(2)} = 0$; and $C^{2}_{(2)} = +1$.

When these data are inserted into equations (14), we obtain ring-currents 1.068706427 for the seven-membered ring, and 1.149752347 for the five-membered ring. These agree with the previous estimates in the first eight decimal-places and so they again round to the same three-decimal-place values as have been obtained above, and in previously published independent calculations on this structure [77, 97]. The results are summarised in Figure 6, in which the diamagnetic ring-current in each of azulene's two rings are appropriately shown circulating in an anti-clockwise direction around that ring.

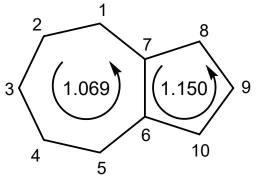


Figure 6. Summary of results of a McWeeny [78] ring-current calculation on azulene (Figure 1) when the constituent rings are assumed to have the areas of the corresponding regular polygons of side equal to the carbon–carbon bond-length in benzene. The 'topological' ring-currents are dimensionless quantities because they are expressed as a ratio to the corresponding ring-current intensity calculated, by the same method, for benzene.

So far as bond currents are concerned, by virtue of Kirchhoff's Law of Conservation of Current at a Junction [19, 35], there is a flow of magnitude 1.069 in the directions indicated in the bonds — in Figure 6 — (7→1), (1→2), (2→3), (3→4), (4→5) and (5→6) and a bond-current of magnitude 1.150 in the bonds (6→10), (10→9), (9→8) and (8→7). Because of the electronic competition in the bond (6–7), which is shared between the two rings, the net direction of flow of a current of magnitude 0.0081 (= 1.150 − 1.069) is in the direction 7→6. As Pople pointed out originally [77] (when he presented a calculation on azulene in order to illustrate application of his own method [77]), although the ring-current intensity in the seven-membered ring is the smaller (by some 7%, below that in the five-membered ring), this ring will, nevertheless, make the greater contribution to the London contribution to χ^{π}, by virtue of its much larger ring area; this is more than twice the area of the five-membered ring — approximately 1.399 benzene hexagons for the seven-membered ring compared with *ca.* 0.662 benzene-hexagon units for the five-membered ring. This observation is evident, from example, from a consideration of equation (9).

Finally, bearing in mind that, as previously observed, in the case of azulene there are 34 graph-theoretically distinct spanning-trees [90–92] on which the ring-current calculation could have been based, we draw attention to the following previous remarks [31] of the present authors that

> '. . . an HLPM ring-current calculation that capitalises on the McWeeny [78] and Gayoso–Boucekkine [94] unitary-transformations on the basis orbitals can be effected by beginning the computation starting from *any* spanning-tree whatsoever. This means, in the case of Coronene [31], that *any one* of 176400 spanning trees may be selected as the starting point. Furthermore, the remarkable fact is that, because of the myriad of relationships [46, 78, 81, 84] that exist between the Coulson bond-orders and the self- and mutual imaginary bond-bond polarisabilities for the 'circuit-completing' bonds, the final calculated ring-current intensities are independent of this overwhelming choice of starting spanning-tree that is available. No matter what spanning tree is chosen, the same ring-current intensities will, in the end, always result.'

6. The early 1960s – the late 1980s

A few years after McWeeny's work [78], Veillard, in a much-neglected paper [98], elegantly adapted it so that it could be applied to hetero-conjugated systems and to calculate ring currents in hydrocarbons without the restriction of having all resonance integrals [9] the same as the benzene value (or, indeed, having all Coulomb integrals [9] the same as the benzene Coulomb integral). Veillard's extension [98] can be expressed by the formulation below (first explicitly presented in ref. [84]) :

$$\left(\frac{J_i}{J_{\text{benzene}}}\right) = 9\left\{\sum_{(\mu)}\left[P_{(\mu)}\eta_{(\mu)} + \beta\bar{\pi}_{(\mu)(\mu)}\eta^2_{(\mu)}\right]S_{(\mu)}\,C^i_{(\mu)} + \sum_{(\mu<\nu)}\sum_{(\nu)}\beta\bar{\pi}_{(\mu)(\nu)}\eta_{(\mu)}\eta_{(\nu)}\left[S_{(\mu)}C^i_{(\nu)} + C^i_{(\mu)}S_{(\nu)}\right]\right\} \qquad (15),$$

where the symbols that also occur in equation (10) have the same meaning as they have there, and there are now two new symbols, $\eta_{(\mu)}$and $\eta_{(\nu)}$. The resonance integral, $\beta_{(\mu)}$, of the μ^{th} cycle-completing bond in the absence of an external magnetic field is given by

$$\beta_{(\mu)} = \beta\eta_{(\mu)} \qquad (16),$$

in which β is, as usual, the standard, Hückel resonance-integral in benzene [9]. It should be noted that any non-standard values chosen for some, or all, of the Coulomb integrals manifest themselves only *implicitly* in equation (15), by means of the effect that they have on the eigenvalues and eigenvectors of the molecular graph — that is, of the Hückel Hamiltonian matrix for the conjugated system — by virtue of changing some (or, possibly, all) *diagonal* elements of that matrix. These eigenvectors and eigenvalues then themselves, in turn, determine the values of those Coulson bond-orders, $P_{(\mu)}$, (*via* equation (11)) and imaginary bond-bond polarisabilities, $\bar{\pi}_{(\mu)(\nu)}$, (*via* equations (12) and (13)) that *do* feature explicitly in equation (15). Accordingly, setting some (or all) Coulomb integrals to a value different from the standard benzene value, α, does *not* give rise to any *explicit* mention, in equation (15), of any such non-standard Coulomb integrals *per se*. Any *resonance* integrals that are different from the standard benzene value, β, (as per equation (16), above) likewise have an implicit influence on the eigenvalues and eigenvectors of the molecular graph — by virtue of the change that they cause in some of the *off*-diagonal elements of the vertex-adjacency matrix/Hückel Hamiltonian matrix — thus affecting $P_{(\mu)}$ (*via* equation (11)) and $\overline{\pi}_{(\mu)(\nu)}$ (*via* equations (12) and (13)). However, any modified *resonance*-integrals ($\beta\eta_{(\mu)}$ — equation (16)) associated with the cycle-completing bonds are (unlike the modified *Coulomb* integrals) additionally — and *explicitly* — referred to in equation (15).

Figeys [99, 100] exploited the above facility, in the context of hydrocarbons, whilst one of the present authors (RBM) provided what have subsequently turned out to be rare examples of the application of Veillard's approach [98] to heterocycles (which, in these cases, yielded estimates of ring currents in some sulphur-heterocyclic analogues of fluoranthene [101] and some nitrogen analogues of certain carcinogenic, polycyclic hydrocarbons [102]). These calculations adopted the parameters suggested by Streitwieser [103] for Coulomb and resonance integrals that involve sulphur atoms and nitrogen atoms. Gayoso [104] further introduced the refinement of variation of resonance and Coulomb integrals into the original McWeeny [78]–Veillard [98] method — the reader is referred to p. 1359 of ref. [30] for more information about extensions and applications of the Veillard approach [98]. We do not go into further details here because, elegant as it is, the Veillard [98] formalism takes us away from purely 'topological' aspects because it is necessary to adopt (possibly subjective) parameters, such as Streitwieser's [103], or empirical/possibly subjective schemes for making wave-functions self-consistent with respect to iteratively calculated charges and bond-orders [105–109], specifically applied to magnetic properties by Gayoso [104] and (with Coulson [110] and with de Castro and with Gomes [111, 112]) by one of the present authors (RBM). Another major extension of the London method at this time was by Hall and Hardisson [113], who refined the McWeeny formalism [78] by using a self-consistent-field molecular orbital; however, as this is also somewhat removed from the realms of topological ring-currents, we do not discuss this approach any further, here.

The unmodified methods of Pople [77] and McWeeny [78] were applied to a wide range of conjugated systems from the early 1960s until the late 1980s [110–112, 114–128]. The majority of these calculations concerned the condensed, benzenoid hydrocarbons, ring-current intensities in large numbers of which were summarised in ref. [87]. The uptake of the McWeeny formalism [78] in these computations was much more frequent than the adoption of Pople's [77] method; to the authors' knowledge, the latter was used only three times — in refs. [115, 118 & 119]. In that latter reference, Jung [119] made a very important remark (these days very seldom cited) — namely, that π-electron systems exist which sustain diamagnetic currents in some rings and at the same time paramagnetic ring-currents in others. Jung therefore concluded [119] that *aromaticity cannot be defined in terms of* *ring current for such systems*. This pertinent observation was re-emphasised by one of the present authors (RBM) a decade later [124] and further given prominence in a major review (p. 1362 of ref. [30]); nevertheless, Jung's conclusion [119] appears not to be taken into account very frequently when modern authors invoke 'ring-current' criteria for 'aromaticity'.

It has been observed on several occasions [110–112, 123, 124, 126, 129, 130] that calculated *para*magnetic currents — which are especially sensitive to HOMO–LUMO separations — tend to be over-estimated by methods (such as the topological, non-iterative version of the HLPM [31] approach) which do not make Hückel resonance-integrals iteratively self-consistent with respect to the corresponding calculated Coulson bond-orders, and which, likewise, do not make Coulomb integrals iteratively self-consistent with calculated charge-densities on the carbon atoms. Again, however, we do not further discuss these refinements here because we are specifically reviewing concepts (topological ring-currents and bond-currents) that claim *to depend on no empirical or subjective parameters or prescriptions whatsoever.*

Before (in the next section) we move specifically to a consideration of what we call 'topological ring-currents' *per* se, we make brief mention of an explicitly graph-theoretical formalism, also based on the Hückel [9]–London [21–23] method, proposed by Aihara and co-workers [131–134]. This couches the London equations ((1) – (10)) in terms of graph-theoretical characteristic polynomials [9, 86, 89], $P_G(E)$, of the molecular graph, G, representing the conjugated system in question, and of graphs obtained from it by appropriately deleting certain cycles, r_k. Thus, in the notation of Aihara *et al*. [131–134]:

$$\left(\frac{I_k}{I_{\text{benzene}}}\right) = 18\left(\frac{c_k}{c_{\text{benzene}}}\right)\sum_{K}^{\text{occ}} \frac{P_{G-r_k}(E_K)}{P_G'(E_K)} \tag{17}$$

In equation (17), I_k is the current associated with the k^{th} cycle, r_k, within G — which is not in general just a single ring — and I_{benzene} is the corresponding current around the single cycle in benzene. In addition, c_k and c_{benzene} (the latter previously referred to in this Review as S_{benzene}) are the areas of the cycle r_k and of a standard benzene ring, respectively; $G - r_k$ is the graph remaining when the cycle r_k is deleted from G, and $P_G(E)$ and $P_{G-r_k}(E)$ are the characteristic polynomials [9, 86, 89] of the graphs G and $G - r_k$, respectively. $P_G'(E)$ is the derivative, with respect to E, of $P_G(E)$. E_K (with the same meaning as in equation (4)) is the K^{th} largest root of $P_G(E)$ and the summation runs over all occupied molecular orbitals, K, which, here, are assumed to be doubly occupied. (If $P_G(E)$ has repeated roots, this situation, too, can appropriately be accommodated — as described in refs. [131–133]). The ring-current intensity in the i^{th} ring, relative to benzene (J_i/J_{benzene} — *cf.* equation (10)), is then obtained by just *adding* the quantities I_k/I_{benzene} — some of which may be negative — computed from equation (17), over all cycles, r_k, that *contain* a specified *ring*, *i*, in which the *ring* current is required [131−134]. This approach, in the form of equation (13), gives numerical results that are entirely equivalent (within the limits of machine error) to those obtained from, for example, equations (7) and (10), when comparable Hückel assumptions [9] are made and the same molecular geometry is adopted. This now conveniently brings us to the central idea of a 'topological ring-current'.

7. The Concept of Topological Ring-Current

For more than fifty years it has been widely acknowledged (*e.g*., refs. [4−12]) that computing the Hückel energy-levels and Linear-Combination-of-Atomic-Orbitals Molecular Orbitals (LCAO MOs) for a given conjugated hydrocarbon is isomorphically equivalent to finding the eigenvalues and eigenvectors, respectively, of the associated (labelled) molecular graph [11] — that is to say, the eigenvalues and eigenvectors [89] of the vertex-adjacency matrix [86] of that molecular graph. Because that matrix is sometimes called the 'topological matrix' (*e.g.* refs. 4 and 7) of the graph in question, there has been a tendency — perhaps, in retrospect, an unfortunate one — to describe Hückel calculations as being 'topological' (*e.g.*, refs. [4−12]). However, as was emphasised right at the beginning of this Review, in our present context the term 'topological' does *not* have the connotations that are associated with it in the realms of Algebraic Topology (*e.g.*, ref. [1]): here, by contrast, it effectively means, simply, 'graph-theoretical'.

This much is, perhaps, intuitively self-evident to anyone who has ever actually carried out a Hückel calculation in practice. Less well emphasised and less frequently referred to is the fact that the *Aufbau* process is, in the context of Hückel Theory [*e.g.*, 9, 34], itself also entirely 'topological' (graph-theoretical) in nature [10, 12, 51−53], depending, as it does, on the relative *order* of the calculated HMO energy-levels. Application of the *Aufbau Prinzip* is needed [10, 12, 51−53], once the Hückel energy-levels/eigenvalues and LCAO-MOs have been calculated, in order to obtain a ground-state configuration for the π-electrons so that Hückel quantities — such as charge densities [9, 51], Coulson bond-orders [9] (equation (11)) and other indices such as imaginary bond-bond polarisabilities [12, 31, 78, 85] (equations (12) and (13)) — can be calculated; (see also especially Appendix A of ref. [85]). It is therefore important to emphasise that the *Aufbau* procedure *may itself also be mimicked by means of an entirely abstract*, *graph-theoretical algorithm*; for full details on this claim, please see refs. [10, 12, 51−53].

Coulson and one of the present authors (RBM) described some of the ring currents that they reported in ref. [110] not as being, in themselves, explicitly 'topological', but nevertheless being based on a 'topological *wave-function* (such as the simple Hückel one [9]). The same present author had earlier [85] considered whether ring currents were themselves topological quantities and concluded that, manifestly, they were not, because the expressions for ring currents (such as equations (10) and (15)) involve terms (the quantities $\{S_{(\mu)}\}$ in equations (10) and (15)) that represent *areas* which are, thereby, dependent on the actual *geometrical* areas that are assumed for the rings that comprise the conjugated system under study. *Prima facie*, therefore, it seemed that the ring currents themselves could not properly be described as being topological quantities, even when a topological *wave-function* (such as the simplest Hückel one with all Coulomb integrals and all resonance integrals set at the corresponding benzene values) has been used to calculate them. In 1976, Coulson and one of the present authors (RBM) put it this way [110].

