EXTENSION OF THE PAIRING THEOREM TO MÖBIUS NON-ALTERNANT HYDROCARBONS

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Abstract

It is proved that an eigenvalue pairing theorem applies to the molecular graphs associated with Möbius *non-*alternant hydrocarbons that contain exactly two symmetry-related odd-membered rings, one of which is Möbius (i.e. has the equivalent of precisely one edge weighting of -1 somewhere within it) and the other of which is Hückel (i.e. may be considered to have all its edge weightings $+1$).

1. General introduction

The much celebrated Pairing Theorem of Coulson and Rushbrooke [1,2], which was first formally proven some fifty years ago, continues to spark considerable interest within the chemical community [3]. In its original form, the Theorem related to so-called *alternant* hydrocarbons – that is, to hydrocarbons in which the carbon atoms could be consistently labelled or "starred" in such a way that every other carbon atom in the carbon skeleton would bear a star, and that no two "starred" atoms would be directly bonded together *via* a carbon–carbon "sigma" bond. The "pairing" part of the Theorem states that the π-electron energy levels of all alternant-hydrocarbon species are symmetrically distributed in complementary "plus–minus" pairs about the zero energy level. The same Theorem may be expressed in slightly different, but equivalent, language by making use of graph-theoretical concepts. The Theorem then becomes the following: any conjugated hydrocarbon possessed of a bipartite molecular graph will have eigenvalues that exist in positive and negative complementary pairs about the zero eigenvalue. The various elaborations of the Theorem that have been advanced since its initial publication have recently been reviewed in this journal by two of the present authors [3].

In addition to its considerable extension and reformulation, the Pairing Theorem has also been shown to apply in a wide range of different chemical contexts [4]. For instance, the Theorem is now known to hold for many species other than alternant hydrocarbons. As examples, mention may be made of both positive and negative hydrocarbon ions [5], various classes of hetero-conjugated molecules such as the triazines [6] or the inorganic cumulenes [7], high-spin hydrocarbon and other systems [8], and chemical species having a Möbius-strip type of topology [9,10]. It is on the latter that we focus attention here. Such Möbius species were defined by Heilbronner [11] as cyclic arrays of orbitals in which there is an odd number of sign inversions because of negative overlaps between adjacent π-orbitals of differing sign. Reviews that have considered the applicability of the Pairing Theorem to Möbius systems have been presented by Graovac et al. [12], Zimmerman [13], and Day et al. [10]. It is our purpose here to demonstrate how the Pairing Theorem can be further extended to a previously unstudied family of molecules of this type, namely, to a certain class of non-alternant Möbius hydrocarbons.

2.   Mathematical introduction

For a graph G on N vertices, the Pairing Theorem may be stated in the following form [14]:

$$x_i + x_{N-i+1} = 0, \qquad \text{for all } i = 1, 2, \ldots, N, \tag{1}$$

where $\{x_i\}_{i=1,2,\ldots,N}$ are the roots (not necessarily distinct) of the characteristic polynomial $\phi(G, x)$ of G. The latter may be represented in expanded form thus:

$$\phi(G, x) = \sum_{n=0}^{N} a_n x^{N-n}, \tag{2}$$

where a_n is the scalar coefficient of the $(N-n)$th power of x in the characteristic polynomial. It is then well known [14] that the Pairing Theorem, as stated above, is equivalent to the property that

$$a_n = 0, \qquad \text{for all } odd \ n. \tag{3}$$

The long observed fact [1–4,15] that the Pairing Theorem holds for bipartite graphs but not for non-bipartite ones may then be rationalised on the basis of Sachs' Theorem [16–20]. This is because odd-membered circuits (necessarily present in a non-bipartite parent graph G) imply the existence of Sachs graphs with an odd number of vertices when Sachs' Theorem is applied, and such Sachs graphs inevitably make contributions to a_n, where n is odd. (They *may* also contribute to a_n where n is even, but they *must* in general have an effect on a_n when n is odd.) In the case of molecular graphs which have neither weighted edges nor weighted self-loops, the

Pairing Theorem holds if and only if the graph in question is bipartite [15]. In the case of certain edge-weighted non-bipartite graphs, however, these contributions from odd circuits, although individually non-zero, may *sum* to zero; in such circumstances, the Pairing Theorem would then continue to hold, even though the graph in question may be non-bipartite. In this paper, we draw attention to one particular such special case by considering a class of edge-weighted (although vertex-*un*weighted) molecular graphs that represent certain *Möbius* non-alternant hydrocarbons, to which the Pairing Theorem *does* apply.

