

Some Observations on Triplet Ground-States in the Context of ‘Topological’ (HLPM) Ring-Currents in Conjugated Systems

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 DEDICATED TO THE MEMORY OF DR EDWARD CAMERON KIRBY (1934–2019)

Abstract: When the quasi graph-theoretical Hückel–London–Pople–McWeeny (HLPM) approach is used to calculate ‘topological’ π -electron ring-currents and bond-currents in conjugated hydrocarbons, a problem is identified that occurs whenever application of the *Aufbau* process gives rise to a π -electronic ground-state configuration that is a *triplet*. This circumstance seems to occur only occasionally and, even when it does, the generally somewhat *outré* molecular graphs in question appear unlikely to represent extant or viable conjugated systems. The molecular graphs of four examples are used to illustrate this ‘triplet ground-state problem’, only one of which represents a hydrocarbon that has actually been synthesised. It is pointed out that the ‘triplet ground-state problem’ does constitute an intrinsic limitation of the HLPM approach. It is, though, a limitation that is also necessarily inherent in other equivalent (though ostensibly different) methods of calculating magnetic properties due to π -electron ring-currents — methods that are likewise founded on the Hückel molecular-orbital conventions. When a triplet ground-state arises, topological ring-currents and bond-currents cannot be calculated by the HLPM method and its equivalents. Infinite paramagnetism is formally to be predicted in such situations.

Keywords: Topological Ring-Currents in Conjugated Systems, π -Electron Triplet Ground-States, *Aufbau* Principle, Infinite Paramagnetism.

INTRODUCTION

FOR a period of some 25 years, one of us (RBM) was privileged to work with the late Edward Cameron Kirby (1934–2019), the honorand of this Session of MATH/CHEM/COMP 31 (Dubrovnik, 2019). A considerable proportion of our collaboration was devoted to the idea of spanning trees in graphs,^[1–7] especially of chemical graphs^[8] that represent conjugated hydrocarbons (extant or hypothetical). A prominent application of these ideas in Mathematical Chemistry has been in the context of what the present authors have named^[9,10] the Hückel^[11,12]–London^[13]–Pople^[14]–McWeeny^[15] (HLPM) formalism for calculating what are frequently called ‘topological’ ring-currents and bond currents^[9,10] — for reviews please see Refs. [16–19].

In the course of performing calculations on individual molecules by means of this HLPM approach a problem has, from time-to-time, been encountered whenever, on application of the *Aufbau* Principle,^[11,20–24]

the π -electronic ground-state configuration of the conjugated hydrocarbon in question is found to be a *triplet* ground-state. We have occasionally noted specific examples of this phenomenon as we have serendipitously come across them in our previously reported work.^[16,25]

Such structures have, however, arisen only very occasionally and, even then, they have been associated with somewhat *outré* molecular graphs^[8] that are unlikely to represent the carbon–carbon connectivities^[8] of extant or viable conjugated hydrocarbons — examples are (3,12)-Coronene^[25,26] (structure 1, on the left-hand side of Figure 1) and^[16] what Agranat *et al.*^[27] call Corannulene [6¹, 6¹, 6¹, 6¹, 6¹, 6¹] (structure 2, on the right-hand side of Figure 1).

The problem also arose in some recent calculations (not yet published) in which, following the *ab initio* calculations of Monaco and Zanasi,^[28,29] we attempted to extend our earlier studies of the neutral *altans* and multiple (‘iterated’) *altans* of corannulene and coronene,^[30] and their dianions,^[31] to the tetra-anions and hexa-anions of the same parent species.

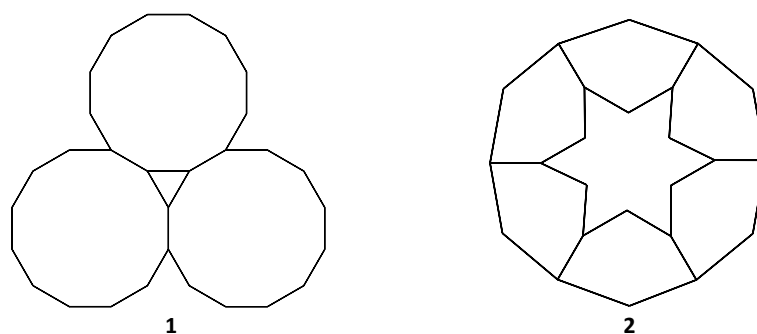


Figure 1. Carbon–carbon connectivities ('molecular graphs'^[8]) of hypothetical conjugated hydrocarbons (3,12)-Coronene^[25,26] (**1**) and Corannulene [6¹, 6¹, 6¹, 6¹, 6¹, 6¹]^[16,27] latent in both of which is the 'triplet ground-state problem', discussed in the text.