> 'The Hückel matrix, with all α's the same and all β's equal, is isomorphic with [*the*] topological adjacency matrix. An attractive feature of the use of such an MO is that once given the *areas* of the various rings, *no* subjective or arbitrary parameters whatsoever are involved in the ring-current *ratios* (expressed relative to the benzene value). . . all are immediately and automatically determined (*via*, for example, [*equation* (*10*), *here*]. . .) once the carbon-atom connectivity and ring areas have been specified' [110].

After that, although the topic was briefly alluded to in a review [30] a quarter of a century later, little more was said on the matter for some thirty years until one of the present authors (RBM) revived the idea [87] of a 'topological ring-current' by initially restricting the concept only to ring currents calculated for, specifically, *benzenoid* hydrocarbons, in which all rings are hexagonal and are taken to be of equal area. It was pointed out that [87]

(a) when the Hückel [9, 34]–London [21–24]–Pople [77]–McWeeny [78] (HLPM) method is used, and

(b) when only benzenoid hydrocarbons are considered, and

(c) when all Hückel [9, 34] Coulomb integrals (α) and resonance integrals (β) are fixed at the respective benzene values, and

(d) when the benzenoid hydrocarbon under study (assumed to be geometrically planar) is considered to consist of regular hexagons of carbon atoms of benzene dimensions, and, finally,

(e) when ring-current intensities (as calculated, for example, from equation (10)) are expressed as a ratio to the ring-current intensity evaluated, by the same method, for benzene,

then [87]

> '. . . once the carbon–carbon connectivity of a benzenoid system has been specified, the (topological) ring-current intensities so-calculated are predetermined and do not further depend on any subjective (or other) parameters. In that sense, the ring-current intensity that characterises each of the diverse rings in benzenoid molecules is a purely graph-theoretical index that depends solely on the knowledge of a vertex-adjacency matrix for the graph representing the connectivity of the carbon atoms in the particular benzenoid molecule under study' [87].

The idea of a topological ring-current, at one time abandoned after due consideration [85], was thus retrieved by restricting attention just to benzenoid hydrocarbons. However, as a result of a casual suggestion from Professor T. Pisanski at the MATH / CHEM / COMP meeting at Verbania in June, 2009, the idea of a topological ring-current was soon extended so as to encompass conjugated systems containing rings of more than one size. The definition of 'topological ring-current' was, thereby, generalised [135] so that any rings in an arbitrary conjugated system — still, however, assumed to be geometrically planar — that are N-membered *are considered to be regular N-sided polygons of side equal in length to the carbon–carbon bond-length in benzene.* This effectively meant adopting the following relationship for the areas of regular polygons of equal side-length, a result [77] that may easily be demonstrated by appeal to elementary trigonometry:

$$\left(\frac{\text{Area of a Regular Polygon with } N \text{ Sides}}{\text{Area of a Regular Hexagon with Sides of the Same Length}}\right) = \left(\frac{N\cot\left(\frac{\pi}{N}\right)}{6\cot\left(\frac{\pi}{6}\right)}\right) \qquad (18).$$

This, therefore, replaces conditions (b) and (d), in the list presented above, to give *the generalised definition of a topological ring-current* [135]. With the adoption of this convention about molecular geometry, Balaban *et al.* [135] thus concluded that the topological ring-current, so defined,

> '. . . *is a purely graph-theoretical index* that depends solely on the knowledge of a vertex-adjacency matrix [86] for the graph representing the connectivity of the carbon atoms in the particular . . . molecule under study. The values of the topological ring-currents . . . are, in a sense, "latent", as soon as the system's structure has been written down' [135].

These authors also emphasised that [135]

> '. . . once the eigenvectors and eigenvalues of the system's (arbitrarily labelled) adjacency-matrix [86] are known, their use for the calculation of the HMO quantities needed for the ring-current computations [*as in equations* (*10*) *and* (*15*), *here*] also requires knowledge of the ground-state π-electronic configuration for the conjugated system in question, determined by an application of the *Aufbau* Principle — a process which . . . may itself be simulated [10, 12, 51–53] by an entirely graph-theoretical algorithm based solely on knowledge simply of the *order* of the eigenvalues possessed by the system's adjacency matrix, arbitrarily labelled' [135].

Another intrinsic aspect of the concept of topological ring-current concerns the planarity (in the geometrical, rather than the graph-theoretical, sense) of the conjugated system under study. Some structures are so severely overcrowded because of steric interactions amongst their peripheral protons or between carbon atoms actually within their network (such as in the helicenes [50]) that they are non-planar (*e.g.*, ref. [50] — see also the Appendix of ref. [136]). Strictly, the unmodified HLPM method should not be applied to these because the concept of 'ring-current' in the HLPM model is precisely defined as an exact quantity only for *planar* molecules [50]. The topological ring-currents calculated for such geometrically non-planar structures are thus, in effect, those for a *hypothetical* species having the same carbon–carbon connectivity as the actual molecule under consideration, but envisaged as if it were (geometrically) *planar*. The justification for this is that the topological ring-current is here essentially being regarded purely as a mathematical, *graph-theoretical* index, and *not* as an assumed 'physical' quantity *per se* [87, 135]. That said, even if there *is* some non-planarity, the idea of a ring current may still conceptually and semi-quantitatively — if not strictly mathematically [50] — be maintained provided that molecular overcrowding is such that '. . . the skeletal distortion *about any bond* is comparatively mild.' (Please see ref. [50] and the Appendix to ref. [136] for further discussion of this aspect). Haigh and one of the present authors (RBM) [50] have claimed that

> '. . . because of the way in which the strains from overcrowding are spread over many degrees of freedom, this condition does appear to be satisfied in the case of the helicenes [50], even though the overall non-planarity between well-separated parts of such molecules may in fact be very large.'

Topological ring-currents thus depend only on the following properties of an arbitrary conjugated hydrocarbon system:

(a) The occurrence/assumption of a (geometrically) planar structure;
(b) The carbon–carbon connectivity in the network represented by the system's molecular graph;
(c) The areas of its constituent rings, as determined by an application of equation (14).

In his recent instructive and entertaining essay entitled 'What I like about Hückel Theory', Kutzelnigg [36] has asked whether Hückel theory [9, 34] should be regarded as 'semi-empirical' or 'parameter-free'. As he puts it:

> 'These days, when *ab-initio* calculations to any desired accuracy are almost routinely possible, the label *semiempirical* is regarded as a stain.'

Kutzelnigg [36] goes on to argue that closer examination reveals that the most important results in Hückel theory depend only on the resonance integral, β. He thus concludes that

> '. . . HMO is effectively a one-parameter theory. . . .'

and he further observes that

> '. . . one can decide to discuss only parameter-free quantities within the HMO model'.

This is precisely what the present authors have argued for topological ring-current. In ref. [137] we claimed that

> '. . . topological ring-currents and bond-currents are even independent of whatever value might be assumed for the Hückel resonance-integral, β, because "topological" currents (proportional, as they are, to β) are conventionally expressed as a ratio to the corresponding values calculated, by the same method, for benzene, and so β cancels.'

This is so because [137], although it looks, from equation (10), as though topological ring-currents do explicitly depend on β, the quantities $\beta\bar{\pi}_{(\mu)(\mu)}$ and $\beta\bar{\pi}_{(\mu)(\nu)}$ are in fact dimensionally independent of β, despite explicitly mentioning this parameter, because [137] $\bar{\pi}_{(\mu)(\mu)}$ and $\bar{\pi}_{(\mu)(\nu)}$ are themselves — from their very definitions, in, for example, equations (A1) and (A2) of the Appendix of ref. [85], and in equations (12) and (13), here — expressed in units of 1/β. Hence our claim that topological ring-currents, as defined, are *latent* in a conjugated structure and are immediately pre-determined at the moment when its molecular graph has been specified, *without the need for knowledge of any parameters*.

8. Recent Considerations Concerning of the Concept of Topological Ring-Current

The present authors [19, 31, 87, 97, 135–145], and others [130, 146–148], have applied these ideas in several studies within the last five years. The aims of our own calculations have mainly been (a) to test the veracity of the so-called 'Annulene-Within-an-Annulene Rule' (AWA, now largely discredited) — refs. [31, 136–138 & 140–142] — and (b) to see how well a simple-minded theory such as is our subject (the topological HLPM model [87, 135]) in this Review can mimic the trends predicted by much more sophisticated *ab initio* calculations (please see refs. [19, 97, 140, 143 & 145]).

8.1. Assumptions about Ring Areas

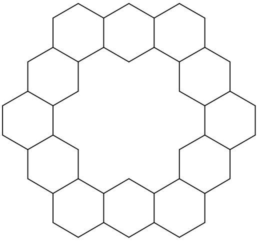


Figure 7. The molecular graph [11] of kekulene. The area of the ([18]-membered) central ring is considered to be that of seven benzene rings, rather than the area of a regular polygon with 18 sides.

Not all of the calculations reported in the papers just cited give rise to strictly 'topological' ring-currents in the sense defined here, in that relation (18) has not always been used to estimate all ring areas. For example, the central ring of kekulene (Figure 7) is [18]-membered but, in our own calculations [31, 97, 138], and in those performed by others [149–152], it was clearly considered to be more intuitive to estimate the central ring as being the area of the hexagons that are missing from an otherwise perfectly tessellated hexagonal network — in the case of kekulene, seven of them — rather than the area of an [18]-sided regular polygon. A similar consideration applies to the central rings of several other benzenoid structures (*e.g.*, the conjugated systems studied in refs. [149–152]). The approximation of assuming regular polygons for the central rings of the *p*-coronenes (defined in ref. [142]) would also seem somewhat unrealistic, as was discussed in ref. [142]. In the majority of cases, however — *e.g.*, in refs. [19, 31, 87, 97, 130 & 135–148] — the ring currents reported *are* genuinely toplogical ring-currents, in the sense defined here [87, 135], with ring areas effectively estimated from equation (18).

It should finally be said, on this subject of areas, that what little experimentation there has been on varying the assumptions about ring areas — for example, using ring areas experimentally determined by means of X-ray crystallography — has concluded that such refinements affect the HLPM ring-currents only very marginally: in refs. [121 & 153], a change of < 3% was reported as a result of taking into account actual ring areas rather than using idealised ones.

8.2. The Relative Merits of Considering Topological Ring-Currents or Topological Bond-Currents

It is appropriate to insert at this point a brief consideration of the pros and cons of contemplating topological *bond*-currents as an alternative to topological *ring*-currents. Over the years, ring currents have been discussed far more frequently than have bond currents (especially by organic chemists), despite the fact that bond currents were thoroughly considered by early pioneers in the field such as Longuet-Higgins and Salem [25, 154] — and their ideas on 'line currents' and application of the Biot-Savart Law were taken up, in a limited way, by the next generation (*e.g.,* refs. [84 & 155]). In recent years, however, much more attention has been devoted to bond currents than to ring currents.

As has been pointed out [19, 29], the collection of *ring*-currents for an arbitrary conjugated system (which may be considered [29] classically as a microscpic electrical network) represents the anaolgy of the family of *loop* currents [29, 156, 157] in a macroscopic network such as is encountered in the laboratory; the list of *bond* currents, on the other hand, is the analogy of the various currents in the wires forming the *arms* of a macroscopic network of the type considered by Kirchhoff [19, 35, 156, 157]. Both are rigorously equivalent representations if (as is precisely the case with HLPM topological bond-currents) Kirchhoff's Law of Conservation of Current at a Junction is respected.

We have, however, remarked [19] that ring currents do represent a more efficient way of characterising a structure, because a list of r ring currents, one for each of the r rings of that structure, constitutes a minimal and independent family of quantities containing all the required information about π-electron currents. The list of all bond currents in the structure, on the other hand, contains some redundances: because of applicability of the Kirchhoff Conservation Law at Junctions, if all but one of the bond currents entering and leaving a given junction are known, then the last one is automatically predetermined, by virtue of Kirchhoff's Law.

By contrast, consideration of individual bond-currents rather than overall ring-currents may frequently give more insight [19, 97, 137, 143, 144]. This is because it is possible [137]

> '. . . for structures to have very different ring-currents and yet — because the bond currents in bonds shared by two rings are the result of algebraic summation of the ring currents in those adjacent rings — for them still to exhibit corresponding bonds that bear . . . comparable *bond*-currents' [137].

An extreme example of this is [10,5]-coronene (the left-hand structure of Figure 8) and its so-called '*altan*', structure (Figure 8, right-hand side). Remarkably, this qualitative similarity of *bond* currents between the inner and perimeter cycles of [10,5]-coronene, on the one hand, and (respectively) the corresponding bonds in the innermost and middle cycles of *altan*-[10,5]-coronene, on the other hand, arises even though *all* rings in [10,5]-coronene bear *dia*magnetic topological ring-currents and *all* rings in *altan*-(10,5)-cononene support *para*magnetic topological ring-currents [137], as emphasised in Figure 8. (It may be noted in passing that Monaco [158] has suggested that what we have called altan-[10,5]-coronene, above, might more appropriately be regarded as a 'double' *altan* of [10]-annulene and thus called *altan*^{2}-[10]-annulene.) The question of these so-called '*altan*' structures will be discussed further, in §9.

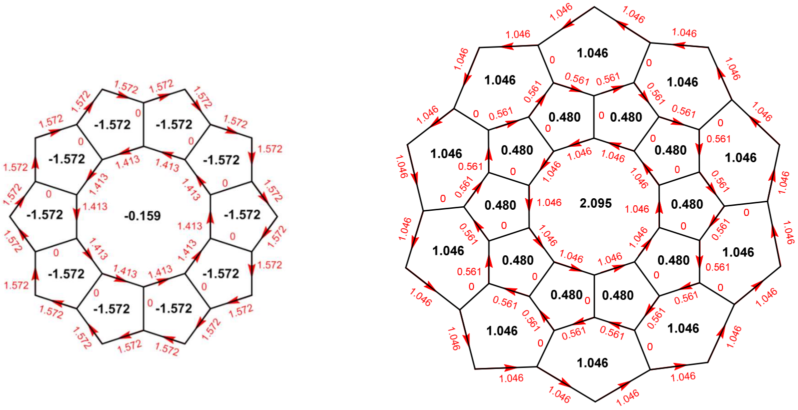


Figure 8. HLPM Topological bond-currents and ring-currents for [10,5]-coronene (left) and *altan*-[10,5]-coronene (also called [158] *altan* ^{2}-[10]annulene) (right), taken from ref. [137]. The topological ring-currents are depicted in black, written in the centre of the relevant ring, and the associated topological bond-currents are illustrated in red. The topological ring-currents and bond-currents are dimensionless quantities. Positive (diamagnetic) ring-currents are considered to circulate anti-clockwise around their respective rings whilst negative (paramagnetic) ring-currents flow in the clockwise sense around those rings. The various bond-currents flow in the direction indicated by the arrow pointing along each bond. Reproduced from T.K. Dickens & R.B. Mallion, *Chem. Commun.* **51** (2015) 1819−1822 with permission from The Royal Society of Chemistry.