DEFINITION OF OUR CLASS OF MOLECULAR GRAPHS

The graph G is defined to belong to the special class in question if it represents a conjugated hydrocarbon containing exactly two symmetry-related odd-membered rings, one of which is Möbius (i.e., has the equivalent of precisely one edge weighting of -1 somewhere within it) and the other of which is Hückel (i.e., in the present context, it may be considered to have all its edge weightings $+1$). Two odd-membered rings in a molecule, represented by the circuits R^* and R^{**} in the molecular graph G, are said to be *symmetry related* if the subgraphs $G - R^*$ and $G - R^{**}$ are isomorphic. Some examples of such molecular graphs are illustrated in fig. 1.
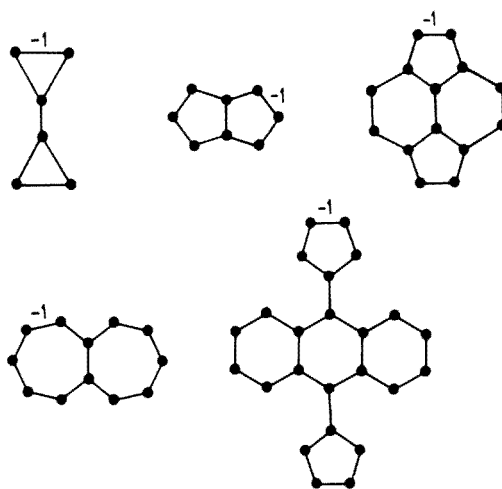

Fig. 1. Some examples of molecular graphs representing Möbius non-alternant hydrocarbons of the type to which the theorem under discussion applies.

THEOREM

The Pairing Theorem applies to the molecular graphs associated with Möbius non-alternant hydrocarbons of the class just defined.

3.   Preliminaries on Sachs' Theorem

Before proving this, we need to remind the reader of Sachs' Theorem for edge-weighted graphs [19]. In what follows, we make extensive use of the notation and the results of ref. [19], where what is here frequently referred to as a "Sachs graph" is there called a "mutation graph". The essentials are summarised below, but complete details may be found by consulting ref. [19]. Three types of mutation graphs were defined there [19]; since, however, we are here concerned with edge-weighted graphs, but not with vertex-weighted ones, consideration and definition of the loop graph L (fig. 2(a)) as a Sachs (mutation) graph (one of those invoked as such in ref. [19]) will *not* be required. By the term "Sachs (mutation) graph" in *this* paper, we shall mean only a subgraph of the parent molecular graph G that is
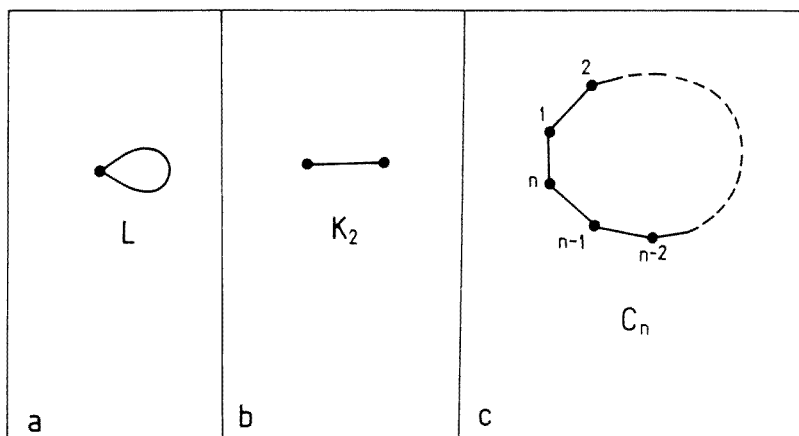

Fig. 2. Sachs (mutation) graphs [19].