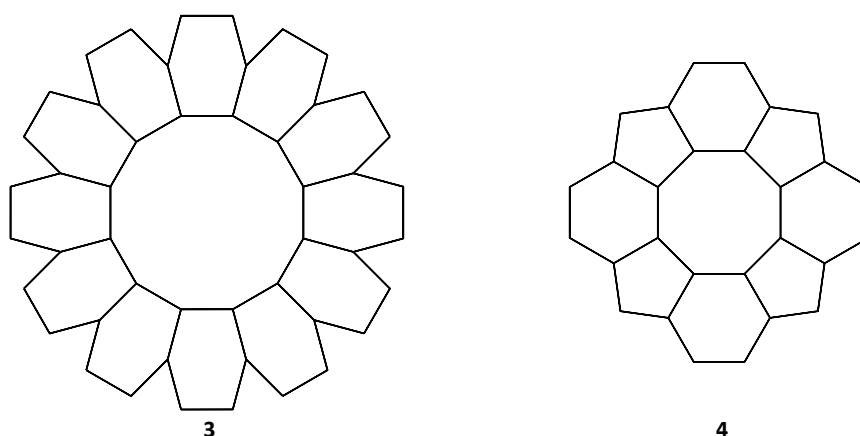


Figure 2. Carbon–carbon connectivities ('molecular graphs'^[8]) of (left) a hypothetical conjugated hydrocarbon (**3**) that we have 'designed', and (right) structure **4**, the extant [8]-circulene labelled '**9**' by Baryshikov *et al.* in Ref. [32]. The di-anion and the di-cation of **3**, and the neutral species **4**, are used here in order to illustrate the 'triplet ground-state problem', discussed in the text.

We have also noted this occurrence of what we are somewhat colloquially calling 'the triplet ground-state problem' in some charged species of a hypothetical conjugated system (structure **3**, on the left-hand side of Figure 2) and in the case of an extant hydrocarbon of the [8]-circulene family (structure **4**, on the right-hand side of Figure 2), the latter of which was recently considered by Baryshikov *et al.*^[32] These two structures will be used in this presentation, along with structures **1** and **2** (in Figure 1), in order to illustrate the observations that are being documented here about the 'triplet ground-state problem'.

The overall aim of the present communication is to describe the problems that a triplet ground-state brings about, to record some specific examples of this problem's occurrence, and to emphasise that it represents an intrinsic limitation of the HLP approach. It is, furthermore, also a limitation that is necessarily inherent in other equivalent (though ostensibly different) methods^[13–15,33–38] of calculating magnetic properties due to π -electron ring-

currents — methods that are likewise founded on the Hückel molecular-orbital conventions.^[11,12,39]

THE OVERALL STRUCTURE OF HLP RING-CURRENT CALCULATIONS

HLP 'topological' ring-current and bond-current calculations are carried out in the following four stages:^[16–19]

- (a) Hückel^[11,12,39] energy-levels and molecular-orbitals — the latter consisting of appropriate linear-combinations of the atomic orbitals (LCAO) that are centred on each of the carbon atoms — are first calculated from an arbitrarily labelled molecular-graph^[8,16–19] representing the carbon–carbon connectivity of the particular conjugated hydrocarbon under study. In the graph-theoretical^[8,16–19] language in which the HLP

approach^[9,10] is frequently cast, these are the eigenvalues and eigenvectors,^[11,21] respectively, of the vertex-adjacency matrix^[8] of that associated labelled molecular-graph.^[8]

- (b) Then the *Aufbau* process^[20–24] is applied, during the course of which the available π -electrons are distributed amongst these calculated energy-levels in order to determine a π -electron ground-state configuration for the hydrocarbon in question. If the *Aufbau* procedure has been successful — which is not always the case, as is discussed in Refs. [21–23] — then, at this stage, each energy level is known to have been unambiguously assigned either *two* π -electrons (in which case that energy level is said to be ‘fully occupied’ or ‘filled’), or just *one* π -electron (when it is ‘singly occupied’), or *no* π -electrons at all (in which latter case the molecular orbital in question is said to be ‘unoccupied’, or ‘empty’). This is all as described on pp. 123–125 of Cotton.^[20]
- (c) Once this π -electronic ground-state has been established, the π -electron energy-levels and the LCAO molecular-orbitals (determined in stage (a), above), together with the ground-state π -electron configuration (determined in (b), above, by invoking the *Aufbau* process^[20]), are used to calculate certain quantities that are referred to as^[16–19] Coulson bond-orders^[11,40] and self- and mutual imaginary bond-bond polarisabilities^[15,40] (all of which are explicitly defined in the next section).
- (d) These purely *graph-theoretical* quantities are then combined with *geometrical* information (in the form of the *areas* of the various rings within the conjugated system being studied) in order to calculate the HLPm ring-currents and bond-currents.

