

# Electron delocalization and aromaticity measures within the Hückel molecular orbital method

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## Abstract

In this paper, we review the electronic aromaticity measures from the perspective of the Hückel molecular orbital (HMO) theory. The analysis of FLU, PDI,  $I_{\text{ring}}$  and SCI in the framework of the HMO theory provides an interesting scenario for the interpretation of these indices. Within the Hückel theory the formulas for the Coulson bond orders are easily obtained in a closed form for annulenes, which enables the production of analytical expressions for some of the aromaticity measures. These analytical functions are used to study the ring size dependence of current aromaticity indices. Besides, HMO calculations of polycyclic benzenoids complete the analysis of the electronic aromaticity indices reviewed in this paper, by showing how HMO theory explains the changes in aromaticity due to annulation. All these results help grasping the meaning and the behavior of the electronic aromaticity indices.

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## 1. Introduction

In his seminal work Coulson [1] put forward a measure of the order of a bond, which he applied within Hückel molecular orbital (HMO) theory to explain the electronic structure of some polyenes and aromatic molecules. This measure of the *order of a bond*, more commonly known as Coulson bond order (CBO), has been connected with HMO calculations done so far. Despite the approximations inherent in the HMO approach, organic aromatic molecules are specially well described within this method. It is thus of common practice to learn simultaneously some of the aromaticity measures given in the HMO method, as the resonance energy (RE), the RE per electron (REPE) or even the topological REPE (TREPE) [2].

Nowadays very few calculations are performed within the HMO method, as more sophisticated (and now computational affordable) methods are easily available. As a consequence, the CBO has been replaced by what we could call electron sharing indices (ESI), which measure at which extent a couple of atoms are sharing the electrons lying between them. Likewise, in the present, several measures from different aromaticity manifestations (magnetic, energetic, structural or electronic) are used to play the role RE does in HMO calculations.

Unlike current electronic structure methods, HMO enables easy understanding of the aromaticity measures associated with the method. Due to its simplicity, we believe that the projection of some current electronic aromaticity measures into the HMO approach, may shed some light into the real meaning and behavior of these quantities. This hypothesis bases on the fact that though several drastic approximations are taken into account, the essence of organic aromaticity, driven by the  $\pi$ -electron current, remains for a HMO wavefunction. Moreover, HMO is said to be a good approximation for conjugated molecules and

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yield correct electron density, bond orders and valences [3], as well as ring currents [4].

The purpose of this paper is to study the FLU,  $I_{\text{ring}}$ , MCI and PDI indices of aromaticity at the HMO level for some organic molecules. The paper is organized as follows: Section 2 introduces the aforementioned aromaticity indices, Section 3 is devoted to the study of annulenes, for which closed-form expressions for some aromaticity indices are derived, Section 4 presents some numerical results for linear polyacenes and Section 5 studies the behavior of the indices for a benzenoid macrocycle as we increase its size by annulating benzenoid rings in two dimensions.

## 2. Methodology

Aromaticity is usually claimed to be a multifold property [5–9], because of its different manifestations which range from purely energetical to structural ones. Furthermore, even the use of different aromaticity measures based on the same manifestation is recommended because, as some of us have recently proved [10], no aromaticity index is infallible. Lately aromaticity measures based on the electronic structure of molecules are becoming popular, and several research groups have contributed to the issue by providing new electronic aromaticity indices. Among others we can mention the  $I_{\text{ring}}$  [11] of Giambiagi et al., the SCI [12] of Bultinck and coworkers or the  $\theta$  [13] of Matta. Our group has been also extensively working in this issue [14], and the latest efforts have provided the PDI [15] and FLU [16,17] aromaticity measures.

Some of the aromaticity indices have been proposed without an exhaustive justification further from the fact that these indices correlate well with previously reported aromaticity indices. Taking into account the simplicity and the reduced computational expense of the HMO method, we can here analyze the behavior of these indices for a series of compounds, at the time we can afford large carbon skeleton molecules, which would be completely unfeasible with current *ab initio* calculations.