constituted solely from one or more complete graphs K_2 (fig. 2(b)) and/or any circuit graph C_n, $3 \leq n \leq N$ (fig. 2(c)). Sachs' Theorem and its extension to edge-weighted graphs [21,22,19] then prescribe that

$$a_0 = 1$$

and

$$a_n = \sum_{H \in M_n} 2^{c(H)}(-1)^{k(H)}t(H), \quad \text{for } n \geq 1. \tag{4}$$

Here, M_n denotes the set of all mutation graphs of G on n vertices, $k(H)$ is the number of components in any one particular such Sachs graph H, $c(H)$ is the number of circuit graphs in this subgraph, and $t(H)$ is the *traversal* of H, defined as follows [19]:

(a)   For our purposes, a *traversal* is a function defined on the following edge-weighted graphs:

(i) the complete graph K_2, with edge weighting b_{ij} (fig. 3(a)): the traversal, $t(K_2) = b_{ij} b_{ji} = b_{ij}^2$;

(ii) the circuit graph C_n (fig. 3(b)):

$$t(C_n) = b_{12} b_{23} \ldots b_{n-1\,n} b_{n1}.$$
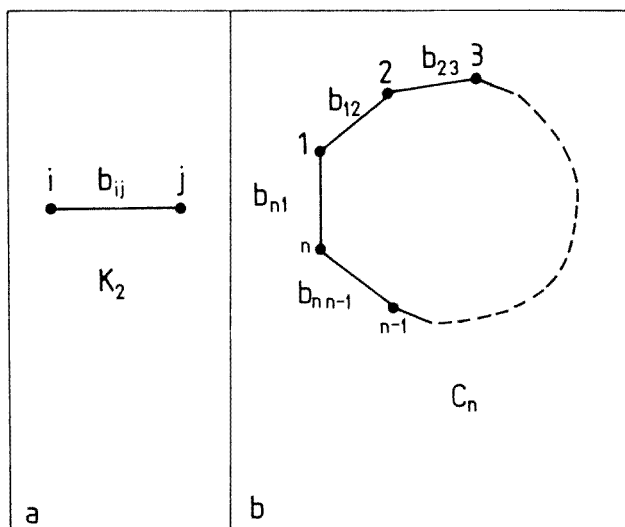

Fig. 3. The edge-weighted Sachs (mutation) subgraphs: (a) K_2, (b) C_n.

(b)   We finally define the traversal $t(H)$ of a mutation (Sachs) graph H to be *the product of the traversals of all the components of H.*

In all that follows, it will be helpful for the reader to bear in mind that for the particular molecular graphs G that we are considering here, all edge weightings b_{ij} are $+1$, with the sole exception of the one edge in the Möbius ring that has a weighting of -1. Consequently, in these special cases, $t(K_2) = 1$ for *all* Sachs graphs K_2, because

$$t(K_2) = (-1)^2 = 1 \qquad \text{for the edge with weight } -1,$$

and

$$t(K_2) = (+1)^2 = 1 \qquad \text{for all the other edges.}$$

Furthermore,

$$t(C_n) = 1 \times 1 \times 1 \times \ldots \times 1 = 1 \qquad \text{for any Hückel circuit in } G,$$

and

$$t(C_n) = 1 \times 1 \times \ldots \times (-1) \times 1 \times \ldots \times 1 = -1 \quad \text{for any Möbius circuit in } G.$$

4.   Proof of the Theorem

As we have already remarked, to prove the Theorem it is sufficient to show that $a_n = 0$ whenever n is odd [14]. In all that follows, therefore, n is assumed to be odd. Since the parent graph G is taken to be edge-weighted but not vertex-weighted (so that, as was mentioned earlier, the loop graph L (fig. 2(a)) is not admitted as a possible Sachs graph in the present discussion), it follows that any mutation graph H on n vertices (n odd) must in general contain an odd number of odd-membered circuits among its components; in the context of the class of molecular graphs we have defined for treatment in this paper, these considerations determine that each $H \in M_n$ must contain *exactly one* odd circuit, be it either of Hückel type (in which every edge weighting around it is taken to be $+1$) or of Möbius type (in which exactly one edge weighting is taken to be -1 and all the others are assumed to be $+1$).