In the present paper, we shall not be concerned at all with stage (d). We do, however, now consider stages (a)–(c) in more detail.

DETAILS OF STAGES (a)–(c)

(a) Hückel Energy-Levels and LCAO Molecular-Orbitals

The first task in a ring-current calculation carried out by means of the HLPm method is to find the eigenvalues and the corresponding eigenvectors of the vertex-adjacency matrix^[8,21] of the molecular graph^[8] representing the conjugated hydrocarbon under consideration. If that hydrocarbon has N carbon atoms, then

$$\{\mathbf{c}_J\}_{J=1,2,\dots,N} \left(= \left\{ \left(c_{J1} \ c_{J2} \ \dots \ c_{JN} \right)^T \right\}_{J=1,2,\dots,N} \right)$$

denotes the set of eigenvectors (*i.e.*, the standard, field-

free Hückel coefficients in each of the N LCAO molecular-orbitals), and $\{E_J\}_{J=1,2,\dots,N}$ denotes the family of eigenvalues of that molecular graph — that is, they are the Hückel energy-levels, ϵ_J , when expressed in the conventional form $\epsilon_J = \alpha + E_J\beta$, where α and β are the standard Hückel Coulomb-integrals and resonance-integrals, respectively.^[11,12,39]

It is assumed in the above that the eigenvectors are (a) normalised and (b) orthogonalised (if degeneracies amongst the energy levels — that is, repetitions within the eigenvalues — make this latter operation necessary because the eigenvectors of the real-symmetric vertex-adjacency matrix are then no longer all automatically mutually orthogonal). This matter is gone into in considerable detail on pp. 63–65 of Ref. [21].

(b) The *Aufbau* Process and the Possibility of a Triplet Ground-State

Once the energy levels are established, as in stage (a), above, they may notionally be thought of as being arranged vertically in (from the bottom to the top) increasing order of energy, and the available π -electrons (N for a neutral species, $(N+2)$ for a di-anion, $(N-2)$ for a di-cation, *etc.*) are then assigned to occupy the energy-levels, beginning with the one of lowest energy, according to the well-known *Aufbauprinzip*, which incorporates the Pauli Exclusion Principle and Hund’s Rules of Maximum Multiplicity (*e.g.*, Ref. [20]). This process yields a family of N numbers, $\{v_J\}_{J=1,2,\dots,N}$ (which are the occupations numbers assigned, by the *Aufbau* process, to the energy levels/eigenvalues); the elements of the family $\{v_J\}_{J=1,2,\dots,N}$ are all either 0, 1 or 2.

Rouvray and one of the present authors (RBM)^[22,23] showed many years ago that the *Aufbau* process may effectively be simulated by means of an algorithm, the outcome of which depends only on *the relative order* of the eigenvalues/energy levels computed (as in (a), above) for the structure. In that sense, therefore, since the order of the energy levels/eigenvalues — being latent, as they are, in the vertex-adjacency matrix — depends only on the carbon-atom connectivity in the molecular graph in question, the *Aufbau* procedure^[20] may itself be thought of as *an entirely graph-theoretical* process. (Please see Refs. [21–23] for full details of this idea.)

Now, our purpose in this communication is to point out that there are occasions — after an attempt is made by application of the *Aufbau* Process^[20–23] to determine a π -electronic ground-state configuration — when that ground-state turns out to be a *triplet*, in which the highest-occupied levels are doubly degenerate and each is singly occupied (*i.e.*, $v_J = 1$ for both of those degenerate energy-levels). This case arises when the last two π -electrons to be distributed in the course of applying the *Aufbau* process^[20–23] have to be assigned to a pair of doubly degenerate

molecular-orbitals (that is, a pair of repeated eigenvalues of the molecular graph^[8,17,21]) — thereby necessarily resulting in two unpaired spins and thus a triplet ground-state. This is where there is a problem with the HLP approach — a problem that is shared with other ostensibly different formalisms^[33–38] that also rely on the simple Hückel model.^[11,12,39] How this comes about is explained in the next sub-section.

A referee has pointed out that there are wider and more sophisticated considerations concerning the *Aufbau* process than are addressed here — see, for example, Refs. [41–43] — which involve predicting spin by use of a variety of different techniques. In this work, however, we are avowedly using Hückel Theory only. We are also strictly adhering to Hund's rule^[20]. Consideration of species such as extended graphite and graphene-like structures — together with concomitant boundary-conditions — is, therefore, not directly relevant to our work here on discrete molecules. Furthermore, neither are we doing configuration interaction nor valence bond calculations. We are merely establishing the circumstances under which application of the HLP approach, in its originally proposed form,^[9,10] exposes certain pathological cases. In addition, it should be noted that the HLP formalism is explicitly *defined*^[9,10,17] to incorporate the graph-theoretical algorithm of Refs [17, 21–23] in order to mimic the conventional *Aufbau* process.^[20] That is why no other form of *Aufbau* scheme is entertained here.