8.3 Conceptual and Numerical Equivalence of the 'Topological HLPM' Method and the 'Graph-Theoretical HL-CD' Approach

For the avoidance of possible confusion, it ought perhaps explicitly to be mentioned at this stage that what the present authors have defined and called [87, 135] 'the Hückel–London–Pople–McWeeny (HLPM) procedure for calculating topological ring-currents' has recently been dubbed by Fowler *et al*. [146–148] 'the graph-theoretical current-density Hückel–London (CD–HL)' method. It is, however, clear from refs. [87 & 135] on the one hand, and from refs. [146–148] on the other hand, that the 'HLPM' and the 'CD–HL' approaches are theoretically and numerically equivalent, being based, as the two are, on the simplest Hückel model [9] and employing, as they both do, the assumption of regular polygons for the constituent rings. Both formalisms end by expressing calculated ring-currents and bond-currents as a ratio to the corresponding values computed, by the same method, for benzene — thereby both properly giving rise to dimensionless ring-currents and bond-currents. As the present authors understand it, in refs. [146–148] ring currents (bond currents) are effectively calculated from equation (7) of the present Review, which simultaneously takes into account carbon–carbon connectivity *and* molecular geometry, the latter by means of input information on the Cartesian coordinates of the constituent carbon-atoms, through which ring areas are implicitly pre-determined and from which they may subsequently explicitly be calculated. In the HLPM approach, by contrast, the calculation is carried out, following the philosophy of one of the formulations of the McWeeny method [78], in *two* distinct stages (which the present authors find conceptually helpful [31]):

(a) the *topological* (Hückel) quantities required are first calculated from the vertex-adjacency matrix [86] of the associated labelled molecular graph [11], and an application of the *Aufbau* process [10, 12, 51–53], and then

(b) these topological quantities are combined with separately inputted *geometrical* information supplied by explicitly specifying the *area* of each individual ring of the conjugated system in question and, thereby, the areas of the cycles in the Fundamental System [31, 88] that contain these rings; (information about how individual rings feature in the Fundamental System of Cycles (§5) is also inputted in the course of this second stage).

This process was fully described in detail in ref. [31] and, more briefly, in our 'Worked Example' (§5) in this present Review (and elsewhere — *e.g.*, ref. [30]).

Given the same geometrical and Hückel assumptions, the two alternative strategies for calculation ('HLPM' and 'CD–HL') should, therefore, yield identical numerical ring-currents and bond-currents (within the machine error of the computation.) When it comes to actual application of the Hückel–London method, it would thus seem to be a matter of taste which approach is adopted. As just stated, we ourselves find the two-stage process described above conceptually helpful. This is indeed all very satisfactory when relatively small conjugated systems are studied. It has to be conceded, however, that one practical disadvantage of the two-stage calculation is that, as the number of rings in the conjugated systems under study increases — and we have recently studied systems containing as many as 43 rings — the amount of data that has to be transferred from the first stage to the second stage begins to become extensive enough to make the procedure too labour-intensive.

Nevertheless, despite this latter small reservation — which, if desired, could be obviated by automating the process of joining the two stages computationally — these considerations are all consistent with the fact that Fowler *et al.* [146–148] have implicitly agreed with our own previous claim [30, 31, 87, 135] by observing that, in the case of benzenoid hydrocarbons, the Hückel–London (HL) model is based on '. . . a single graph-theoretically defined matrix. . .' [146] and that, with the assumption of regular hexagons, it '. . . becomes a purely graph-theoretical approach' [148].

9. Use of HLPM Topological Currents in Assessing the 'Annulene-Within-an-Annulene' (AWA) Model (with Special Reference to '*Altan*' Structures)

9.1 Formal Construction of 'Altan' Systems

Much of the subsequent discussion will draw on the so-called '*altan*s' of various 'parent' structures in order to illustrate recent applications of the HLPM topological approach. The idea of an *altan* seems first to have been proposed by Monaco & Zanasi [159] as a means of 'designing' conjugated systems that might have intriguing ring-current properties and, subsequently, the concept was further developed by them and Memoli [160–162]. The general mathematical properties of the process of what the present authors have (somewhat inelegantly) called [97] '*altanisation*' have recently been exhaustively studied, by Gutman [163, 164] and by Bašić & Pisanski [165].

The *altan* derivative of a given conjugated hydrocarbon is constructed so that each peripheral hydrogen atom in it is considered to be replaced by a vinyl group, and each pair of adjacent vinyl groups is then thought of as being condensed into a new (outer) cycle. Gutman [163] has illustrated the process of forming the *altan* of phenanthrene by means of Figure 9.

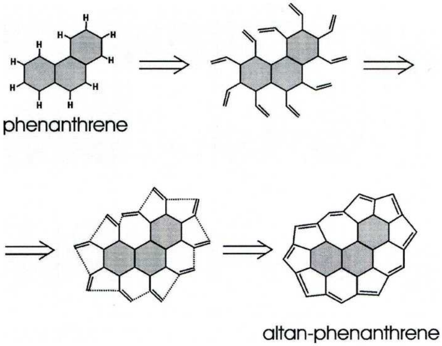


Figure 9. Construction of *altan*-phenanthrene from phenanthrene. Note that the perimeter of *altan*-phenanthrene is a [20]-annulene, encircling the 'parent' phenanthrene structure (shaded). Reproduced from I. Gutman, *J. Serb. Chem. Soc.* **79** (2014) 1515–1521 with the kind permission of Academician Professor Dr Ivan Gutman and the Serbian Chemical Society. [© 2014 Serbian Chemical Society]

The entire process may formally be thought of [97] as notionally placing the parent hydrocarbon 'inside' a [4*n*] annulene of appropriate size — in the phenanthrene example, above, it is a [20]-annulene — and then altering the bonds in such as way that an outgoing C–H bond from the inner ('parent') structure and an internal C–H bond from the (outer) annulene are replaced by a C–C bond [97]; at the end of the process, such C–C bonds join certain carbon atoms of the inner (parent) structure to *alternating* carbon-atoms of the surrounding annulene (and *only* to those carbon atoms.) Hence, the appellation '*altan*'. For example, in *altan*-phrenanthrene (Figure 9), the inner structure (shaded, in Figure 9) has the carbon-atom connectivity of phenanthrene, and the outer structure, to which the inner one is joined as just described, has the carbon–carbon connectivity of [20]-annulene. The (shaded) inner moiety, and the outer ([20]-) annulene are thereby joined by the connecting bonds that are sometimes referred to as 'spokes' bonds, as can be seen in Figure 9. These spokes bonds have been shown [159, 161, 163–165] to be formally fixed as *single* bonds in all Kekulé structures that may be devised for the conjugated system as a whole [97]. In this respect, the inner cycle and the outer perimeter are often said to be 'uncoupled'.

9.2 The ‘Annulene-Within-an-Annulene’ (AWA) Model

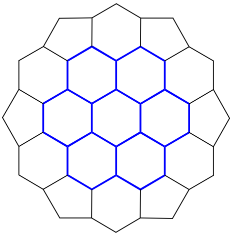


Figure 10. The molecular graph of *altan*-coronene, with the coronene ‘parent’, which constitutes the ‘inner core’, highlighted in blue.

The ‘Annulene-Within-an-Annulene’ (AWA) ‘Rule’ arises from Pople & Unch’s 1966 idea [118] that for (monocyclic) annulenes (only) [4*n*]-annulenes should bear paramagnetic currents (circulating clockwise around the annulenic ring) whilst [4*n*+2]-annulenes should bear diamagnetic (anti-clockwise) ring-currents. The idea was extended to conjugated systems that did not consist of just a single annulenic ring. According to the AWA ‘Rule’, [4*n*]-membered cycles in these polycyclic systems should bear paramagnetic currents and [4*n*+2]-membered cycles should bear currents that circulate in the diamagnetic direction. For example, in *altan*-coronene (Figure 10, above), which may be considered to be ‘a [6]-annulene-within-an-[18]-annulene-within-a-[24]annulene’, the bonds in the innermost ([6]-membered) cycle would be predicted by the AWA ‘Rule’ to bear diamagnetic currents, the bonds in the middle ([18]-membered) cycle would also be expected (on the basis of the ‘Rule’) to bear diamagnetic currents (flowing in the anti-clockwise direction around that cycle), whilst the bonds in the [24]-membered perimeter cycle would be predicted to bear currents circulating in the clockwise (paramagnetic) sense. In other words, the AWA Rule would predict (for cycles listed outwards from the central one):

Diamagnetic/Diamagnetic/Paramagnetic

in the three cycles. Figure 11 shows that what is actually found by means of HLPM calculations — and the HLPM [143] conclusions are confirmed by an *ab initio* [160] approach (the so-called ‘*ipso*-centric’ [166–170] one) — is:

Paramagnetic/Diamagnetic/Paramagnetic.

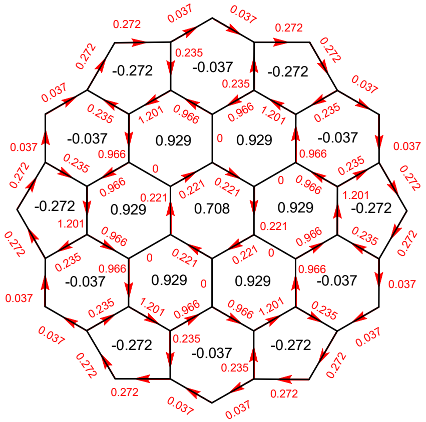


Figure 11. HLPM Topological bond-currents and ring-currents for *altan*-coronene taken from ref. [143]. For the conventions on displaying bond currents and ring currents please see the caption to Figure 8. Reprinted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **118** (2014) 933–939. Copyright 2014 American Chemical Society.

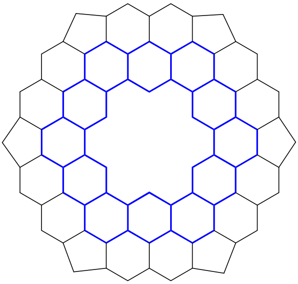


Figure 12. The molecular graph of *altan*-kekulene, with the kekulene 'parent', which constitutes the 'inner core' of the *altan*-structure, highlighted in blue.

Another example is *altan*-kekulene (Figure 12, above). This can be considered as 'an [18]-annulene-within-a-[30]-annulene-within-a-[36]annulene'. The innermost cycle is [18]-membered, the middle one is [30]-membered and the perimeter is [36]-membered. If the AWA model held, we should thus expect (again, with cycles being listed from the innermost one, outwards — the last one listed being the perimeter):

Diamagnetic/Diamagnetic/Paramagnetic.

The topological ring-current and bond-current maps (taken from ref. [97]) are presented in Figure 13. From this it is seen that the HLPM approach predicts the pattern

Paramagnetic/Diamagnetic/Diamagnetic.

This qualitative conclusion is supported by calculations [158] based on the (*ipso*-centric) [166–170] *ab initio* approach. Once again, therefore, the AWA 'Rule' is seen *not* to be respected.

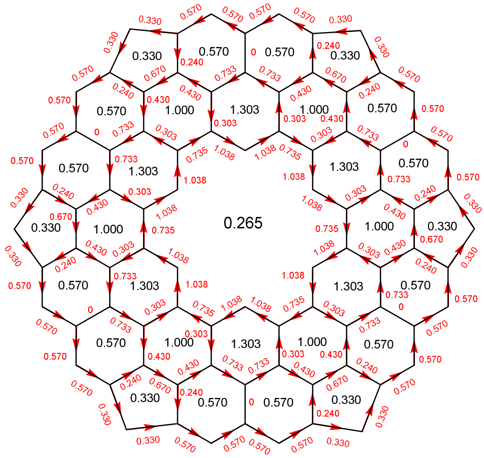


Figure 13. HLPM Topological bond-currents and ring-currents for *altan*-kekulene taken from ref. [97]. For the conventions on displaying bond currents and ring currents please see the caption to Figure 8. Adapted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **118** (2014) 3688–3697. Copyright 2014 American Chemical Society.

There are, however, occasional examples of compliance with the AWA 'Rule'. [10,5]-coronene (illustrated on the left-hand side of Figure 8) is a case in point. The ring-current and bond-current maps for this structure have already been presented in Figure 8: although the *ring*-current intensities in all rings in [10,5]-coronene are paramagnetic (negative), the net currents in the bonds of the inner ([10]-membered) cycle flow in the diamagnetic (anti-clockwise) sense, and the circulation in the [20]-membered perimeter is strongly paramagnetic (clockwise). *Altan*-[10,5]-coronene (dubbed *altan*^{2}-[10]-annulene by Monaco [158]) — whose HLPM bond-current and ring-current maps are depicted on the right-hand side of Figure 8 — does *not* obey the AWA Rule, as the perimeter cycle should bear currents in the paramagnetic direction in order to comply with the 'rule' but this perimeter cycle is actually predicted by the HLPM computations to bear a diamagnetic current. This apparent anomaly arising from our unsophisticated topological calculations [97] has also been definitively confirmed by Monaco [158], who applied the much more sophisticated *ab initio ipso*-centric [166–170] formulation to the same structure.

We finish this section on the AWA Rule on a positive note by drawing attention to what might be regarded as the ‘paradigm’ *altan* structure: namely, *altan*-benzene [31] (Figure 14).

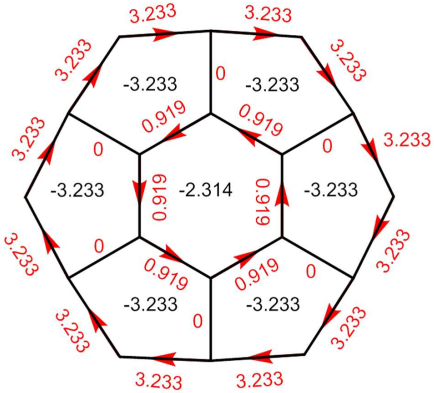


Figure 14. Ring-current and bond-current maps for *altan*-benzene [31], having a [6]-membered central ring ([4*n*+2], with *n* = 1) and [12]-membered periphery ([4*m*], with *m* = 3). For conventions on ring currents (black) and bond currents (red) please see the caption to Figure 8. Taken from T. K. Dickens & R. B. Mallion, *Croat. Chem. Acta* **86** (2013) 397–406 and reproduced with the kind permission of the Croatian Chemical Society [© 2013 The Croatian Chemical Society]

The HLPM topological ring-current and bond-current maps exhibited in Figure 14 indicate that *altan*-benzene respects the AWA model because (a) the bonds in the [6]-membered central ring bear currents, of magnitude of approximately the benzene value, that flow in the diamagnetic direction, whilst (b) the bonds that form the [12]-membered periphery bear a substantial current (more than three times the benzene value) that flows in the paramagnetic (clockwise) sense.