We denote by M_n^* the subset of those Sachs graphs belonging to M_n that contain a Hückel circuit and by M_n^{**} the subset of those Sachs graphs from within M_n that include a Möbius circuit. Then:

$$M_n = M_n^* \cup M_n^{**}; \qquad M_n^* \cap M_n^{**} = \varnothing. \tag{5}$$

There is a one-to-one mapping between M_n^* and M_n^{**}, described as follows. As a consequence of the assumed symmetry of the molecular graph that was stated in its definition, for each $H^* \in M_n$ such that H^* contains an *odd* Hückel circuit C^* and is of the form

$$H^* = h^* \oplus C^*,$$

there exists

$$H^{**} \in M_n$$

such that H^{**} contains the *odd* Möbius circuit C^{**} which is symmetrically equivalent to C^* and is of the form

$$H^{**} = h^{**} \oplus C^{**}.$$

Here, h^* and h^{**} stand for Sachs graphs contained within the subgraphs $G - C^*$ and $G - C^{**}$, respectively; h^* and h^{**} are chosen to be isomorphic. Furthermore, $h^* \oplus C^*$ symbolises the Sachs graph having h^* and the circuit C^* as its components; $h^{**} \oplus C^{**}$

analogously stands for the Sachs graph having h^{**} and C^{**} as its components. We note in passing that if h^* and h^{**} contain circuits, these must necessarily be even-membered. Then:

$$a_n = \sum_{H \in M_n} 2^{c(H)}(-1)^{k(H)} t(H)$$

$$= \sum_{H^* \in M_n^*} 2^{c(H^*)}(-1)^{k(H^*)} t(H^*) + \sum_{H^{**} \in M_n^{**}} 2^{c(H^{**})}(-1)^{k(H^{**})} t(H^{**}). \quad (6)$$

Now,

$$\sum_{H^* \in M_n^*} 2^{c(H^*)}(-1)^{k(H^*)} t(H^*) = - \sum_{H^{**} \in M_n^{**}} 2^{c(H^{**})}(-1)^{k(H^{**})} t(H^{**}), \quad (7)$$