(c) Coulson Bond-Orders and Self- and Mutual Bond-Bond Polarisabilities

The third stage in the HLP approach is to take the graph-theoretical data — the eigenvalues and the eigenvectors of the vertex-adjacency matrix of the molecular graph — that have been obtained in stage (a), above, and the ground-state π -electronic configuration — the family of eigenvalue/energy-level occupation-numbers, $\{v_j\}_{j=1,2,\dots,N}$ — established by an application of the *Aufbau* process in stage (b), in order to calculate two types of graph-theoretical Hückel molecular-orbital indices that are needed in the ring-current calculations.^[17] These are the well-known Coulson bond-order,^[11,12,40] $P_{(rs)}$, for the bond between carbon atoms r and s (defined in equation (1), below) and the imaginary mutual- (and self-) bond-bond polarisabilities, $\bar{\pi}_{(rs)(tu)}$ and $\bar{\pi}_{(rs)(rs)}$, respectively, originally defined by McWeeny in Ref. [15] (with some misprints that are corrected in the Appendix of Ref. [40]). The imaginary mutual bond-bond polarisabilities, $\bar{\pi}_{(rs)(tu)}$, between bonds (rs) and (tu), are defined in equations (2) and (3), below; the imaginary self bond-bond polarisability for the bond (rs) is obtained by replacing ' tu ' everywhere with ' rs ' in equations (2) and (3). All the symbols in equations (1) – (3) have been defined in the previous sub-section, with the

exception of M , which is the number of *doubly-occupied* orbitals. It should be emphasised that, for equations (2) and (3) to be valid, there must be *no* singly-occupied orbitals; the number of unoccupied orbitals is thus $(N-M)$

$$P_{(rs)} = \sum_{j=1}^N v_j c_{jr} c_{js} \quad (1)$$

$$\bar{\pi}_{(rs)(tu)} = \pi_{rs,tu} - \pi_{rs,ut} + \pi_{sr,ut} - \pi_{sr,tu}, \quad (2)$$

where

$$\pi_{rs,tu} = \frac{2}{\beta} \sum_{i=1}^M \sum_{j=M+1}^N \frac{c_{ir} c_{js} c_{jt} c_{iu}}{E_i - E_j}. \quad (3)$$

The actual fine details of the calculations — such as equations (1)–(3), above — are, however, not necessary for the present considerations and, for any interested reader, they may be found in our earlier reviews^[16–19]; the crucial points that we emphasise here are that

- (i) Bond order is defined for open-shell states — see pp. 63–64 of Ref. [11]: some of the $\{v_j\}_{j=1,2,\dots,N}$ in equation (1) may thus be equal to 1 for certain values of the running-index, J .
- (ii) The imaginary bond-bond polarisabilities, $\bar{\pi}_{(rs)(tu)}$, by contrast, are defined (by equations (2) and (3)) *only for closed-shell ground-states* — that is, *only when every energy level is either unoccupied or doubly occupied*. In particular, we observe that, in equation (3), M denotes the number of *doubly-occupied* orbitals and the other $(N-M)$ orbitals are *all unoccupied*; there must be no singly occupied orbitals.

Triplet ground-states are, accordingly, not catered for in the HLP method, nor are they by other methods^[33–38] that are based on the Hückel approach. As a very special case of the more-general scenario outlined here, the first explicit encounter with this phenomenon was in the context of the $[4n]$ -annulenes *without* 'bond-alternation', studied by Pople and Untch^[44] in their classic paper of more than fifty years ago. Consequently, in these 'triplet ground-state' situations, *infinite paramagnetism is formally to be predicted* — as was pointed out originally by Pople and Untch,^[44] was re-iterated and further discussed in Note 21 on Page 170 of Ref. [11], and as was also more recently re-emphasised by Aihara.^[45]

EXAMPLES OF CASES IN POINT

(i) Structure 1 (shown on the left-hand side of Figure 1)

The left-hand section of Scheme 1, labelled 'I', shows the energy levels (eigenvalues) for the neutral species of structure 1 (which is depicted on the left-hand side of Figure 1). They are presented according to the conventions explained in the caption to Scheme 1.