We are concerned with the calculation of the local aromaticity of a given molecule which possesses at least one ring structure. Let us suppose such ring structure consists of  $n$  atoms, represented by the following string  $\mathcal{A} = \{A_1, A_2, \dots, A_n\}$ , whose elements are ordered according to the connectivity of the atoms in the ring. For such system we can calculate the following electronic aromaticity indices.

### 2.1. The Aromatic Fluctuation Index: FLU

Based on the comparison with cyclic electron delocalization of typical aromatic molecules, FLU index is defined as follows [16,17]:

FLU( $\mathcal{A}$ )

$$= \frac{1}{n} \sum_{i=1}^n \left[ \left( \frac{V(A_i)}{V(A_{i-1})} \right)^\alpha \left( \frac{\delta(A_i, A_{i-1}) - \delta_{\text{ref}}(A_i, A_{i-1})}{\delta_{\text{ref}}(A_i, A_{i-1})} \right) \right]^2 \quad (1)$$

where  $A_0 \equiv A_n$  and  $V(A)$  is the atomic valence that for a closed-shell system reads:

$$V(A) = \sum_{B \neq A} \delta(A, B) \quad (2)$$

and  $\alpha$  is a simple function to ensure the first term in Eq. (1) is always greater or equal to 1,

$$\alpha = \begin{cases} 1, & V(A_{i-1}) \leq V(A_i) \\ -1, & V(A_i) < V(A_{i-1}) \end{cases} \quad (3)$$

$\delta(A, B)$  and  $\delta_{\text{ref}}(A, B)$  are quantities that account for the electron sharing of  $A$  and  $B$ ; the latter is taken from an aromatic molecule which has the pattern of bonding  $A - B$ . In the present case, where only C–C bonds will be taken into account, the molecule chosen as an aromatic reference is benzene. FLU is close to zero in aromatic species, and greater than zero for non-aromatic or antiaromatic species.

### 2.2. A multicenter based index: $I_{\text{ring}}$

Based on the multicenter index (which account for the simultaneous electron sharing of various centers) Giambiagi and coworkers, proposed this quantity,  $I_{\text{ring}}$ , as a measure of aromaticity. The formula reads as follows [11]:

$$I_{\text{ring}}(\mathcal{A}) = \sum_{i_1, i_2, \dots, i_n}^{\text{occ}} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2), \dots, S_{i_n i_1}(A_n) \quad (4)$$

where  $S_{ij}(A)$  is the overlap of molecular orbitals  $i$  and  $j$  in the atom  $A$ .  $I_{\text{ring}}$  will provide large values (larger simultaneous electron sharing of atoms in the ring) for aromatic molecules.

### 2.3. The Multicenter Index: MCI

With the aim to improve the  $I_{\text{ring}}$ , Bultinck and coworkers [12] proposed to sum not only the contribution from the Kekulé structures (as  $I_{\text{ring}}$  does), but also the contribution from all possible structures generated by permuting the position of all the atoms in the ring. Such possibility was already discussed by Ponec and coworkers [18,19] among others [20]. Thus, the formula reads:

$$\text{MCI}(\mathcal{A}) = \sum_{\mathcal{P}(\mathcal{A})} I_{\text{ring}}(\mathcal{A}) \quad (5)$$

$$= \sum_{\mathcal{P}(\mathcal{A})} \sum_{i_1, i_2, \dots, i_n}^{\text{occ}} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2), \dots, S_{i_n i_1}(A_n) \quad (6)$$

where  $\mathcal{P}(\mathcal{A})$  stands for  $n!$  permutations of elements in the string  $\mathcal{A}$ . Although the original proposal of MCI differs from this one in a numerical factor, we will skip it for the reasons already commented in Ref. [21]. As  $I_{\text{ring}}$ , MCI produces large numbers for aromatic species, and the authors claim negative numbers are produced by antiaromatic species [22].

#### 2.4. The para-Delocalization Index: PDI

Based on the finding of Fulton [23] and Bader [24], which showed that benzene has larger para-related atoms electron sharing than meta-related one, the index uses the para-related atoms electron sharing as a measure of aromaticity for six-membered rings:

$$\text{PDI}(\mathcal{A}) = \frac{\delta(A_1, A_4) + \delta(A_2, A_5) + \delta(A_3, A_6)}{3} \quad (7)$$

thus, the larger the index the greater the aromaticity.