because

$$t(H^*) = t(h^*) \cdot t(C^*),$$

$$t(H^{**}) = t(h^{**}) \cdot t(C^{**}),$$

$$t(h^*) = t(h^{**}) = 1,$$

$$t(C^*) = -t(C^{**}) = 1,$$

and therefore

$$t(H^{**}) = -t(H^*),$$

whereas

$$c(H^{**}) = c(H^*)$$

and

$$k(H^{**}) = k(H^*).$$

Hence, eqs. (6) and (7) lead to

$$a_n = 0, \qquad \text{for all } n, \text{ as required.} \qquad \square$$

5. Example

We illustrate the theorem by giving as an example its application to the graph G in fig. 4, in which are also depicted all the Sachs graphs of G on an odd number of vertices. In the notation introduced in this figure,
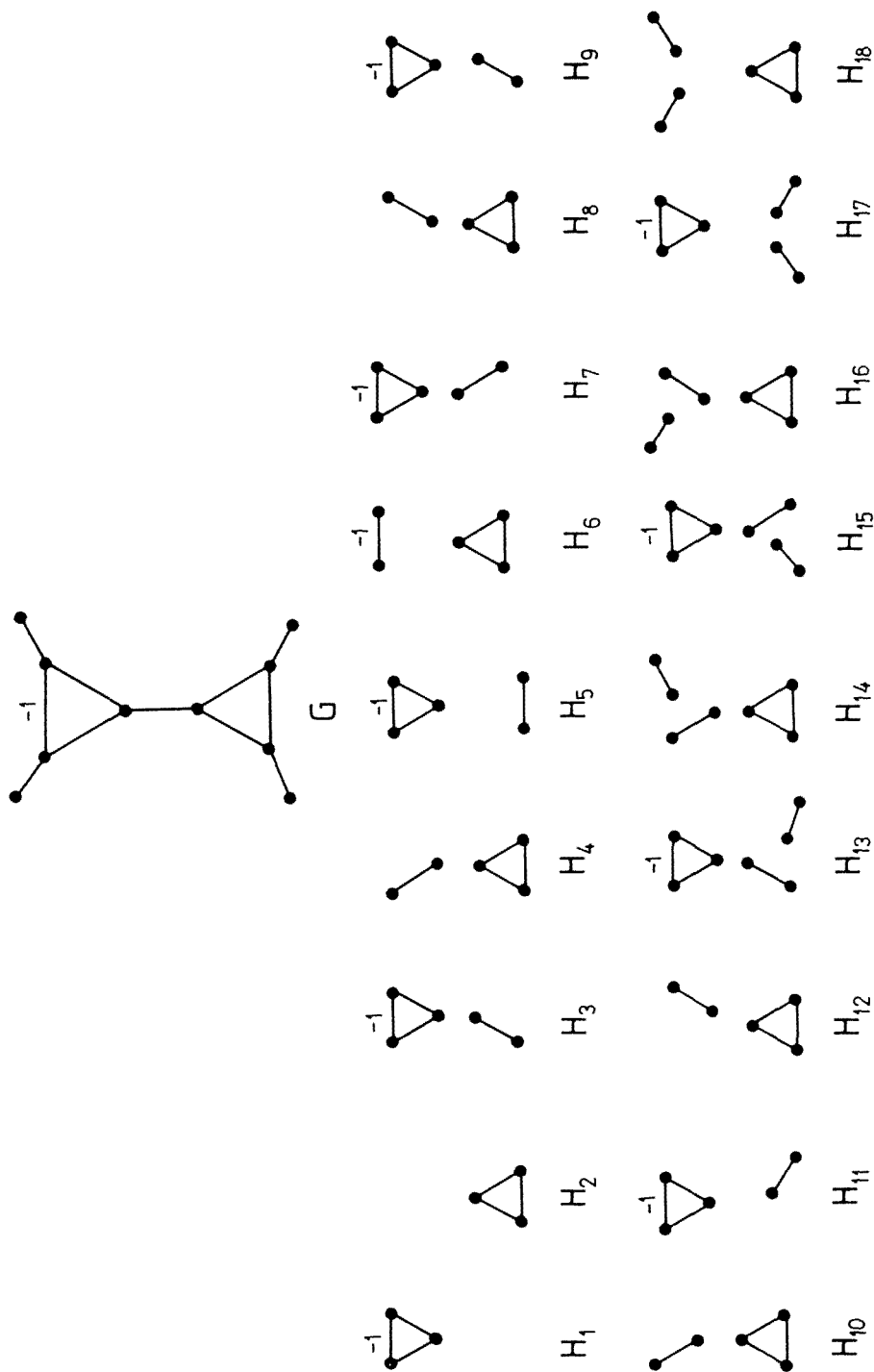
Fig. 4. Example of application of the theorem under discussion to a particular Möbius non-alternant conjugated system with molecular graph G containing exactly two symmetry-related odd-membered rings, one of which is Möbius (i.e., has the equivalent of precisely one edge weighting of -1 somewhere within it) and the other of which is Hückel (i.e., may be considered to have all its edge weightings $+1$).

$$M_3 = \{H_1, H_2\},$$

$$M_5 = \{H_3, H_4, \ldots, H_{12}\},$$

$$M_7 = \{H_{13}, H_{14}, \ldots, H_{18}\}.$$

Each Sachs graph H_i, $i = 1, 2, \ldots, 18$, assigned an even subscript belongs to M_n^*, whereas each Sachs graph with an odd suffix belongs to M_n^{**}. In particular, $M_7^* = \{H_{14}, H_{16}, H_{18}\}$ and $M_7^{**} = \{H_{13}, H_{15}, H_{17}\}$. Hence, for $n = 7$, the first sum on the right-hand side of eq. (6) is equal to

$$\sum_{H^* \in M_7^*} 2^{c(H^*)} (-1)^{k(H^*)} t(H^*) = \left(2^1 \times (-1)^3 \times (1 \times 1 \times 1)\right.$$

$$+ 2^1 \times (-1)^3 \times (1 \times 1 \times 1)$$

$$+ 2^1 \times (-1)^3 \times (1 \times 1 \times 1)\left.\right)$$

$$= -6.$$

The second sum on the right-hand side of eq. (6) is

$$\sum_{H^{**} \in M_7^{**}} 2^{c(H^{**})} (-1)^{k(H^{**})} t(H^{**}) = \left(2^1 \times (-1)^3 \times (1 \times 1 \times (-1))\right.$$