After an application of the *Aufbau* process to the neutral species of structure **1** — in the course of which 30 π -electrons are notionally to be assigned to the energy levels — the first 28 electrons go into the orbitals (labelled 1–14) coloured in **red** in the section of Scheme 1 labelled 'I'; each of these orbitals is therefore **fully occupied** with two electrons. The last two electrons of the 30 to be distributed are then available to be placed, with paired spins, in the non-bonding energy-level 15. However, level 16 is also a non-bonding orbital; according, therefore, to the rules of the *Aufbau* procedure, the two non-bonding orbitals (15 and 16, coloured in **green** in section I of Scheme 1) are consequently both **singly occupied**. The remaining (anti-bonding) orbitals — which are denoted in **black** in section I of Scheme 1 and are labelled 17–30 — are **unoccupied**. The result is a *triplet* π -electronic ground-state for the neutral species of structure **1**. (It should be noted, however, that, for example, the *di-anion* (1^{2-}) of structure **1** would have a closed-shell ground-state, as the two extra π -electrons that it possesses would be accommodated in levels 15 and 16, thereby completing the double occupation of both of these two non-bonding orbitals, and thus resulting in a closed-shell structure.)

(ii) Structure 2 (shown on the right-hand side of Figure 1)

The section of Scheme 1 headed 'II' shows the energy levels (eigenvalues) for the neutral species of structure **2** (depicted on the right-hand side of Figure 1). They are likewise presented according to the conventions explained in the caption to Scheme 1. It should be noted that, in accordance with the Coulson–Rushbrooke Theorem (please see Chapter 6, pp. 88–110, and Appendix D, pp. 159–166, of Ref. [11]), the eigenvalues of the *bipartite* graph^[8,11] that represents structure **2** are seen to occur in \pm pairs, around zero.

After an application of the *Aufbau* process, in which 24 π -electrons are notionally to be distributed, the first 22 electrons go into the bonding orbitals (labelled 1–11) coloured in **red** in section II of Scheme 1 and each of these is therefore **fully occupied** with two electrons. The last two electrons are then available to be assigned to the non-bonding energy-level 12. However, in an exact analogy with what happened in the case of structure **1** in Scheme 1, level 13 in section II of Scheme 1 is also a non-bonding orbital; according, therefore, to the rules of the *Aufbau* procedure, the two non-bonding orbitals (12 and 13, coloured in **green** in section II of Scheme 1) are, as a result, **singly occupied**. The remaining orbitals — namely, the anti-bonding orbitals, denoted in **black** in section II of Scheme 1 and labelled 14–24 — are all **unoccupied**. The result is once again a triplet π -electronic ground-state for the neutral species of structure **2**. (It should be noted that — as was the case with structure **1** — the *di-anion* (2^{2-}) of structure **2** would have a

closed-shell ground-state, as the two extra π -electrons that it possesses would complete the full occupation of the two non-bonding orbitals 12 and 13.)

(iii) Structure 3 (shown on the left-hand side of Figure 2)

The section of Scheme 1 headed 'III' presents the energy levels (eigenvalues) for the neutral species of the 'designed' structure **3** (shown on the left-hand side of Figure 2). They are likewise displayed according to the conventions explained in the caption to Scheme 1. Once again, as with structure **2**, the eigenvalues of the *bipartite* graph^[8,11] that represents structure **3** occur in \pm pairs, around zero (in accordance with the Coulson–Rushbrooke Theorem,^[11] referred to above).

After an application of the *Aufbau* process, in which 48 π -electrons are notionally to be distributed, all 48 may straight away be accommodated in the (bonding) energy levels labelled 1–24 and coloured in **red** in the section of Scheme 1 headed 'III'; each of these orbitals is therefore **fully occupied** with two electrons. The remaining orbitals — which are anti-bonding ones and which are denoted in **black** in Scheme 1 and are labelled 25–48 — are **unoccupied**. The result is — in contrast to what occurred in the case of the neutral species **1** and **2** — a *closed-shell* π -electronic ground-state for the neutral species of structure **3**. This means that, by use of the standard HLP procedures (of which full details are given in, for example, Refs. [9,10,16–19]), 'topological' ring-currents and bond-currents may be computed for the neutral species of structure **3** (which is illustrated on the left-hand side of Figure 2). For the record, we note that the calculated ring-current intensities (expressed as a ratio to the benzene value) are -0.161 — the negative sign indicates that the ring current is paramagnetic — for the inner, 12-membered ring and $+1.113$ (diamagnetic) for each of the 12 peripheral six-membered rings. As for the bond currents, a current of magnitude 1.113 flows around the perimeter (of length $36 = [4n]$, with $n = 9$), in the anti-clockwise (diamagnetic) direction, and one of magnitude 1.274 flows around the inner, 12-membered ring ($[4n]$, with $n = 3$), in the clockwise (paramagnetic) sense. By symmetry, the ring-current intensity in all the 'spokes' bonds,^[46,47] connecting the inner ring to the perimeter, is precisely zero.