### 3. Annulenes

#### 3.1. HMO approach: The Coulson bond

Let us take a cyclic polyene of  $n$  member rings and  $n$   $\pi$ -electrons. Within the HMO approach [25,26] the MO energies can be given analytically:

$$\epsilon_l = \alpha + 2\beta \cos\left(\frac{2\pi l}{n}\right) \quad (8)$$

with  $l = 0, \pm 1, \dots, \pm(n-1)/2, n/2$ . Likewise the eigenfunctions read:

$$\phi_l = \sum_{\mu=1}^n \chi_{\mu} c_{\mu l} = \frac{1}{\sqrt{n}} \sum_{\mu=1}^n \chi_{\mu} \exp\left[\frac{2\pi i(\mu-1)l}{n}\right] \quad (9)$$

where  $\chi_{\mu}$  is the atomic orbital  $2p_z$  of the carbon atom with number  $\mu$  and energy  $\alpha$ .

Let us divide the molecular space into non-penetrating atomic domains,  $\{\Omega_{\mu}\}_{\mu=1, \dots, n}$ . The atomic boundary in a cyclic polyene is given by the symmetry of the system, which is  $D_{nh}$ . Since HMO assumes non-overlapping  $2p_z$  as atomic functions, the integration within an atomic domain of the atom  $\mu$  is quite simple:

$$\begin{aligned} S_{\lambda\nu}(\Omega_{\mu}) &= \int_{\Omega_{\mu}} \chi_{\lambda} \chi_{\nu} d\tau = \int_0^{\infty} \int_0^{\pi} \int_{\Phi_{\mu}} \chi_{\lambda} \chi_{\nu} dr d\theta d\phi \\ &= \delta_{\lambda\nu} \delta_{\mu\nu} \end{aligned} \quad (10)$$

Thus, from Eq. (9) it is easy to prove:

$$\int \phi_l^* \phi_m d\tau = \frac{1}{n} \sum_{\mu=1}^n \exp\left[\frac{2\pi i\mu(m-l)}{n}\right] = \delta_{lm} \quad (11)$$

provided the following relationship is fulfilled for  $p$  integer:

$$\frac{1}{n} \sum_{\mu=1}^n \exp\left[\frac{2\pi i\mu p}{n}\right] = \delta_{p0} \quad (12)$$

In the same way, one can prove:

$$S_{lm}(\Omega_{\mu}) = \int_{\Omega_{\mu}} \phi_l^* \phi_m d\tau = c_{\mu l}^* c_{\mu m} \quad (13)$$

Since MO are orthonormal, the Coulson bond order (CBO) [1] reads:

$$\begin{aligned} P_{\mu\nu} &= \frac{1}{2} \sum_p n_p \left( c_{\mu p}^* c_{\nu p} + c_{\nu p}^* c_{\mu p} \right) \\ &= \frac{1}{n} \sum_p n_p \cos\left[\frac{2\pi p(\mu-\nu)}{n}\right] \end{aligned} \quad (14)$$

where  $p = 0, \pm 1, \dots, \pm(n-1)/2, n/2$ . It is fair saying Coulson only recommended the use of CBO for bonded pairs of atoms  $\mu, \nu$ . After algebraic manipulations of Eq. (14) we can reach the following closed-form expressions for  $4N$  and  $(4N+2)\pi$ -electrons annulenes:

$$P_{\mu\nu}^{4N+2} = \frac{2 \sin\left[\frac{(\mu-\nu)\pi}{2}\right]}{n \sin\left[\frac{(\mu-\nu)\pi}{n}\right]}, \quad P_{\mu\nu}^{4N} = \frac{2 \sin\left[\frac{(\mu-\nu)\pi}{2}\right] \cos\left[\frac{(\mu-\nu)\pi}{n}\right]}{n \sin\left[\frac{(\mu-\nu)\pi}{n}\right]} \quad (15)$$

for  $\mu - \nu \neq 0$ ; the particular case of auto-CBO can be derived directly from Eq. (14), and is  $P_{\mu\mu} = N_{\mu} = 1$ . We can easily recognize the classical CBO results (contiguous atoms,  $\mu - \nu = 1$ ) for annulenes. The reader should notice that the denominators in Eq. (15) will never vanish, and as a consequence, the CBO never reaches infinity regardless the value of  $\mu - \nu$ . As the size of the ring of the annulene goes to infinity the CBO tend to  $2/\pi$  for contiguous atoms, as one can deduce from both formulas.