10. Application to the *Altans* of '*K*-Factorisable' Conjugated Systems Containing 'Fixed' Single-Bonds

Structures classically described by Clar [171] as having bonds that are 'fixed' as single bonds (because they never appear other than as single bonds in any Kekulé structure that may be devised for the system as a whole) have recently been referred to as '*K*-Factorisable' [130,159]. The paradigm for a benzenoid structure of this type is perylene (depicted on the left-hand side of Figure 15), in which the unshared bonds in the central ring are fixed as single (in the sense just defined). This is to be compared (and *contrasted*) with the ostensibly similar but electronically very different central ring of peropyrene (illustrated on the right-hand side of Figure 15) in which there is no such bond-fixation. In his renowned book *The Aromatic Sextet*, Clar [171] claimed that perylene '. . . can be considered to be built up from two naphthalenic complexes connected by two single bonds, whereas peropyrene '. . . consists of three sextets and four fixed double bonds.' The Clar description is exemplified by Figure 16.

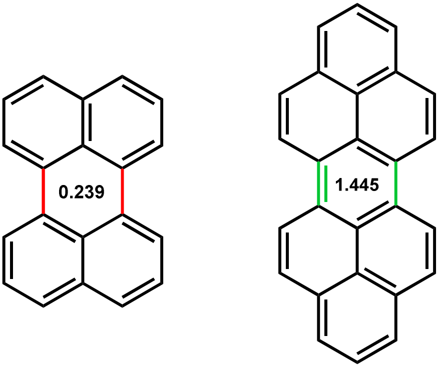


Figure 15. Kekulé structures for perylene (left), with the bonds depicted in red 'fixed' as single bonds and peropyrene (right), with no such bond-fixation in the central ring. The topological ring-current intensity in the central ring of perylene (in which there is this 'bond fixation') is only 0.239 (expressed as a ratio to the benzene ring-current), whereas the analogous central ring of peropyrene, in which there is no such 'bond fixation', the ring-current intensity is *six* times the size, (1.445). Reprinted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **119** (2015) 5019–5025. Copyright 2015 American Chemical Society.

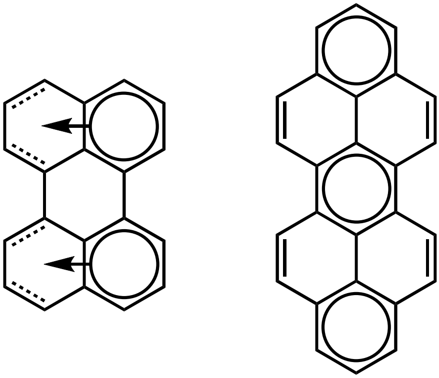


Figure 16. Clar structures [171–173] for perylene (left)) and peropyrene (right). Perylene is considered (by Clar [171]) '. . . to be built up from two naphthalene complexes connected by two single bonds . . .' and the peropyrene structure is regarded as consisting '. . . of three sextets and four fixed double-bonds.' Reprinted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **119** (2015) 5019–5025. Copyright 2015 American Chemical Society.

Forty-five years ago, one of us (RBM) [122] drew attention to the fact that the HLPM topological ring-current in the central ring of peropyrene (1.445) is more than six times that (0.239) [115, 116, 139, 153] in the (superficially) analogous central-ring of perylene. Much later, in collaboration with Haigh [128], this observation was rationalised. Very recent work by the present authors [144] has asked the question as to whether this pattern of currents in the 'red' bonds and the 'green' bonds in Figure 15 survives the process of altanisation. The *altans* of perylene and peropyrene are depicted in Figure 17.

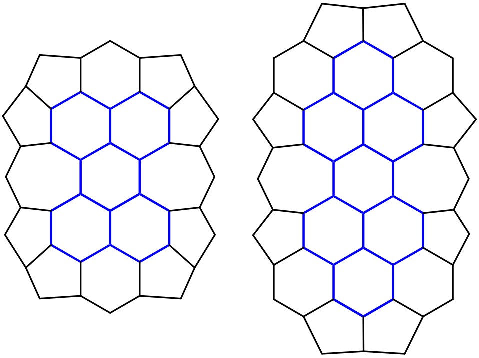


Figure 17. The molecular graphs of *altan*-perylene (left) and *altan*-peropyrene, with the respective 'parent' inner-cores highlighted in blue. Adapted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **119** (2015) 5019–5025. Copyright 2015 American Chemical Society.

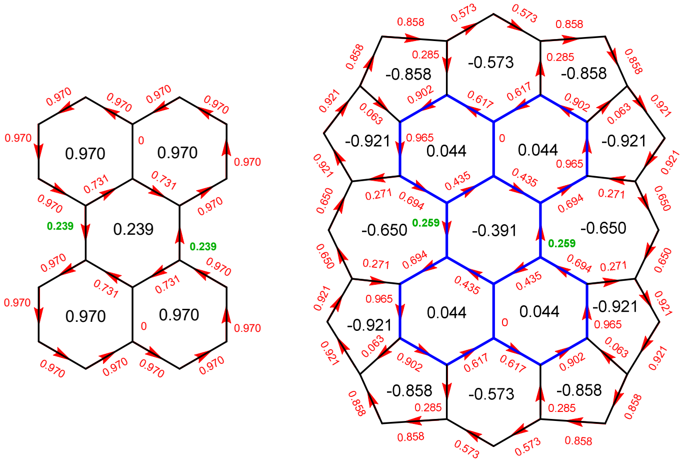


Figure 18. Topological HLPM bond-currents and ring-currents in perylene (left) and *altan*-perylene (right). Note that the unshared bonds in the central ring of perylene bear currents of size 0.239 (depicted in green figures) and the currents associated with the corresponding bonds in the central ring of *altan*-perylene (also depicted in green figures) are of comparable magnitude (0.259). For the other conventions on displaying bond currents and ring currents please see the caption to Figure 8. Adapted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **119** (2015) 5019–5025. Copyright 2015 American Chemical Society.

It is manifest from Figure 18 that the unshared bonds in the central ring of perylene bear currents of size 0.239 (depicted in green figures) and that the currents borne by the corresponding bonds (which, here, are *shared* bonds) in the central ring of *altan*-perylene (also depicted in green figures) are of comparable magnitude (0.259). A similar comparison may be made between the unshared bonds in the central ring of peropyrene and the corresponding (shared) bonds in the central ring of *altan*-peropyrene. This is presented in Figure 19.

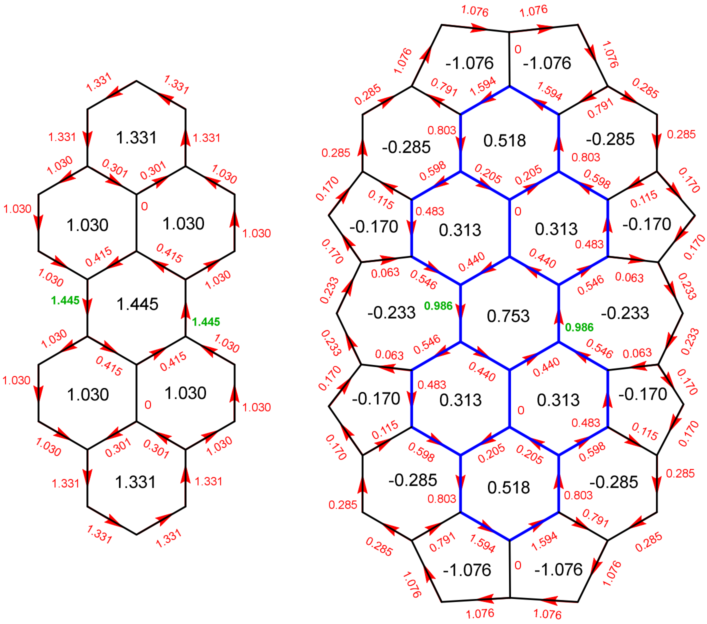


Figure 19. Topological HLPM bond-currents and ring-currents in peropyrene (left) and *altan*-peropyrene (right). Note that the unshared bonds in the central ring of peropyrene bear currents of size 1.445 (depicted in green figures) and the currents associated with the corresponding bonds in the central ring of *altan*-peropyrene (also depicted in green figures) are 0.986. For the other conventions on displaying bond currents and ring currents please see the caption to Figure 8. Adapted with permission from T. K. Dickens & R. B. Mallion, *J. Phys. Chem. A* **119** (2015) 5019–5025. Copyright 2015 American Chemical Society.

It is seen from Figure 19 that the unshared bonds in the central ring of peropyrene bear currents of 1.445 (depicted in green figures) and the currents borne by the corresponding bonds in the central ring of *altan*-peroyrene (also depicted in green figures) are approximately the same as the benzene current — not as large as the 1.445 in peropyrene, but still substantial, at just under the benzene value. As the present authors observed in ref. [144]: 'This [0.986] is still almost four times the current [0.259] in the analogous bonds of *altan*-perylene. . .' and that '. . .the phenomenon previously observed concerning the starkly contrasting magnitudes of the currents in the unshared bonds in the central rings of perylene and peropyrene is thus also seen to be displayed in the corresponding bonds of the respective *altans* of these two structures.'

As we also pointed out in ref. [144], because it has been proved [159, 163–165] that the bonds joining the parent to the peripheral [4n]-annulene in an *altan*-structure are also all fixed as single bonds, it follows that the bonds in *altan*-perylene corresponding to the unshared bonds in the central ring of perylene are themselves *also* ‘fixed’ as single — even when they are embedded in the *altan*. As we stated in ref. [144], this rationalises, albeit only intuitively, the empirical observation that the currents in the bonds of *altan*-peropyrene that correspond to the unshared bonds in peropyrene are some four times the size of the HLPM currents in those bonds in *altan*-perylene that correspond to the central, unshared bonds in perylene.

The HLPM topological studies reported in refs. [97, 143 & 144] thus generally support the conclusions of Monaco & Zanasi [159–162] that ‘. . . current patterns in the parent structures frequently remain semi-quantitatively intact when the parent is converted to the corresponding *altan*.’

11. Comparisons with the Predictions of *Ab Initio* Calculations

11.1 Qualitative and Semi-Quantitative Comparisons

Having carefully defined, in §7, the graph-theoretically calculated ‘HLPM topological ring-currents’ (and bond-currents), and, in §§8–10, having considered their use and application in some considerable detail, we are naturally then led to ask how well these compare, both qualitatively and numerically, with *ab initio* calculations of the corresponding quantities. Such an assessment is the subject of this sub-section of the Review, and the next one (§11.2).

The *ab initio* techniques that we consider are confined to those formulations that have been applied in the literature to calculate the current maps of conjugated hydrocarbon systems, which can then be compared with the corresponding maps calculated by the HLPM method. This determines that we shall focus on

(a) what has become known as the ‘*ipso*-centric’ *ab initio* formulation [166–170] to molecular magnetic-response theory. This approach was pioneered more than two decades ago by Keith & Bader [166] and by Lazzeretti *et al.* (*e.g.*, ref. [167]) and, in the succeeding 20 years, it has been much taken up by Fowler *et al.* (Please see refs. [168 & 169] for representative early examples, ref. [170] for complete details, and pp. 230–235 of ref. [29] for a review of the first fifteen years of what was there called ‘the *ab initio* era’ in this field). The main philosophy of this method is characterised by the fact that the origin of vector potential — for calculation of the current density induced at any point — is placed actually *at* the point itself (hence, the appellation ‘*ipso*’). Later, a computationally more economical ‘pseudo-π’ approximation to this formalism was proposed [174], which can often numerically mimic predictions of the ‘computationally more expensive’ *ipso*-centric calculations [146–148];

(b) what is known as the method of 'gauge-including magnetically induced current' (GIMIC), also an *ab initio* approach, which has recently been developed by the Sundholm group [*e.g.*,175–177].

Until recently, these *ab initio* approaches were capable of providing only pictorial current-density maps (*e.g.* refs. [168–170]) and so any comparison with topological HLPM calculations had, necessarily, to be qualitative or, at best, semi-quantitative; (see, for example, refs. [178] & [179], corresponding with refs. [145] & [140], respectively). In recent years, however, it has become possible [180], in the context of these *ab initio* formalisms, to calculate the analogy of what the graph-theoretical HLPM approach calls 'bond current'. This so-called 'integrated current strength' [177] is achieved by numerical integration of the current density passing through planes at right angles to the bonds in question, selected from the conjugated system under study [177]. Kirchhoff's Law of Current Conservation at Junctions [19, 35] — automatically guaranteed to be rigorously obeyed in the case of the (graph-theoretical) 'topological HLPM' [19, 31] and the (graph-theoretical) 'HL–CD' [146–148] bond-currents — is, however, *not*, in general, precisely respected in the *ab initio* calculations [177] (except [181] in the ideal case of a complete basis-set) [182, 183].