However, consultation of section III of Scheme 1 shows that (for example) the dianion (3^{2-}) of structure **3** would again have a triplet ground-state, because the 'extra' two electrons that the di-anion possess — but which the neutral species does not possess — would have to be assigned, by the *Aufbau* process, so that one was accommodated by level 25 and the other by the degenerate level 26, as both anti-bonding levels 25 and 26 are of energy ($\alpha - 0.51764\beta$). A similar situation would be encountered on considering the di-cation (3^{2+}) of **3**. This has

two fewer electrons than does the neutral **3** and so, with only 46 electrons now to be assigned when the *Aufbau* process is invoked, 44 of them would be accommodated by double occupation in each of levels 1–22, but the last two would have to sit, each on its own, in the two degenerate bonding-levels 23 and 24, which are both of energy ($\alpha + 0.51764\beta$). Hence, a triplet ground-state would once again be encountered.

(iv) Structure 4 (shown on the right-hand side of Figure 2)

Finally, the section of Scheme 1 headed 'IV' shows the energy levels (eigenvalues) for the neutral species of structure **4** (shown on the right-hand side of Figure 2). They are likewise displayed according to the conventions explained in the caption to Scheme 1. This extant structure (**4**), along with some doubly-charged species related to it, was recently discussed by Baryshikov *et al.*^[32]

During an application of the *Aufbau* process, in which 28 π -electrons are notionally to be distributed, the first 26 electrons conveniently go into the bonding orbitals (labelled 1–13) that are coloured in red in the section of Scheme 1 headed 'IV'; each of these orbitals is therefore **fully occupied** with two electrons. The last two electrons are then available to be assigned to the energy-level labelled 14 (also a bonding orbital). However, by analogy with what happened with structure **1** in section I of Scheme 1 and with structure **2** in section II of Scheme 1, this level 14 in section IV of Scheme 1 is degenerate with level 15, both bonding orbitals having energy ($\alpha + 0.13446\beta$). According, therefore, to the rules of the *Aufbau* procedure, these two degenerate bonding-orbitals (14 and 15), coloured in green in section IV of Scheme 1, are, as a result, **singly occupied**. The remaining orbitals — one (labelled 16) which is non-bonding and the rest (labelled 17–28) which are all anti-bonding — are denoted in black in section IV of Scheme 1 and are all **unoccupied**. The result is once again a *triplet* π -electronic ground-state for the neutral species of structure **4**.

It should be noted that — as was the case with, for example, structure **1** — the *dianion* (4^{2-}) of structure **4** would have a closed-shell ground-state, as the two extra π -electrons that it possesses when compared with the neutral species would completely fill the two bonding orbitals labelled 14 and 15, each of which, in neutral structure **4** itself, is only singly occupied, as is evident from section IV of Scheme 1. The topological ring-currents and bond-currents of 4^{2-} can, therefore, be computed, by the standard methods described in detail in our previous reviews.^[16–19] Since this charged species is an extant structure recently discussed in Ref. [32], we take the opportunity to present, in Figure 3, the topological HPLM ring-currents and bond-currents of the di-anion of structure **4**. For the full details of how these bond currents

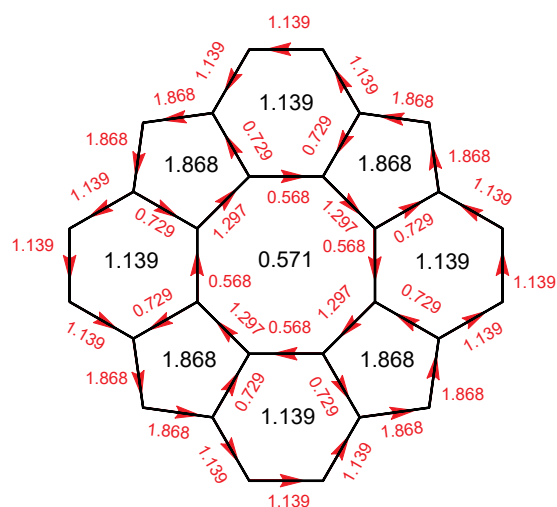


Figure 3. HPLM ring-current and bond-current maps for 4^{2-} , the di-anion of structure **4** (introduced in Ref. [32]). Figures in black in the centres of rings denote the corresponding (diamagnetic) ring-current intensities (expressed as a ratio to the benzene value), whilst red figures written along the bonds denote the bond-currents (in the directions indicated by the arrows) that are consistent with them

and ring currents were computed, the reader is referred to extensive and fully-worked examples in two reviews^[16,17] and to several briefer, but still substantial, examples presented in Refs. [9,18 and 19].

All ring-currents in 4^{2-} are diamagnetic; bond currents are such that there is a diamagnetic flow (that is, in the anti-clockwise direction) around the perimeter, which is of length 20 ($= [4n]$, with $n = 5$), and a flow in the clockwise (paramagnetic) sense around the inner 8-membered ring (which is $[4n]$, with $n = 2$). In 4^{2-} , the spokes bonds^[46,47] connecting the inner (8-membered) ring to the 20-membered perimeter do *not* (as, by contrast, was the case with the spokes bonds of structure **3**) carry zero current by symmetry but, as can be seen from Figure 3, they do in fact bear a substantial current — some 73 % of the benzene value.