$$+ 2^1 \times (-1)^3 \times (1 \times 1 \times (-1))$$

$$+ 2^1 \times (-1)^3 \times (1 \times 1 \times (-1))\left.\right)$$

$$= +6,$$

and, consequently,

$$a_7 = 0.$$

It is straightforward to check in a similar way that a_3 and a_5 are also equal to zero. Application of Sachs' Theorem to calculate the coefficients a_i, where i is even, can then be shown ultimately to give

$$\phi(G, x) = x^{10} - 11x^8 + 37x^6 - 45x^4 + 15x^2 - 1$$

as the characteristic polynomial of the graph G shown in fig. 4. It will be noted that this is an even polynomial which, therefore, will have paired roots. The characteristic equation of G factorises to [23]

$$(x^4 - 3x^2 + 1)(x^6 - 8x^4 + 12x^2 - 1) = 0,$$

and the explicit, exact eigenvalues of G may in this case be shown to be [23]

$$x = \pm \sqrt{\frac{8 + 4\sqrt{7} \, \sin\left[2\pi\varepsilon/3 - \left(\sin^{-1} \frac{187}{112} \sqrt{\frac{1}{7}}\right)/3\right]}{3}} \, ,$$

where $\varepsilon = 0, 1, 2$, together with

$$x = \pm \sqrt{\frac{3 \pm \sqrt{5}}{2}} \, .$$

This leads to the following eigenvalue list:

$$\pm \, 0.297483925,$$

$$\pm \, 0.618033989,$$

$$\pm \, 1.367676394,$$

$$\pm \, 1.618033989,$$

$$\pm \, 2.457837382.$$

6.   Conclusions

We have thus proved that the Pairing Theorem applies to the graphs representing conjugated hydrocarbons that contain exactly two symmetry-related odd-membered rings, one of which is Möbius and the other of which is Hückel. We have done this by the device of arranging for judicious cancellation of the several contributions to terms which, when they arise in an application of Sachs' Theorem, are required identically to be zero in order for an eigenvalue pairing to hold. The cancelling achieved in this way is, therefore, in a sense, an artificial one – it has been specifically *contrived* to occur. Consequently, we wish to emphasise that, in contrast to the circumstances that pertain to the original Pairing Theorem [1] applicable to alternant hydrocarbons, the eigenvalue pairing encountered here does *not* arise from any fundamental symmetry that enables partition of the graph's adjacency matrix into a particular, blocked form. From this, it follows that there is no reason to expect any special relationship between the *eigenvectors* belonging to paired eigenvalues, such as is evident when the original Coulson–Rushbrooke Theorem [1–4] is applied to alternant hydrocarbons. It is clear, therefore, that the present result is unlikely to be susceptible to proof by matrix-partition methods analogous to those employed by Ruedenberg [24], Cvetković [25] and one of us [15] when proving the standard eigenvalue Pairing Theorem [1–3].

We also observe in passing that if a self-loop be considered as a ring of size 1, a previous result of one of the present authors [26] can be understood as a special case of our current theorem.

From a number of potential applications of the new result obtained here, mention should be made of Möbius π-systems in the form of very long (so-called "infinite") strips. Many such systems – for example, the polyacenes and the poly-arenes – are of considerable topical interest as possible starting points for conductors or semiconductors of novel type. It is well known that there exists a relationship between cyclic and extended linear π-systems within the framework of traditional Hückel Theory [27]. The band gap has in fact been shown [27] to be identical for cyclic oligomers and linear polymers composed of the same repeating units. For instance, from the well-established mnemonic devices of Frost and Musulin and others [28–30], it is possible to determine the orbital energies of [12]-annulenes by making use of the molecular orbitals of both the standard (Hückel) and Möbius topologies of the benzene ring. Since the procedure may be extended to infinitely large rings, the gaps in linear polymeric species are obtainable purely from a consideration of cyclic systems. Our theorem could thus be useful in shedding new light on the disposition of the energy levels in a number of polymeric molecules. Of special relevance in this context are those systems constructed from very large rings of non-alternant species possessed of Möbius topology. When such rings become sufficiently large, they are ultimately equivalent to linear strips that consist of repeating units with one (or, in general, an odd number) of Möbius-type twists.

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