In the majority of cases where comparison has been made between qualitative *ab initio* current-density maps and HPLM topological ring-currents and bond-currents, the qualitative and, sometimes, semi-quantitative agreement achieved has been encouraging (not to say surprising) — see, for example, refs. [97, 140, 143 & 145]. The *altan* structures (fully described in §9.1) have been of especial service in this context. These conjugated networks are specifically designed [137, 142, 144, 159–162] to yield two- or three-layered annulenic systems — though not, in general, planar ones: they are thought usually to be 'bowl'-shaped [136, 158–162, 184]. As already discussed for the case of *altan*-coronene in §9.2, by use of topological HLPM calculations the present authors have confirmed [97, 143] the paramagnetic/diamagnetic nature of the π-electron currents circulating around the several 'layers' of some representative *altan*-structures, directions of circulation that had previously been predicted by Monaco, Zanasi and Memoli from their *ipso*-centric *ab initio* computations [159–162] on these same conjugated systems. Furthermore, these *altan* structures have been proved [158–165] always to have outer perimeters of [4*n*] carbon-atoms, where *n* is an integer, no matter what parent conjugated system the *altan* in question has been created from. Intuitively, therefore, as was discussed in §9.1, one would expect — by an extension (not necessarily justified) of the considerations of ref. [118] from monocyclic to polycyclic systems — paramagnetic circulations around the perimeters of all *altan*-conjugated hydrocarbons. With one exception, this anticipation was indeed realised by Monaco *et al.* [159–162] by means of their *ipso*-centric *ab initio* calculations and this exception was independently confirmed [97] by the present authors using the HLPM graph-theoretical approach that is the subject of this Review. The topological HLPM calculations did indeed highlight the same exception to what had been expected: namely, that the outer perimeter of *altan*-kekulene (depicted in Figure 12) was predicted by both approaches (*ipso*-centric *ab initio* [162] *and* topological HLPM [97]) to be unambiguously *dia*magnetic, rather than the *para*magnetic nature that would be anticipated by a naïve extension, to polycyclic systems, of Pople & Untch's pioneering ideas on paramagnetic ring-currents in — specifically – [4*n*]-membered *mono*cycles [118]. Later investigations by the present authors revealed another such exception — the [4*n*]-perimeter of *altan*-[10,5]-coronene (the structure depicted on the right-hand side of Figure 8). According to the HLPM graph-theoretical calculation that the present authors reported in ref. [137], it, too, bears an unmistakable diamagnetic current (of size almost exactly that of the diamagnetic current in the carbon–carbon bonds of benzene) circulating around its outer ([4*n*])-perimeter. Motivated by this, Monaco [158] has since verified the diamagnetic nature of the perimeter of *altan*-[10,5]-coronene (which that author recommends be called *altan*^{2}-[10]-annulene). These more sophisticated calculations thus confirm this unexpected prediction of the much more rudimentary HLPM 'topological' approach. In fact, our current investigations into triple *altans* (inspired by Bašić & Pisanski's recent study [165] of multiple *altans* — or, as those authors call them, 'iterated' *altans*) indicate that *altans* with diamagnetic circulations in their [4*n*] outer-perimeters are, perhaps, not as rare as, until recently, was generally [137, 158] thought. Monaco has recently argued [158] on the basis of his *ab initio* calculations of the current density that diamagnetic circulations in the [4*n*] perimeters of *altan* structures '. . . can be expected whenever the outermost and middle annulenes of the *altan*-molecule have similar sizes' [158]. This claim is consistent with the observation that the two *altan*-structures discussed here that exhibit anti-clockwise (diamagnetic) circulations in their [4*n*]-peripheries — whether these circulations are calculated by the simple-minded HLPM topological approach or by sophisticated *ab initio* formalisms — do in fact fulfil this criterion: *altan*-kekulene (Figure 12) has middle and peripheral annulenic cycles of length 30 and 36, respectively, whilst *altan*-[10,5]-coronene (*altan*^{2}-[10]-annulene), displayed on the right-hand side of Figure 8, has middle and peripheral annulenic cycles of precisely the *same* length (namely, 20). Recent mathematical consideration of 'multiple' (or 'iterated') *altans* has revealed that the latter example is not just a coincidence: the equal size of the middle and outer (peripheral) annulenic cycles in, specifically, *iterated altans* is in fact guaranteed [158, 165]. Our own recent, unpublished HLPM topological calculations on four iterated *altans* — *altan*^{2}- and *altan*^{3}- corannulene and coronene — also bear out the expectation of a diamagnetic (anti-clockwise) flow around the [4*n*]-peripheries of these structures.

11.2 Quantitative Comparisons with the Predictions of Ab Initio Calculations

All the foregoing has been concerned with qualitative or semi-quantitative comparisons between the predictions of the *ipso*-centric [166–170] *ab initio* calculations (or the 'pseudo-π' approximation to it [174]), and those predictions effected by means of the 'topological' [87, 135] HLPM approach. However, potentially of much more interest is the fact that, as was mentioned in the previous sub-section, it has become possible in recent years [142, 160–162, 177, 180] quantitatively to calculate what are called 'integrated current strengths'

[177], which are the analogy, in these more sophisticated methods, of what the HLPM method refers to as 'bond currents'. When all currents are expressed as a ratio the current calculated, by the corresponding method, for a bond in benzene, this facility does, thereby, *now allow direct and quantitative comparison of the predictions of the two approaches* — the one (HLPM) relying only on the knowledge of the carbon-atom connectivity and the areas of the constituent rings of the conjugated system under study, and the other which invokes a full *ab initio* calculation — or, possibly, if the *ipso*-centric approach [166–170] is being employed, the pseudo-π approximation [174] to it — with all that that implies (*e.g.*, refs. [166–170, 174–181]). Accordingly, we now turn attention to such *quantitative* comparisons.

One of the most striking demonstrations of how the topological HLPM [31, 87, 135] (graph-theoretical HL–CD [146–148]) methods can give '. . . predictions of similar quality to those obtained from much more onerous methods. . .' [146] is provided by Figure 3 of ref. [146]. In that Figure, Gershoni-Poranne *et al.* [146] compare the ring currents calculated by the method just referred to with those obtained by the pseudo-π approximation [174] to the *ipso*-centric *ab initio* formalism [166–170] for 143 rings (not all of them necessarily symmetrically distinct) in 17 different conjugated systems that consist of alternatingly condensed four-membered and six-membered rings (all of which may be viewed in Scheme 1 of ref. [146]). The results are presented in Figure 3 of ref. [146] as a least-squares best-fit straight-line whose correlation coefficient is 0.995. As Gershoni-Poranne *et al.* pointed out [146], this shows that ring-currents calculated by the graph-theoretical HLPM/HL–CD method '. . . are remarkably similar to those extracted from the pseudo-π maps [174], which themselves mirror the full *ab initio* maps' [166–170].

The present authors have examined a more limited set of *ab initio* bond-currents provided by Monaco and Zanasi [160] for corannulene and coronene and their respective *altans* (illustrated, along with appropriate bond labellings, in Figure 20). Figure 21 shows a 'comparator' diagram for the predictions of bond currents in these systems by the *ipso*-centric *ab initio* method [160] (the red curve) and the HLPM formalism (the black curve) [143]. For both sets of calculations, the currents (along the vertical axis) are dimensionless, being expressed as a ratio to the bond current/integrated current strength (as the case may be) calculated, by the corresponding method, for benzene. The patterns are seen to be reassuringly similar for the two curves — this observation being consistent with the agreement found in ref. [146], referred to above.

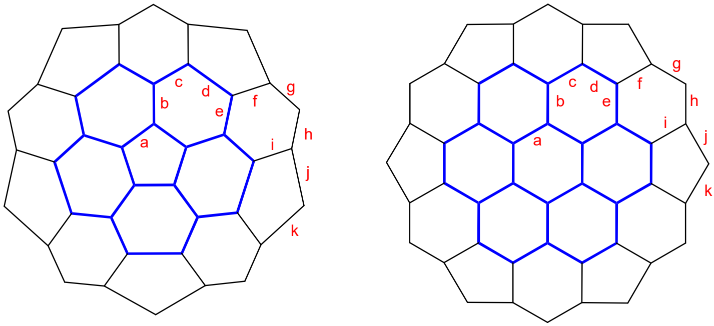
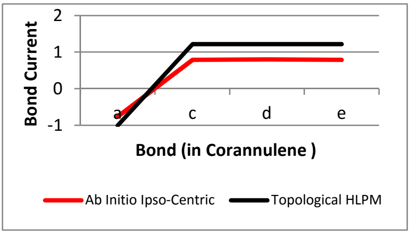
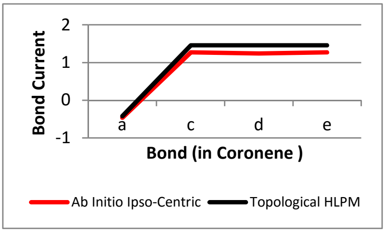


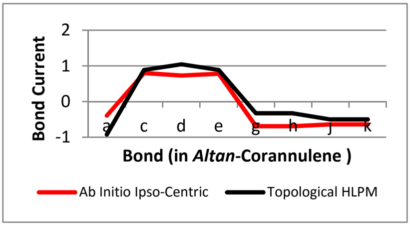
Figure 20. The molecular graphs of four conjugated species: corannulene (the inner-core, highlighted in blue, of the structure on the left), *altan*-corannulene (the entire left-hand structure), coronene (the inner-core, highlighted in blue, of the structure on the right), and *altan*-coronene (the entire right-hand structure). In all cases, symmetrically non-equivalent bonds are labelled according to the scheme adopted by Monaco and Zanasi [160]. Adapted with permission from T. K. Dickens & R. B. Mallion *J. Phys. Chem. A* **118** (2014) 933–939. Copyright 2014 American Chemical Society.

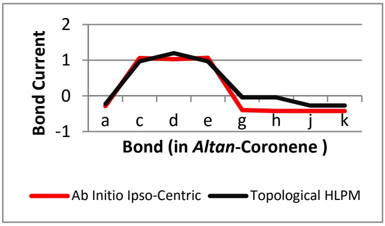




(a)

(b)





(c)

(d)

Figure 21. ‘Comparator’ diagrams for (a) corannulene, (b) coronene, (c) *altan*-corannulene and (d) *altan*-coronene. The comparison in each case is between the predictions of *ab initio ipso*-centric calculations [160] (the red curve) and those of topological HLPM calculations [143] (the black curve). For both sets of calculations, the currents (along the vertical axis) are dimensionless, being expressed as a ratio to the bond current or the integrated current strength (as appropriate) calculated, by the corresponding method, for benzene. The labellings along the horizontal axis — a,b,c, . . — refer to the individual bonds of the four structures, as depicted in Figure 20. Adapted with permission from T. K. Dickens & R. B. Mallion *J. Phys. Chem. A* **118** (2014) 933−939. Copyright 2014 American Chemical Society.

We now examine how the HLPM [87, 135] bond-currents, from various sources [31, 87, 125], compare with analogous quantities (‘integrated current strengths’ [177]) extracted from the calculations based on the GIMIC formalism [175—177] that the Sundholm group has presented [177] for 69 bonds in the ten different condensed, benzenoid hydrocarbons that are illustrated on the left-hand sides of Figures 4, 7 and 10 in ref. [177].

Least-squares regression-lines are presented in Figure 22 between HLPM topological bond-currents [31, 87, 125] (expressed as a ratio to the benzene value) — plotted along the **vertical** axis — and (plotted along the **horizontal** axis) the GIMIC ‘integrated current strengths’ (defined in ref. [177] and likewise expressed relative to the integrated current strength calculated, by the same method, for benzene) for 69 bonds in the ten condensed, benzenoid hydrocarbons illustrated on the left-hand sides of Figures 4, 7 and 10 in ref. [177]; the latter are calculated by the GIMIC *ab initio* formalism [175−177] described by Kaipio *et al.* in that ref. [177]. By means of the GIMIC formalism, the integrated current–strength for a bond in benzene is calculated [177] to be 11.6 nA/T; accordingly, all the integrated current strengths reported for bonds in certain condensed benzenoid hydrocarbons by Kaipio *et al.* in ref. [177] have here been divided by this value to give GIMIC integrated current strengths that are dimensionless numbers expressed as a ratio to this absolute value (11.6 nA/T) calculated as the integrated current strength for benzene. These ratios are the data that were then used in our two regression lines (Figure 22) and in our comparator diagram (Figure 23).

In Figure 22, the left-hand plot (with correlation coefficient 0.977) is for an unrestricted regression, and the right-hand plot (with only a marginally smaller correlation coefficient of 0.976) is for a regression that is additionally constrained to go through the origin. The regression constrained to go through the origin does, nevertheless, have a slope that is somewhat nearer to the ideal of 1 — 0.961, rather than 0.934.

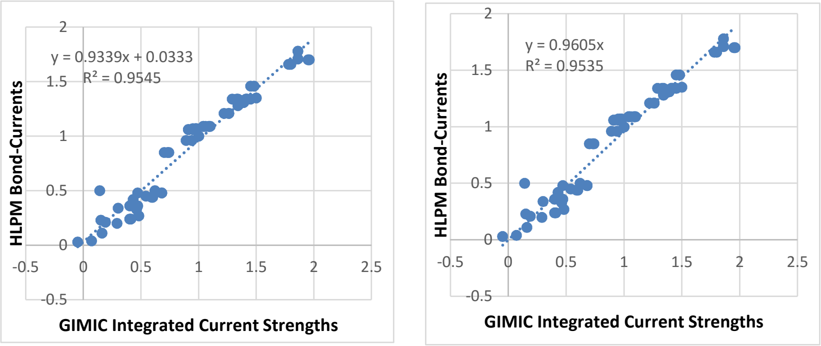


Figure 22. Least-squares regression-lines between HLPM topological bond-currents [31, 87, 135] — plotted along the **vertical** axis — and (plotted along the **horizontal** axis) the integrated current strengths calculated by the GIMIC *ab initio* formalism [175–177] for 69 bonds in the ten condensed, benzenoid hydrocarbons illustrated on the left-hand sides of Figures 4, 7 and 10 in ref. [177]. In each case, the currents plotted along both axes are dimensionless, being expressed as a ratio to the bond current or the integrated current strength (as the case may be) calculated, by the corresponding method, for benzene. The left-hand plot is for an unrestricted regression, and the right-hand plot is for a regression that is additionally constrained to pass through the origin.

As Kaipio *et al*. point out [177], and as we emphasised earlier, the *ab intio* methods do not, in general, enable the calculation of the equivalent of 'bond currents' — the 'integrated current strengths' — that rigorously respect Kirchhoff's Law of Current-Conservation at Junctions [19, 35] (except [181] in the idealised limit of a complete basis-set [182, 183]). Bond currents calculated by the HLPM/HL–CD approach are, by contrast, automatically guaranteed to be entirely consistent with the ring currents calculated for the system as a whole because, by the very way in which they are constructed, the ring currents and bond currents calculated by that method do all strictly obey Kirchhoff's Law. It seems, therefore, that, in the topological model, the conjugated system under study really does behave as it if were a microscopic version of a macroscopic Kirchhoff network [19, 29, 156, 157]. Because of this general non-compliance with the Conservation Law when *ab initio* calculations are envisaged, integrated current strengths calculated for what are in fact symmetrically equivalent bonds are not in general quite the same — in, for example, the data presented in ref. [177]. It should be mentioned in passing that Professor Sundholm has confirmed (in a personal communication to RBM on March 13th, 2015) our suspicion that there is a transcription error in one integrated current strength reported in ref. [177]: the integrated current strength for one of the bonds in anthanthrene (the one given as '13.8' (nA/T) on the left-hand side of Figure 7 in ref. [177]) should in fact be '16.4'. The latter value was, accordingly, the one used in our correlations presented in Figures 22 and 23.