In Figure 3, the numbers in black in the centres of the rings are the corresponding topological ring-currents (expressed as a ratio to the benzene value). The positive nature of all of these ring currents indicates, on the convention being used, that they are diamagnetic and thus are considered to circulate in the anti-clockwise direction around their respective rings. Figures written in red along the bonds denote the corresponding HPLM bond-currents (which, again, are expressed as a ratio to the corresponding bond-current calculated, by the same method, for benzene). The arrow pointing along each bond indicates the direction of flow of the bond current in that bond. By

virtue of the validity of Kirchhoff's Law of Conservation of Currents at Junctions,^[6] all *bond-currents* — the quantities depicted in red in Figure 3 — are automatically predetermined once the *ring currents* in all rings — the quantities in black, in Figure 3 — have been specified.^[48–50] As we have previously pointed out,^[17,18,50] the strict observance of the Kirchhoff Conservation Law in the case of the HLP approach is essentially because, on the assumptions made, a conjugated hydrocarbon really is mimicked as if it were a microscopic version of a standard macroscopic Kirchhoff network, with EMFs and 'arms' consisting of macroscopic wires, loop currents (the macroscopic analogy of ring currents) around the closed regions, and currents (the macroscopic analogy of bond currents) in the individual wires. Conservation of currents at junctions in *ab-initio* calculations is, by contrast, strictly observed *only in the limit of an infinite basis set*.^[51–54]

ARTIFICIALLY OBTAINING THE TRIPLET GROUND-STATE PROBLEM BY DELIBERATELY BREAKING SYMMETRY

A referee has pointed out that a renowned example of a system for which Hückel molecular-orbital (HMO) theory predicts a triplet ground state is square cyclobutadiene, with all four resonance integrals, β , being the same. In this case, the non-bonding energy-level is doubly degenerate and this, of course, is what gives rise to the triplet ground-state — see, for example, Page 78 of Ref. [11]. Another well-known example is cyclooctatetraene, the HMO description of which behaves in very much the same way, although, in practice, the most important aspect of this structure is that, on steric grounds, it is severely non-planar; (please see Page 81 of Ref. [11]). In addition, we have ourselves already drawn attention in the present paper to an analogous situation that obtains in the case of the $[4n]$ -annulenes; (please see Ref. [44] and Note 21 on Page 170 of Ref. [11]). However, as the above-mentioned referee has reminded, if the resonance integrals — in, say, cyclobutadiene — are allowed to alternate as $\beta(s)$ and $\beta(l)$, mimicking 'short' and 'long' bonds, respectively, this degeneracy disappears by means of a pseudo Jahn–Teller/Renner distortion to a rectangular shape (as described by Coulson *et al.* on Pages 79–80 and in Note 13 on Page 172 of Ref. [11]); as a result, the total π -electron energy goes down. This has led to the referee's suggestion of investigating whether the examples considered in this paper in which a triplet ground-state is encountered might not behave in a similar way, if given the opportunity to lower the symmetry of the problem by the introduction of

alternation in the values of the resonance integrals. Returning again to our structure **2**, illustrated on the right-hand side of Figure 1, we have taken up the referee's suggestion and (somewhat arbitrarily) we have effected the following changes:

- For those bonds around the periphery the resonance integrals have been changed so that they alternate between 0.90 and 1.10 (in units of β).
- For those bonds forming the 'inner star', the resonance integrals alternate between 0.85 and 1.15.
- For the 'spokes bonds', connecting the inner star to the periphery, the resonance integrals have been left at 1.00.

This results in the ordered eigenvalue/energy-level list depicted in Scheme 2 (with the same colour conventions as in Scheme 1: **red** indicates doubly-occupied orbitals and **black** denotes empty energy-levels).

This, therefore, is seen to result in a closed-shell ground-state, as desired. This situation is to be compared with column II of Scheme 1, which shows the outcome of the

Eigenvalues/Energy Levels for Structure 2 (in Figure 1) when alternating values are assigned to Resonance Integrals (as described in the text), and the Occupation of those Levels by π -Electrons. Structure 2 has 24 carbon atoms.	
24	-2.5615528
23	-2.3072793
22	-2.3072793
21	-1.6396742
20	-1.6396742
19	-1.5615528
18	-1.3072728
17	-1.3072728
16	-1.0615108
15	-0.6395066
14	-0.6395066
13	-0.0565232
12	0.0565232
11	0.6395066
10	0.6395066
9	1.0615108
8	1.3072728
7	1.3072728
6	1.5615528
5	1.6396742
4	1.6396742
3	2.3072793
2	2.3072793
1	2.5615528

Scheme 2. Disposition of Eigenvalues/Energy-Levels for Structure **2** (in Figure 1) together with their corresponding occupation by π -electrons after the *Aufbauprinzip* has been applied. The Colour Convention is as in Scheme 1: **Doubly ('fully') occupied** orbitals are depicted in **red**, and **unoccupied ('empty')** orbitals are denoted in **black**.

original HLPm calculation on structure **2**, when all resonance integrals were assigned the standard value, 1.00β .