It is worth noticing how  $P_{\mu\nu}^{4N}$  can be actually written as  $\cos\left[\frac{(\mu-\nu)\pi}{n}\right] P_{\mu\nu}^{4N+2}$ , and providing  $0 \leq \cos\left[\frac{(\mu-\nu)\pi}{n}\right] < 1$  the CBO for a  $4N$ -annulene is lower than the  $4N+2$  counterpart, being equal only in the limit of infinite member rings. Despite  $4N\pi$ -electrons annulenes have lower CBO, their value is still appreciable, which may seem in direct contradiction with the so-called Hückel rule. Such rule, actually designed from the HMO approach, states that those compounds with  $(4N+2)\pi$ -electrons are aromatic, whereas  $4N\pi$ -electrons compounds are antiaromatic. Antiaromatic compounds have localized bonds, usually with bond order alternation (BOA), however, at the HMO level  $4N\pi$ -electrons compounds do not present such BOA. This problem was already noticed by the own Coulson [1] with cyclobutadiene. Due to the symmetry of the system ( $D_{nh}$ ), the wavefunction must stick with this symmetry. However, the possible singlet wavefunctions of  $4N\pi$ -electrons annulenes have an orbital scheme with 2 electrons either on one degenerate orbital, or on the other, but both singlet wavefunctions break the symmetry of the system. Both singlet wavefunctions must be compounded together to give a singlet wavefunction of the correct symmetry (see Fig. 1). This compromised wavefunction has the same CBO as the corresponding triplet one, and also the same HMO energy than the other singlet ones, but with the proper symmetry. Hence the resulting CBO cannot exhibit the BOA as it is a  $D_{nh}$  wavefunction with all CBO equal.

This fact arises as a surprising feature of HMO calculations; whereas energy parameters (such as RE) indicate which compounds are aromatic and can be separated clearly from those which are antiaromatic, the electronic structure according to CBO does not predict antiaromatic



Fig. 1. Both orbital schemes break the symmetry of the wavefunction, but compounded together provide a correct symmetry wavefunction. Nevertheless, such wavefunction will never exhibit bond order alternation.

compounds as such. We must bear in mind that such limitation is easily overcome in current *ab initio* calculations where the geometry may change to  $D_{(n/2)h}$  symmetry, and thus lead to correct BOA. Therefore, for the HMO calculations of this paper, we will restrict ourselves to the application of the aromaticity indices to aromatic molecules, namely those with  $(4N + 2)\pi$ -electrons.

We have already studied the behavior of CBO when the number of  $\pi$ -electrons increases steadily with the size of the ring. Let us assess the effect of the CBO formula when the number of  $\pi$ -electrons keeps frozen, and the size of the ring increases. The formula for the classical-CBO (contiguous atoms) for  $6\pi$ -electrons annulenes is as follows:

$$P_{\mu,\mu+1}^{6e^-} = \frac{2 \sin \left[ \frac{(n-3)\pi}{n} \right]}{n \sin \left[ \frac{\pi}{n} \right]} \quad (16)$$

Table 1 collects some results regarding this and the latter formulas for the classical CBO. The results indicate a progressive decrease of all values with the size of the ring, no matter which formula:  $(4N + 2)$ ,  $(4N)$  or  $6\pi$ -electrons annulenes. However, when number of electrons is kept to six, the CBO goes to zero as the size of the ring increases, whereas for an increasing number of electrons with the ring size, the limit reached is  $2/\pi$ . Both results are consistent with the common sense, and demonstrate that the value of CBO for annulenes have correct asymptotics. It is thus expected that the aromaticity indices derived are reliable.

With these results in mind, let us try to find the HMO analogous of the so-called electron sharing indices.