In addition to the regression lines displayed in Figure 22, a comparator diagram was also constructed in which the integrated current strengths of Kaipio *et al*. [177] (expressed as a ratio to the benzene value of 11.6 nA/T) were compared with the corresponding HLPM topological bond-currents (also expressed relative to benzene), accumulated from various sources [31, 87, 125]. This comparator diagram is illustrated in Figure 23. In each case, the two sets of bond currents/integrated current strengths (along the vertical axis) are dimensionless, being expressed as a ratio to the bond current/integrated current strength (as the case may be) calculated, by the corresponding method, for benzene. The red curve depicts the GIMIC integrated current strengths and the black curve represents the HLPM topological bond-currents. Once again, a very gratifying visual agreement is found between the two approaches, concerning the relative variation of the currents borne by the 69 bonds considered in these ten condensed benzenoid hydrocarbons.

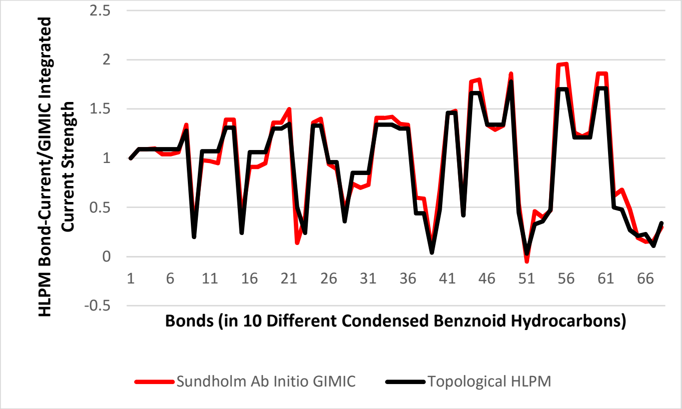


Figure 23. Comparator diagram between relative integrated current strengths from the GIMIC data reported in ref. [177] for 69 bonds in ten different condensed, benzenoid hydrocarbons (the red curve) and the corresponding relative HLPM topological bond-currents, selected from various sources [31, 87, 125], (the black curve). In each case, the currents (along the vertical axis) are dimensionless, being expressed as a ratio to the bond current/integrated current strength (as the case may be) calculated, by the corresponding method, for benzene. The labellings along the horizontal axis refer to the 69 bonds in the ten condensed benzenoid structures for which integrated current strengths are documented in ref. [177]; these labellings are thus arbitrary and hence are of no consequence: the 69 bonds could equally well have been listed in any desired order whatsoever and an equivalent comparator diagram, just as valid, would have resulted from each and every possible such permutation.

12. Conclusions

It will be seen from the previous two sections that there is growing evidence (and agreement) for a belief in what an anonymous referee to ref. [97] described as '. . . the remarkable ability of the topological approach to reproduce complex patterns of current in large polycyclic hydrocarbons.' Gershoni-Poranne *et al.* [146] have also noted '. . . the surprising ability of Hückel-based models to capture essential features of delocalised systems . . .'

Ab initio procedures frequently depend first on the application of elaborate software in order to optimise starting geometries [145] and then on the choice of wave-function basis-set employed; (see, for example, 'Computational Details' [p. 848] of ref [185], 'Ab Initio Calculations' [p. 7448] of ref. [186] and 'Method' [p. 655] of ref. [178]). It is clear, therefore, that such approaches '. . . still require prescriptions for specific wave-functions and possibly other assumptions . . .' [31]. We claim, therefore, that, even with the present-day routine availability of *ab initio* calculations, the simple topological HLPM approach [31, 87, 135] still has intuitive and even quantitative contributions to make [30] to our understanding of the magnetic properties of conjugated systems, displaying, as it does, a possibly unexpected capacity to account for such properties. Application of this approach depends on knowledge only

(a) of the molecular graph [11] of the conjugated system in question (in the form of a vertex-adjacency matrix [86] that describes its carbon–carbon connectivity) and

(b) of the areas of its constituent rings.

According to common belief, this impressive predictive success should ostensibly be the preserve only of sophisticated, and much more complex — both conceptually and computationally — *ab initio* calculations [137]. We have previously suggested [137] that

> '. . . for any given particular molecule, *ab initio* methods may well give rise to more accurate numerical predictions that might more closely mirror observed experimental data. . .',

but they do not so readily afford the more basic physical insight that is appreciated by the wider chemical community. We have also observed [97] that

> '. . . the fact that a simple-minded theory (the HLPM formalism)…' can yield '. . . the same . . . conclusions as a more sophisticated *ab initio* one . . . brings to mind Coulson's celebrated remark [187] about the conceptual value, even in . . . this "*ab initio* age", of *simple* theories that bring about intuitive and ". . . primitive patterns of understanding'".

In the same vein, Kutzelnigg [36] has emphasised that the HMO model is these days used

> '. . . to give a simple interpretation *a posteriori* to *ab initio* calculations, because these give too detailed information. So, HMO is used as a filter to extract relevant features.'

Furthermore, as Haigh and one of the present authors (RBM) [28] put it, many years ago: the ring-current model itself

> '… is so pictorial that one can almost *feel* what is happening when a molecule is subjected to a magnetic field.'

Be that (somewhat anthropomorphic) observation as it may, we finish by emphasising three important and incontrovertible facts:

(a) Kutzelnigg's [36] point that Hückel Theory may be regarded as a 'one-parameter theory' (the parameter in question here being β, the standard Hückel resonance integral in benzene), and that

(b) even granted point a), just mentioned, topological bond-currents and ring currents are themselves independent of β because, when the results are expressed as a *ratio* to the corresponding quantities calculated (by the same HLPM approach) for benzene, β *cancels* [137].

(c) Computed numerical values of topological ring-currents and bond-currents are thus, to use Kutzelnigg's [36] terminology, the fruits of a *parameter-free theory.*

We conclude by coming full circle and pointing out that such observations are not new: even London, in one of his pioneering papers [23] in the field from nearly eighty years ago, properly and succinctly claimed that his calculation '. . . makes no use of any adjustable parameter.'

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References

[1] E. C. Kirby, R. B. Mallion, P. Pollak, P. Skrzyński, Extensions of Euler's polyhedron formula, *Int. J. Chem. Mod.* **6** (2014) 255–274.

[2] J. A. N. F. Gomes, Topology of the electronic current density in molecules, *Phys. Rev. At. Mol. Opt. Phys.* **A28** (1983) 559–566.

[3] M. Gordon, W. H. T. Davidson, Theory of resonance topology of fully aromatic hydrocarbons, *J. Chem. Phys.* **20** (1952) 428–435.

[4] K. Ruedenberg, Quantum mechanics of mobile electrons in conjugated bond systems. III Topological matrix as a generatrix of bond orders, *J. Chem. Phys.* **34** (1961)1884–1891.

[5] L. Spialter, The atom connectivity matrix characteristic polynomial (ACMCP) and its physicso-geometric (topological) significance, *J. Chem. Doc.* **4** (1964) 209–274.

[6] H. H. Schmidtke, Die Bestimmung von Orbitalreihenfolgen in symmetrischen Molekülen auf Grund der Topologie und Struktur, *Theor. Chim. Acta* **9** (1968) 199–209.

[7] D. H. Rouvray, The topological matrix in quantum chemistry, in: A. T. Balaban, (Ed.), *Chemical Applications of Graph Theory*, Academic Press, London, 1976, pp. 175–221.

[8] A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules*, Springer Verlag, Berlin (West), 1977, pp. 1−123.

[9] C. A. Coulson, B. O'Leary, R. B. Mallion, *Hückel Theory for Organic Chemists*, Acad. Press, London, 1978.

[10] R. B. Mallion, D. H. Rouvray, Molecular topology and the *Aufbau* principle, *Mol. Phys.* **136** (1978) 125−128.

[11] N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, Florida, 1992, Chapters 4 & 6, pp. 41−59 and pp. 85−123. (It may be noted that, in a significant and telling change in the technical jargon adopted, Chapter 4, which was entitled 'Topological Matrices' in the original (1983) edition, is, in the current (1993) edition, entitled 'Graph-Theoretical Matrices'.)

[12] R. B. Mallion, The topological nature of the *Aufbau* process and of quantities calculated by simple molecular-orbital theory, in: A. Graovac, I. Gutman, D Vukičević (Eds.), *Mathematical Methods and Modelling for Students of Chemistry and Biology,* HUM, Zagreb, 2009, pp. 55–86.

[13] M. Randić, Conjugated circuits and resonance energies of benzenoid hydrocarbons, *Chem. Phys. Lett.* **38** (1976) 68−70.

[14] J. A. N. F. Gomes, *Some Magnetic Properties of Molecules*, D. Phil Thesis, Univ. Oxford, 1976, especially pp. 69–73.

[15] J. A. N. F. Gomes, R. B. Mallion, A quasi-topological method for the calculation of relative "ring-current" intensities in polycyclic conjugated hydrocarbons, *Revista Portuguesa de Química* **21** (1979) 82−89.

[16] J. Gayoso, A. Boucekkine, Application de la théorie des graphes à la détermination des exaltations de susceptibilité diamagnétique des hydrocarbures conjugués, *Comptes Rend. Acad. Sci.* (*Paris*) **C205** (1979) 327–330.

[17] M. Randić, Aromaticity of polycyclic conjugated hydrocarbons, *Chem. Rev.* **103** (2003) 3449–3605 (especially pp. 3539–3543).

[18] M. Randić, Graph theoretical approach to π-electron currents in polycyclic conjugated hydrocarbons, *Chem. Phys. Lett.* **500** (2010) 123−127.

[19] T. K. Dickens, J. A. N. F. Gomes, R. B. Mallion, Some comments on topological approaches to the π-electron currents in conjugated systems, *J. Chem. Theory Comput.* **7** (2011) 3661−3674.

[20] P. W. Fowler, W. Myrvold, The ‘anthracene problem’: closed-form conjugated-circuit models of ring currents in linear polyacenes, *J. Phys. Chem.* **A115** (2011) 13191−13200.

[21] F. London, Théorie quantique des courants interatomiques dans les combinaisons aromatiques, *J. Phys. Radium* (*7^e Série*) **8** (1937) 397−409.

[22] F. London, *Théorie quantique du diamagnétisme des combinaisons aromatiques*, *Comptes Rend. Acad. Sci.* (*Paris*) **205** (1937) 28−30.

[23] F. London, Superconductivity in aromatic compounds, *J. Chem. Phys.* **5** (1937) 837−838.

[24] G. Berthier, B. Pullman, A. Pullman, *Le diamagnétisme des composés aromatiques*. in: B. Pullman, A. Pullman (Eds.), *Les Théories Électroniques de la Chimie Organique*, Masson, Paris, 1952, Chapter IX, pp. 527−550.

[25] L. Salem, *Molecular Orbital Theory of Conjugated Systems*, W. A. Benjamin, New York, 1966, Chapter 4.

[26] D. E. O’Reilly, Chemical shift calculations, in: J. W. Emsley, J. Feeney, L. H. Sutcliffe (Eds.), *Progress in Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1967, Vol. 2, pp. 1−61; (especially pp. 27−31).

[27] J. D. Memory, *Quantum Theory of Magnetic Resonance Parameters*, McGraw-Hill, New York, 1968 (especially Chapters 5 & 6 and Appendices 5D and 6B).

[28] C. W. Haigh, R. B. Mallion, Ring current theories in nuclear magnetic resonance, in: J. W. Emsley, J. Feeney, L. H. Sutcliffe, (Eds.), *Progress in Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1979/1980, Vol. 13, pp. 303−344.

[29] J. A. N. F. Gomes, R. B. Mallion, The concept of ring currents, in: D. H. Rouvray (Ed.), *Concepts in Chemistry*, Res. Stud. Press Limited, Taunton, Somerset, England, United Kingdom, 1997, *and* Wiley, New York, 1997, Chapter 7, pp. 205−253.

[30] J. A. N. F. Gomes, R. B. Mallion, Aromaticity and ring currents, *Chem. Rev.* **101** (2001) 1349−1383; (especially pp. 1358−1366).

[31] T. K. Dickens, R. B. Mallion, An analysis of topological ring currents and their use in assessing the annulene-within-an-annulene model for super-ring conjugated systems, *Croat. Chem. Acta* **86** (2013) 387−406.

[32] L. Pauling, The diamagnetic anisotropy of aromatic molecules, *J. Chem. Phys.* **4** (1936) 673−677.

[33] K. Lonsdale, Magnetic anisotropy and electronic structure of aromatic molecules, *Proc. Royal Soc.* (*London*) **A159** (1937) 149−161.

[34] E. Hückel, Quantentheoretische Beiträge zum Problem der aromatischen und ungesättigsten Verbindungen III, *Z. Physik* **76** (1932) 628−648.

[35] G. Kirchhoff, Über die Auflösung der Gleichungen, auf welche man bei der Untersuchung der linearen Vertheilung galvanischer Ströme geführt wird, *Annal. Physik u. Chemie* (‘*Poggendorfs Annalen*’) **72** (1847) 497−508.

[36] W. Kutzelnigg, W. What I like about Hückel theory, *J. Comput. Chem.* **28** (2007) 25–34.

[37] A. R. Ubbelohde, Change from aromatic to metallic electrons in organic compounds, *Nature* **132** (1933) 1002–1002.

[38] J. Iball, J. M. Robertson, Structure of chrysene and 1: 2: 5: 6-dibenzanthracene in the crystalline state, *Nature* **132** (1933) 750–751.

[39] R. Peierls, Zur Theorie des Diamagnetismus von Leitungselektronen, *Z. Physik* **80** (1933) 763–791.

[40] P. E. Ehrenfest, Bemerkungen über den Diamagnetismus von festem Wismut, *Z. Physik* **58** (1929) 719–721.

[41] C. V. Raman, Anomalous diamagnetism, *Nature* **124** (1929) 412–412.

[42] R. McWeeny, The diamagnetic anisotropy of large aromatic systems III: Structures with hexagonal symmetry, *Proc. Phys. Soc.* **A64** (1951) 921–930.

[43] H. J. Bernstein, W. G. Schneider, J. A. Pople, The proton magnetic resonance spectra of conjugated aromatic hydrocarbons, *Proc. Royal Soc.* (*London*) **A236** (1956) 515–528.

[44] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford Univ. Press, Oxford, 1932.

[45] R. B. Mallion, *Nuclear Magnetic Resonance Spectroscopy*: *a Theoretical and Experimental Study of the Spectra of Condensed, Benzenoid Hydrocarbons*, Ph.D. Thesis, Univ. Wales, 1969, pp. 10–34.