Even though the quantifying of resonance integrals in the above calculation was subjective and arbitrary, this exercise — suggested by the referee — does allow the claim that there exists at least one set of resonance-integral values that has the effect of splitting the degeneracies of the non-bonding levels labelled 12 and 13 in column II of Scheme 1. In this case, these divide into two new levels — likewise labelled, in Scheme 2, as 12 and 13 — of energies $(\alpha + 0.0565232\beta)$ and $(\alpha - 0.0565232\beta)$, respectively. This splitting of the two previously degenerate non-bonding levels into a bonding orbital and a symmetrically paired anti-bonding one thus enables a ‘closed-shell ground-state’ to be established. This state of affairs thereby obviates the triplet ground-state problem — at least in the case of this particular example.

We noted earlier that structure **2** is an *alternant* species (that is, one whose carbon–carbon connectivity is represented by a *bipartite* molecular-graph),^[8,11,21] and that the ‘pairing’ of eigenvalues prescribed by the Coulson–Rushbrooke Theorem (discussed at length in Chapter 6 and Appendix D of Ref. [11]) is, accordingly, displayed in column II of Scheme 1 (as was observed earlier) and in Scheme 2. It may be noted that Schemes 1 and 2 are also in accord with the observation that the Coulson–Rushbrooke Theorem applies *irrespective of the values assigned to the resonance integrals*; (this point is discussed on Page 164 of Ref. [11]). Most eigenvalues (though not all, as this example shows) do *change* when the resonance integrals are changed, but *all* eigenvalues — whatever their value — continue to comply with the provisions of the Coulson–Rushbrooke Theorem and *are*, accordingly, still ‘paired’, as Scheme 2 shows in this particular example of structure **2**.

In summary, although this excursion into variation of resonance integrals has been instructive, it should be emphasised that not having all resonance integrals set at the standard value of 1.00β contravenes the ‘rules’ of the HLPm approach, as defined in Refs. [9 and 10]. That is why, in this work — as in our other recent applications of the rudimentary, pseudo graph-theoretical, HLPm approach — resonance integrals have not generally been varied from the standard value of 1.00β .

CONCLUSION

In this communication we have drawn attention to a difficulty that arises in the Hückel–London–Pople–McWeeny approach to calculating topological ring-currents and bond-currents in conjugated hydrocarbons. This happens whenever application of the *Aufbau* process to the eigenvalues/energy levels of the vertex-adjacency matrix of the hydrocarbon’s molecular graph results in a triplet

π -electronic ground-state for the system. This difficulty has been illustrated by explicit appeal to four of only about half a dozen examples that the authors, over the years, have come across in the course of carrying out HLPm calculations on scores of different conjugated systems. Not only are instances of this phenomenon apparently rare but, even when they do arise, they have tended to be associated with molecular graphs that are unlikely to represent the carbon–carbon connectivities of existing or potentially viable conjugated hydrocarbons. Of the structures giving rise to the problem that have been dealt with here, for example, only one (structure **4**) is, to our knowledge, an extant species.

Despite its ostensibly infrequent occurrence, we nevertheless emphasise that this ‘triplet ground-state problem’ does represent an intrinsic limitation of the HLPm approach. It is, furthermore, also a limitation that is necessarily inherent in other equivalent (though ostensibly different) methods^[13–15,33–38] of calculating magnetic properties due to π -electron ring-currents — methods that are likewise founded on the Hückel molecular-orbital conventions.^[11,12,39] When a triplet ground-state arises, topological ring-currents and bond-currents cannot be calculated by the HLPm method,^[9,10,13–19] and its equivalents.^[33–38] Infinite paramagnetism is formally to be predicted in such situations.^[11,44,45]

We conclude by drawing attention to an observation that Rouvray and one of the present authors (RBM) made in Refs. [22] and [23] and which was further discussed in Ref. [21]: it was shown in those places that the *Aufbau* process may effectively be simulated by an entirely graph-theoretical algorithm and that, for certain bizarre graphs that are unlikely to represent the carbon–carbon connectivity of viable molecules, no unambiguously defined π -electronic ground-state of *any* sort — let alone a closed-shell one — can be devised when the *Aufbau* process is applied.^[21–23] It is, of course, self-evident that HLPm ring-currents cannot be computed for the network in question in *these* cases, either.

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