Table 1  
Some values of classical CBO for  $4N$  and  $4N + 2$  annulenes

$N$	$4N$	$4N + 2$	$6e^-(4N + 2)$	$6e^-(4N)$
1	0.5000	0.6667	0.6667	0.5000
2	0.6036	0.6472	0.5236	0.6036
3	0.6220	0.6420	0.4003	0.4553
4	0.6284	0.6399	0.3199	0.3560
5	0.6314	0.6388	0.2654	0.2902
6	0.6330	0.6382	0.2263	0.2443
7	0.6339	0.6378	0.1971	0.2107
8	0.6346	0.6375	0.1745	0.1851
9	0.6350	0.6373	0.1565	0.1650
10	0.6353	0.6372	0.1418	0.1488
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$\infty$	$2/\pi$	$2/\pi$	0	0

### 3.2. Electron sharing indices at the HMO level

One of the tools most used to characterize the electron structure of molecules, are those collected under the name of electron sharing indices (ESI); for a recent review see Ref. [27]. The most popular is perhaps the Wiberg–Mayer [28,29] bond order (WMBO), which for a closed-shell single determinant wavefunction reads:

$$\delta(A, B) = \sum_{\lambda \in A} \sum_{\omega \in B} (PS)_{\omega\lambda} (PS)_{\lambda\omega} \quad (17)$$

Providing the approximations given in HMO theory (overlap matrix being the identity matrix, cf. Eq. (10), and a single function per atom) the WMBO simply reads:

$$\delta(\mu, \nu) = P_{\mu\nu} P_{\nu\mu} \quad (18)$$

which fulfills the well-known sum rule:

$$\frac{1}{2} \sum_{\mu, \nu} \delta(\mu, \nu) = n \quad (19)$$

and *unlike* CBO always produces non-negative electron sharing.

Following Eq. (15), for  $(4N + 2)\pi$ -electrons systems, it is also easy to prove that the bond order for bonded pairs is as follows:

$$\delta^{4N+2}(\mu, \mu + 1) = \left[ \frac{2}{n \sin \left( \frac{\pi}{n} \right)} \right]^2 \quad (20)$$

whose value decreases for larger distances, to reach the limit  $4/\pi^2$ . The pairs separated by one atom, are related by a bond order of 0 regardless the dimension of the cyclic polyene. This feature is specially interesting, as it means there is no electron delocalization between non-contiguous atoms for cyclobutadiene ( $n = 4$ ), as one would expect of an antiaromatic system which should exhibit no much electron delocalization. On the other hand, ESI value for benzene ( $n = 6$ ) indicates that meta-related carbons electron sharing is not as important as para-related one, as noticed independently by Fulton and Bader for *ab initio* calculations. This fact gave rise to the so-called PDI as a measure of aromaticity, and thus the validity of this index at the HMO level is confirmed. Moreover, HF/6-31G(d) values<sup>2</sup> for benzene are  $\delta(C, C)_{\text{ortho}}^{\pi} = 0.43$ ,  $\delta(C, C)_{\text{meta}}^{\pi} = 0.04$ , and  $\delta(C, C)_{\text{para}}^{\pi} = 0.09$ , in close agreement with HMO values of  $\delta(C, C)_{\text{ortho}}^{\text{HMO}} = 0.44$ ,  $\delta(C, C)_{\text{meta}}^{\text{HMO}} = 0.00$ , and  $\delta(C, C)_{\text{para}}^{\text{HMO}} = 0.11$ , a clear indication that the electronic picture of benzene is preserved within the HMO approach.

In general, for annulenes, pairs of atoms with an odd number of atoms between them, have no electron sharing, whereas pairs of atoms separated by an even number ( $m$ ) of atoms, share the following number of electrons according to HMO approach:

<sup>2</sup> Values obtained with Atoms-in-Molecules partitioning [30].

$$\delta^{4N+2}(\mu, \mu + m) = \left[ \frac{2}{n \sin\left(\frac{m\pi}{n}\right)} \right]^2 \quad (21)$$

This value decreases for larger distances, to reach the limit of  $4/(m\pi)^2$ , in consistency with the general expectance of lower sharing for larger distances. Altogether we can say that ESI and CBO derived from HMO theory are in a reasonable agreement with first principles calculations, and we thus expect the aromaticity indices derived at the HMO level to be a good approximation to more sophisticated calculations.