[46] R. B. Mallion, *Empirical Appraisal and Graph-Theoretical Aspects of Simple Theories of the Ring-Current Effect in Conjugated Systems*, D.Phil. Thesis, Univ. Oxford, 1979, pp. 23–54.

[47] K. Gavroglu, *Fritz London*: *a Scientific Biography*, Cambridge Univ. Press, Cambridge, 1995.

[48] A. Berson, Erich Hückel and the theory of aromaticity: reflections on theory and experiment, in: A. Berson, *Chemical Creativity. Ideas from the Work of Woodward, Hückel*, *Meerwein and Others*, Wily VCH: Weinheim, Germany, 1999, pp. 33–75.

[49] B. O'Leary, R. B. Mallion, C. A. Coulson's work on a contour-integral approach to the London theory of magnetic susceptibility of conjugated molecules, *J. Math. Chem.* **3** (1989) 323–342.

[50] C. W. Haigh, R. B. Mallion, Proton magnetic resonance of non-planar condensed benzenoid hydrocarbons. II. Theory of chemical shifts, *Mol. Phys.* **22** (1971) 955–970.

[51] R. B. Mallion, D. H. Rouvray, On a new index for characterising the vertices of certain non-bipartite graphs, *Studia Sci. Math. Hungarica* **13** (1978) 229–243.

[52] R. B. Mallion, An analytical illustration of the relevance of molecular topology to the *Aufbau* process, *Croat. Chem. Acta* **56** (1983) 477–490.

[53] A. Ceulemans, E. Lijnen, P. W. Fowler, R. B. Mallion, T. Pisanski, Graph theory and the Jahn−Teller theorem, *Proc. Royal Soc.* (*London*) *A* **468** (2012) 971−989.

[54] L. H. Meyer, A. Saika, H. S. Gutowsky, Electron distribution in molecules. III. The proton magnetic spectra of simple organic groups, *J. Am. Chem. Soc.* **75** (1953) 4567−4573.

[55] C. F. Squire, L' anisotropie diamagnétique d'une molecule aromatique, *Compt. Rend. Acad. Sci.* (*Paris*) **206** (1938) 665−667.

[56] H. Brooks, Diamagnetic anisotropy and electronic structure of aromatic molecules, *J. Chem. Phys*. **8** (1940) 939−949.

[57] H. Brooks, Note on diamagnetic anisotropy and the method of molecular orbitals, *J. Chem. Phys.* **9** (1941) 463−465.

[58] W. B. Jensen, The free-electron model. From Otto Schmidt to John Platt. An invited lecture given as part of the symposium *Pioneers of Quantum Chemistry*, held at the 241st National American Chemical Society Meeting at Anaheim, California, U. S. A., March 28th, 2011, in: E. T. Strom, A. K. Wilson, (Eds.), *Pioneers of Quantum Chemistry*, ACS Books, Washington, D.C., U. S. A., 2013, pp. 117−137.

[59] O. Schmidt, H. Schmidt, Weiter Untersuchungen zum Kastenmodell (Zylinderring Kompression der B-Electronen), *Z. Phys. Chem. B* **44** (1939) 185−193.

[60] A. Pullman, G. Berthier, Sur l' expression analytique des grandeurs de la chimie théorique des chaînes linéaires et cycliques alternées, *Compt. Rend. Acad. Sci.* (*Paris*) **233** (1951) 1035−1037.

[61] M. Mayot, G. Berthier, B. Pullman, Calcul quantique de l'anisotropie diamagnétique des molécules organiques — I. La méthode, *J. Phys. Radium* **12** (1951) 652−658.

[62] G. Berthier, M. Mayot, B. Pullman, Calcul quantique de l'anisotropie diamagnétique des molécules organiques — II. Principaux groupes d'hydrocarbures aromatiques, *J. Phys. Radium* **12** (1951) 717−723.

[63] G. Berthier, M. Mayot, A. Pullman, B. Pullman, Calcul quantique de l'anisotropie diamagnétique des molécules organiques — III. Hydrocarbures aromatiques complexes, *J. Phys. Radium* **13** (1952) 15−20.

[64] E. D. Bergmann, J. Hoarau, A. Pacault, A. Pullman, B Pullman, Structure électronique, propriétés physico-chimiques et chimiques de l'acenaphthylène, du fluoranthène et de composés apparentes, *J. Chim. Phys. Phys. Chim. Biol.* **48** (1951) 359−367.

[65] E. D. Bergmann, J. Hoarau, A. Pacault, A. Pullman, B. Pullman, Recherches expérimentales et théoriques sur l'anisotropie diamagnétique des composés aromatiques non-benzenoides et des systems quinoniques, *J. Chim. Phys. Phys. Chim. Biol.* **49** (1952) 474−480.

[66] M. Mayot, G. Berthier, B. Pullman, Compléments sur le calcul du diamagnétisme des composés aromatiques, *J. Chim. Phys. Phys. Chim. Biol.* **50** (1953) 176−182.

[67] R. McWeeny, Diamagnetic anisotropy of *p*-polyphenyls, *J. Chem. Phys.* **17** (1949) 1341−1341.

[68] R. McWeeny, The diamagnetic anisotropy of large aromatic systems. Parts I and II, *Proc. Phys. Soc. A* **64** (1951) 261−275.

[69] R. McWeeny, The diamagnetic anisotropy of large aromatic systems. IV: The polyacenes, *Proc. Phys. Soc. A* **65** (1952) 839−845.

[70] R. McWeeny, The diamagnetic anisotropy of large aromatic systems V: Interpretation of the results, *Proc. Phys. Soc. A* **66** (1953) 714−720.

[71] M. T. Rogers, The magnetic anisotropy of coronene, naphthazarin, and other crystals, *J. Am. Chem. Soc.* **69** (1947) 1506−1508.

[72] M. G. Evans, J. De Heer, J. Gergely, Structure and diamagnetic anisotropy of *p*-benzoquinodimethane in connection with those of *p*-benzoquinone, *Proc. Phys. Soc. A* **62** (1949) 505−508.

[73] T. Pauncz, F. Berencz, The diamagnetic anisotropy of ovalene, *Acta Chim. Acad. Sci. Hungaricae* **2** (1952) 375−382.

[74] R. Pauncz, F. Berencz, The diamagnetic anisotropy of four-ring condensed benzenoid hydrocarbons, *Acta Phys. Acad. Sci. Hungaricae* **2** (1952) 183−193.

[75] J. Aihara, The origin of counter-rotating rim and hub currents in coronene, *Chem. Phys. Lett.* **393** (2004) 7−11.

[76] J. A. Pople, Proton magnetic resonance of hydrocarbons, *J. Chem. Phys.* **24** (1956) 1111−1111.

[77] J. A. Pople, Molecular orbital theory of aromatic ring currents, *Mol. Phys.* **1** (1958) 175−180.

[78] R. McWeeny, Ring currents and proton magnetic resonance in aromatic molecules, *Mol. Phys.* **1** (1958) 311−321.

[79] C. A. Coulson, C. *Diamagnetic Anisotropy of Aromatics*, an unpublished hand-written document, dated May 16th, 1953. (Later published as a 'Special Paper' in ref. (49)). It is deposited in The Papers of Charles Alfred Coulson FRS 1910–1974 (Collection Reference CSAC 60.4.78), MS. Coulson 58 (B. 38.6), Department of Special Collections and Western Manuscripts, Bodleian Library, University of Oxford. We are very grateful to Mr. Colin Harris (Superintendent, Special Collections Reading Rooms) and Dr. Chris Fletcher (Keeper of Special Collections) for their kind help in establishing the correct reference numbers (quoted above) to the manuscript document under discussion.

[80] C. A. Coulson, On the calculation of the energy in unsaturated hydrocarbon molecules, *Math. Proc. Cambridge Phil. Soc.* **36** (1940) 201−203.

[81] N. Mizoguchi, Characteristic polynomial expression and integral expression for imaginary bond–bond polarizability. Rules for London susceptibility and for ring current, *Bull. Chem. Soc. Jpn*. **60** (1987) 2005−2010.

[82] R. McWeeny, Gauge invariance and the magnetic properties of molecules, *Chem. Phys. Lett.* **9** (1971) 341−342.

[83] T. G. Edwards, R. McWeeny, Magnetic properties of conjugated molecules, *Chem. Phys. Lett.* **10** (1971) 283–286.

[84] R. B. Mallion, On the magnetic properties of conjugated molecules, *Mol. Phys.* **25** (1973) 1415–1432.

[85] R. B. Mallion, Some graph-theoretical aspects of simple ring current calculations on conjugated systems, *Proc. Royal Soc.* (*London*) *A* **341** (1974/1975) 429–449.

[86] D. Janežić, A. Miličević, S. Nikolić, N. Trinajstić, *Graph Theoretical Matrices in Chemistry*, Univ. Kragujevac, Kragujevac, 2007, pp. 6-6.

[87] R. B. Mallion, Topological ring-currents in condensed, benzenoid hydrocarbons, *Croat. Chem. Acta* **81** (2008) 227–246.

[88] R. J. Wilson, *Introduction to Graph Theory*, Oliver & Boyd, Edinburgh, 1972.

[89] D. M. Cvetković, M. Doob, H. Sachs, *Spectra of Graphs — Theory and Application*, Deutscher Verlag der Wissenschaften, Berlin.

[90] R. B. Mallion, On the number of spanning trees in a molecular graph, *Chem. Phys. Lett.* **36** (1975) 170–174.

[91] I. Gutman, R. B. Mallion, J. W. Essam, Counting the spanning trees of a labelled molecular-graph, *Mol. Phys.* **50** (1983) 859–877.

[92] B. O'Leary, R. B. Mallion, Counting the spanning trees of labelled molecular-graphs embedded on the surface of a sphere, in: R. B. King, D. H. Rouvray, (Eds.), *Graph Theory and Topology in Chemistry.* A Collection of Papers Presented at an International Conference held at the University of Georgia, Athens, Georgia, U. S. A., 16th–20th March, 1987, Studies in Physical and Theoretical Chemistry, Elsevier Science Publishers, B. V., Amsterdam, 1987, Vol. 51, pp. 544–551.

[93] F. Harary, R. B. Mallion, An elementary, necessary condition for Hamiltonian graphs, involving connectivity, *Nanta Math.* **7** (1974) 96–101.

[94] J. Gayoso, A. Boucekkine, Sur le calcul de la susceptibilité diamagnétique des systèmes Π, dans le cadre de Hückel, au moyen de la technique des perturbations, *Compt. Rend. Acad. Sci.* (*Paris*) *C* **274** (1971) 184–187.

[95] E. C. Kirby, D. J. Klein, R. B. Mallion, P. Pollak, H. Sachs, A theorem for counting spanning trees in general chemical graphs and its particular application to toroidal fullerenes, *Croat. Chem. Acta* **77** (2004) 263–278.

[96] E. C. Kirby, R. B. Mallion, P. Pollak, Counting spanning trees in toroidal Fullerenes, in: F. Cataldo, P. Milani, (Series Eds.), F. Cataldo, A. Graovac, O. Ori, (Volume Eds.), Sir Harold Kroto, (Foreword), *Carbon Materials: Chemistry and Physics* Volume 4: *The Mathematics and Topology of Fullerenes*, Springer, Dordrecht, Heidelberg, London & New York, 2010, Chapter 10, pp. 187–204.

[97] T. K. Dickens, R. B. Mallion, π-Electron ring-currents and bond-currents in some conjugated *altan*-structures, *J. Phys. Chem. A* **118** (2014) 3688–3697.

[98] A. Veillard, Le déplacement chimique en résonance magnétique nucléaire dans les hétérocycles aromatiques d'intérêt biochimique, *J. Chim. Phys. Phys. Chim. Biol.* **59** (1962) 1056–1066.

[99] H. P. Figeys, Regression analysis of ring-current effects on proton chemical shifts in polycyclic aromatic hydrocarbons, *Tetrahedron Lett.* **7** (1966) 4625–4630.

[100] H. P. Figeys, Proton nuclear magnetic resonance spectroscopic studies of aromatic hydrocarbons: induced paramagnetic ring-current in the four-membered ring of biphenylene and related hydrocarbons, *Chem. Commun.* **1967** (1967) 495–496.

[101] R. B. Mallion, Approximate π-electron 'ring current' intensities in some sulphur-heterocyclic analogues of fluoranthene, *J. Chem. Soc. Perkins Trans. II*, **1973** (1973) 235–237.

[102] R. B. Mallion, Sur les "courants de cycle" d'électrons π de quelques hydrocarbures polycycliques et cancérogènes et de leurs isostères azotés correspondants, *Biochimie* **56** (1974) 187−188.

[103] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961, pp. 127–127.

[104] J. Gayoso, *Contribution aux Méthodes Empiriques et Semi-Empiriques de la Chimie Quantique*, Thesis, Docteur Ès Sciences, Université de Paris, 1973.

[105] C. A. Coulson, A. Gołebiewski, On perturbation calculations for the π-electrons and their application to bond length reconsiderations in aromatic hydrocarbons, *Proc. Phys. Soc.* **78** (1961) 1310–1320.

[106] C. A. Coulson, A. Gołebiewski, The Jahn-Teller effect in aromatic ions and radicals, *Mol. Phys.* **5** (1962) 71−84.

[107] H. Martin, H. D. Fösterling, H. Kuhn, Beschreibung von π-Elektronenzuständen durch zweidimensionale zweielektronen-Wellenfunktionen und durch zweidimensionale einelektronenwellen-Funktionen, *Tetrahedron Suppl. 2* **19** (1963) 243–264.

[108] C. A. Coulson, F. Wille, Notes on Kuhn's ω" molecular orbital method, *Tetrahedron* **22** (1966) 3549–3555

[109] G. Doggett, A study of the ω-technique as applied to unsaturated hydrocarbons, *Mol. Phys.* **10** (1966) 225–232.

[110] C. A. Coulson, R. B. Mallion, On the question of paramagnetic "ring currents" in pyracylene and related molecules, *J. Am. Chem. Soc.* **98** (1976) 592–598.

[111] J. A. N. F. Gomes, R. B. Mallion, Calculated magnetic properties of some isomers of pyracylene *J. Org. Chem.* **46** (1981) 719–727.

[112] B. R. M. de Castro, J. A. N. F. Gomes, R. B. Mallion, π-Electron "ring currents" in dipleiadiene, *J. Mol. Struct.* (*Theochem*) **260** (1992) 123−132.

[113] G. G. Hall, A. Hardisson, Ring currents and their effects in aromatic molecules, *Proc. Royal Soc.* (*London*) *A* **268** (1962) 328–338.

[114] I. J. Maddox, R. McWeeny, Ring currents in aromatic molecules, *J. Chem. Phys.* **36** (1962) 2353–2354.

[115] N. Jonathan, S. Gordon, B. P. Dailey, Chemical shifts and ring currents in condensed ring hydrocarbons, *J. Chem. Phys.* **36** (1962) 2443–2448.

[116] J. D. Memory, T. B. Cobb, High-resolution NMR spectrum of chrysene, *J. Chem. Phys.* **39** (1963) 2386–2387.

[117] J. D. Memory, Ring currents in pentacyclic hydrocarbons, *J. Chem. Phys.* **38** (1963) 1341–1343.

[118] J. A. Pople, K. G. Untch, Induced paramagnetic ring currents, *J. Am. Chem. Soc.* **88** (1966) 4811–4815.

[119] D. E. Jung, Grenzen der Ringstromdefinition der Aromatizität: Ringstromberechnungen in nicht-alternierenden Tri- und Tetracyclen, *Tetrahedron* **25** (1969) 129–134.

[120] C. W. Haigh, R. B. Mallion, Proton magnetic resonance of planar condensed benzenoid hydrocarbons. III. McWeeny calculations on hexacyclic molecules, *Mol. Phys.* **18** (1970) 767–772.

[121] R. B. Mallion, π-Electron "ring currents" in fluoranthene and related molecules, *J. Mol. Spectr*. **35** (1970) 491–493.

[122] R. B. Mallion, Calculation of the π-electron "ring current" properties of some carcinogenic, heptacyclic, condensed, benzenoid hydrocarbons, *J. Med. Chem.* **14** (1971) 824–826.

[123] C. A. Coulson, J. A. N. F. Gomes, R. B. Mallion, Ring magnetic susceptibilities in conjugated hydrocarbons, *Mol. Phys.* **30** (1975) 713–732.

[124] R. B. Mallion, Some comments on the use of the "ring-current" concept in diagnosing and defining "aromaticity", *Pure Appl. Chem.* **52** (1980) 1541–1548.

[125] C. W. Haigh, R. B. Mallion, "Ring-current" effects on ^{1}H-NMR chemical shifts in linear acenes, *J. Chem. Phys.* **76** (1982) 4063–4066.

[126] C. F. Wilcox, E. N. Farley, Dicyclooctabiphenylene. Synthesis and properties, *J. Amer. Chem. Soc.* **106** (1984) 7195–7200.

[127] R. B. Mallion, "Ring-currents" in corannulene, a prototype pattern-molecule for buckminsterfullerene, in: A. Graovac, (Ed.), *Math/Chem/Comp 1988*, Proceedings of an international course and conference on the interfaces between mathematics and computer Science, Dubrovnik, Yugoslavia, 20th–25th June, 1988, Studies in Physical and Theoretical Chemistry, Elsevier Science Publishers, B.V., Amsterdam, 1989, pp. 505–510.

[128] C. W. Haigh, R. B. Mallion, Rationalisation of "ring-current" sizes in polycyclic, conjugated hydrocarbons, *Croat. Chem. Acta* **62** (1989) 1–26.

[129] R. B. Mallion, Ring current effects in C_{60}, *Nature* **325** (1987) 760–761.

[130] J. Aihara, R. Sekine, T. Ishida, Electronic and magnetic characteristics of polycyclic aromatic hydrocarbons with factorizable Kekulé structure counts, *J. Phys. Chem. A* **115** (2011) 9314–9321.

[131] J. Aihara, Graph-theoretical formulation of London diamagnetism, *J. Am. Chem. Soc*. **101** (1979) 5913–5917.

[132] J. Aihara, T. Horikawa, Graph-theoretical formula for ring currents induced in a polycyclic conjugated system, *Bull. Chem. Soc. Jpn*. **56** (1983) 1853–1854.

[133] J. Aihara, Magnetotropism of biphenylene and related hydrocarbons. A circuit current analysis, *J. Am. Chem. Soc.* **107** (1985) 298–302.

[134] J. Aihara, R. Sekine, S. Oe, Partly olefinic reference structure defined to evaluate bond resonance energy and the ring current it would sustain, *Croat. Chem. Acta* **77** (2004) 353–359.

[135] A. T. Balaban, T. K. Dickens, I. Gutman, R. B. Mallion, Ring currents and the PCP rule, *Croat. Chem. Acta* **83** (2010) 209–215.

[136] T. K. Dickens, R. B. Mallion, Ring-current assessment of the annulene-within-an-annulene model for some large coupled super-ring conjugated-systems, *Croat. Chem. Acta* **87** (2014) 221–232.

[137] T. K. Dickens, R. B. Mallion, Topological ring-currents and bond-currents in the *altan*-(*r*,*s*)-coronenes, *Chem. Commun.* **51** (2015) 1819–1822.

[138] T. K. Dickens, R. B. Mallion, Topological ring-current assessment of the 'annulene-within-an-annulene' model in (*N*)-circulenes and some structures related to kekulene, *Chem. Phys. Lett.* **517** (2011) 98–102.

[139] T. K. Dickens, R. B. Mallion, Topological ring-currents in the "empty" ring of benzo-annelated perylenes, *J. Phys. Chem. A* **115** (2011) 351–356.

[140] T. K. Dickens, R. B. Mallion, Topological ring-currents and bond-currents in some nonalternant isomers of coronene, *J. Phys. Chem. A* **115** (2011) 13877–13884.

[141] T. K. Dickens, R. B. Mallion, The regular (*r*,*s*)-coronenes and the 'annulene-within-an-annulene' rule, *RSC Adv.* **3** (2013) 15585–15588.

[142] T. K. Dickens, R. B. Mallion, π-Electron ring-currents and bond-currents in [10,5]-coronene and related structures conforming to the 'annulene-within-an-annulene' model, *Phys. Chem. Chem. Phys.* **15** (2013) 8245–8253.

[143] T. K. Dickens, R. B. Mallion, Topological Hückel–London–Pople–McWeeny ring-currents and bond-currents in *altan*-corannulene and *altan*-coronene, *J. Phys. Chem. A* **118** (2014) 933–939.

[144] T. K. Dickens, R. B. Mallion, Topological ring-current and bond-current properties of the *altans* of certain *K*-factorizable conjugated systems containing "fixed" single-bonds, *J. Phys. Chem. A* **119** (2015) 5019–5025.

[145] T K Dickens, R. B. Mallion, Comparisons of π-electron ring-current and bond-current patterns calculated by topological ('HLPM') and *ab-initio* ('*ipso*-centric') formalisms for two isomeric conjugated hydrocarbons, corazulene and cornaphthalene, *Croat. Chem. Acta* **88** (2015) 221–225.

[146] R. Gershoni-Poranne, C. M. Gibson, P. W. Fowler, A. Stanger, Concurrence between current density, nucleus-independent chemical shifts, and aromatic stabilization energy: the case of isomeric (4)- and (5)phenylenes, *J. Org. Chem.* **78** (2013) 7544–7553.

[147] W. P. Ozimisky, M. Palusiak, J. Dominikowska, T. M. Krygowski, R. W. Havenith, C. M. Gibson, P. W. Fowler, Capturing the elusive aromaticity of bicalicene, *Phys. Chem. Chem. Phys.* **15** (2013) 3286–3293.

[148] P. W. Fowler, S. Cotton, D. Jenkinson, W. Myrvold, W. H. Bird, Equiaromatic benzenoids: arbitrarily large sets of isomers with equal ring-currents, *Chem. Phys. Lett.* **597** (2014) 30–35.

[149] J. Aihara, Is superaromaticity a fact or an artifact? The kekulene problem, *J. Am. Chem. Soc.* **14** (1992) 865–868.

[150] E. Steiner, P. W. Fowler, L. W. Jenneskens, A. Acocella, Visualisation of counter-rotating ring currents in kekulene, *Chem. Commun.* **2001** (2001) 659–660.

[151] J. Aihara, Simple method for estimating the superaromatic stabilization energy of a super-ring molecule, *J. Phys. Chem. A* **112** (2008) 4382–4385.

[152] J. Aihara, M. Makino, R. Ishida, J. R. Dias, Analytical study of superaromaticity in cycloarenes and related coronoid hydrocarbons, *J. Phys. Chem. A* **117** (2013) 4688–4697.

[153] C. W. Haigh, R. B. Mallion, E. A. G. Armour, Proton magnetic resonance of planar condensed benzenoid hydrocarbons. II. A critical evaluation of the McWeeny ‘ring current’ theory, *Mol. Phys.* **18** (1970) 751–766.

[154] H. C. Longuet-Higgins, L. Salem, The alternation of bond length in long conjugated chain molecules III. The cyclic polyenes $C_{18}H_{18}$, $C_{24}H_{24}$, $C_{30}H_{30}$, *Proc. Royal Soc.* (*London*) *A* **257** (1960) 445–456.

[155] R. C. Haddon, The application of the Biot-Savart law to the ring current analysis of proton chemical shifts — I: A comprehensive investigation of the annulenes, *Tetrahedron* **28** (1972) 3613–3633.

[156] H. M. S. Cundy, *S. M. P. Advanced Mathematics Book 3* (*Metric*), Cambridge Univ. Press, London, 1970, pp. 911-911.

[157] D. Smart, *Linear Algebra & Geometry*, Cambridge Univ. Press, Cambridge, England, United Kingdom, 1988. S. M. P. Further Mathematics Series, pp. 307–308.

[158] G. Monaco, On the diatropic perimeter of iterated *altan*-molecules, *Phys. Chem. Chem. Phys.* **17** (2015) 28544–28547.

[159] G. Monaco, R. Zanasi, On the additivity of current density in polycyclic aromatic hydrocarbons *J. Chem. Phys.* **131** (2009) 044126.

[160] G. Monaco, R. Zanasi, Three contra-rotating currents from a rational design of polycyclic aromatic hydrocarbons: *altan*-corannulene and *altan*-coronene, *J. Phys. Chem. A* **116** (2012) 9020–9026.

[161] G. Monaco, R. Zanasi, Anionic derivatives of *altan*-coronene, *J. Phys. Org. Chem.* **26** (2013) 730–736.

[162] G. Monaco, M. Memoli, R. Zanasi, Additivity of current density patterns in *altan*-molecules, *J. Phys. Org. Chem.* **26** (2013) 109–114.

[163] I. Gutman, Topological properties of *altan*-benzenoid hydrocarbons *J. Serb. Chem. Soc.* **79** (2014) 1515–1521.

[164] I. Gutman, *Altan* derivatives of graphs, *Iranian J. Math. Chem.* **5** (2014) 85–90.

[165] N. Bašić, T. Pisanski, Iterated *altans* and their properties, *MATCH Commun. Math. Comput. Chem.* **24** (2015) 653–666.

[166] T. Keith, R. F. W. Bader, Calculation of magnetic response properties using a continuous set of gauge transformations, *Chem. Phys. Lett.* **210** (1993) 223–231.

[167] P. Lazzeretti, M. Malagoli, R. Zanasi, Computational approach to molecular magnetic properties by continuous transformation of the origin of the current density, *Chem. Phys. Lett.* **220** (1994) 299–304.

[168] E. Steiner, P. W. Fowler, Patterns of ring currents in conjugated molecules: A few-electron model based on orbital contributions, *J. Phys. Chem. A* **105** (2001) 9553–9562.

[169] E. Steiner, P. W. Fowler, Four- and two-electron rules for diatropic and paratropic ring currents in monocyclic π systems, *Chem. Commun.* **2001** (2001) 2220–2221.

[170] E. Steiner, A. Soncini, P. W. Fowler, Full spectral decomposition of ring currents, *J. Phys. Chem. A* **110** (2006) 12882–12886.

[171] E. Clar, *The Aromatic Sextet*, Wiley, New York, 1972, pp. 59 & 89.

[172] I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin, 1989, pp. 93–117.

[173] S. J. Cyvin, I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer-Verlag, Berlin,1988, pp. 2 & 293.

[174] P. W. Fowler, E. Steiner, Pseudo-π currents: rapid and accurate visualisation of ring currents in conjugated hydrocarbons, *Chem. Phys. Lett.* **364** (2002) 259–266.

[175] J. Jusélius, D. Sundholm, J. Gauss, Calculation of current densities using gauge-including atomic orbitals *J. Chem. Phys.* **121** (2004) 3952–3963.

[176] H. Fliegl, O. Lehtonen, D. Sundholm, V. R. Kaila, Hydrogen-bond strengths by magnetically induced currents, *Phys. Chem. Chem. Phys.* **13** (2011) 434–437.

[177] M. Kaipio, M. Patzschke, H. Fliegl, F. Pichierri, D. Sundholm, Effects of fluorine substitution on the aromaticity of polycyclic hydrocarbons, *J. Phys. Chem. A* **116** (2012) 10257–10268.

[178] M. Lillington, P. W. Fowler, M. V. Diudea, Patterns of counter-rotating ring-currents in two valance isomers of corazulene, *Polish J. Chem.* **81** (2007) 653–662.

[179] A. T. Balaban, D. E. Bean, P. W. Fowler, Patterns of ring currents in coronene isomers, *Acta Chim. Slov.* **57** (2010) 507–512.

[180] G. Monaco, R. Zanasi, Investigation of the *p*-coronene series in the context of the ‘annulene-within-an-annulene’ model by means of *ipso*-centric *ab-initio* calculations of π-electron currents, *Phys. Chem. Chem. Phys.* **15** (2013) 17654–17957.

[181] S. Taubert, D. Sundholm, J. Jusélius, Calculation of spin-current densities using gauge-including atomic orbitals, *J. Chem. Phys.* **134** (2011) 054123.

[182] S. T. Epstein, Gauge invariance, current conservation, and GIAOs *J. Chem. Phys.* **58** (1973) 1592–1595.

[183] S. T. Epstein, *The Variation Method in Quantum Mechanics*, Academic Press, New York, 1974.

[184] P. W. Fowler, A. Soncini, Visualising aromaticity of bowl-shaped molecules, *Phys. Chem. Chem. Phys*. **13** (2011) 20637–20643.

[185] G. V. Baryshnikov, B. V. Minaev, M. Pittwlkow, C. B. Nielson, R. Salcedo, Nucleus-independent chemical shifts criterion of aromaticity in the π-extended tetraoxa(8)circulenes, *J. Mol. Model.* **19** (2013) 847–850.

[186] G. Monaco, R. Viglioni, R. Zanasi, P. W. Fowler, Designing ring-current patterns: [10,5]-coronene, a circulene with inverted rim and hub currents, *J. Phys. Chem. A* **110** (2006) 7447–7452.

[187] C. A. Coulson, Present state of molecular structure calculations, *Rev. Mod. Phys.* **32** (1960) 170–177.