### 3.3. Aromaticity indices at HMO level

Now we are in position of studying the aromaticity indices in question. Let us start with the FLU. By virtue of Eqs. (1) and (20), and providing the symmetry of the system makes all carbons equivalent, FLU index at HMO level reads:

$$\text{FLU}(C_nH_n)^{4N+2} = \left[ \left( \frac{3}{n \sin\left(\frac{\pi}{n}\right)} \right)^2 - 1 \right]^2 \quad (22)$$

On the other hand  $I_{\text{ring}}$  can be obtained combining Eqs. (4) and (13), and by taking into account the l.h.s. of Eq. (14) together with Eq. (15):

$$I_{\text{ring}}(C_nH_n)^{4N+2} = \left[ \frac{2}{n \sin\left(\frac{\pi}{n}\right)} \right]^n \quad (23)$$

$I_{\text{ring}}$  goes like the  $n$  power of the classical CBO, and some of us recently showed [21] that is convenient to use  $I_{\text{ring}}^{1/n}/n$  instead of the original proposal, to correctly account for the ring size dependence. This finding was based on the correlation between the TREPE and  $I_{\text{ring}}$ , as both contain CBO on its formula. Unhopefully there is no direct relationship between CBO (or TREPE) and FLU which may help to find the proper normalization factor to account for ring size effects with this index. Our own experience indicates that usually FLU values change roughly with small changes in the system, and frequently we have suggested the use of  $\text{FLU}^{1/2}$  to properly appreciate the differences (see for example Ref. [10]). FLU formula has some resemblance with the variance of the ESI of adjacent atoms in a given ring when the reference value would play the role of the average value; in this sense we prefer  $\text{FLU}^{1/2}$  as it is more similar to its standard deviation. This hypothesis is strongly supported by the perfect correlation between classical CBO and  $\text{FLU}^{1/2}$  for  $(4N+2)\pi$ -electrons annulenes, given in Fig. 2. Therefore, the correct normalization of FLU should be  $\text{FLU}^{1/2}/n$  to account for the ring size effects.<sup>3</sup> Since in the following sections we will deal always with rings of six centers, we will calculate FLU as usual.

<sup>3</sup> Following [21] we can further normalize FLU with respect to number of  $\pi$ -electrons,  $N_\pi$ , so that it perfectly agrees with TREPE. It would thus read  $\frac{\text{FLU}^{1/2}}{nN_\pi}$ .

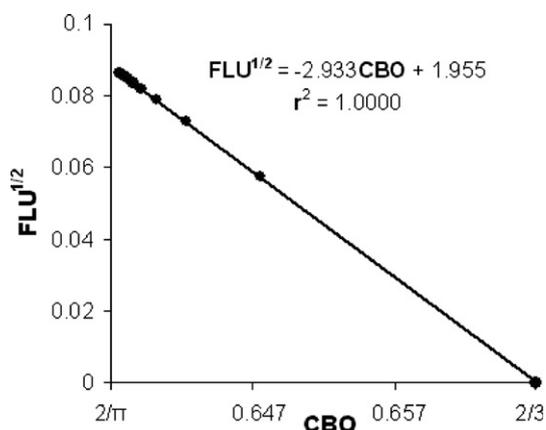


Fig. 2. Correlation between  $\text{FLU}^{1/2}$  and CBO for annulenes.

Unfortunately the generation of a closed-form expression for MCI is not a trivial task, neither for annulenes where the value of CBO is available. Since some of us [21] have recently studied the values of MCI at the HMO for annulenes, we will only give here a brief comment on how to qualitatively analyze the contributions that enter MCI. In Ref. [31] some results for carbon skeleton molecules of MCI at the HMO level are given.

Let us take benzene, which CBO formula is given in Eq. (15). At the HMO level CBO for meta-related carbons is zero. As a consequence, from all possible permutations of atoms that enter the expression of MCI we can discard any which is not composed by para-related or ortho-related positions. Namely, it is easy to prove that the only structures which contribute to MCI are those collected in Fig. 3. Any other permutation is actually equivalent to some of these three. Since the permutations run over all possible connected structures, for each structure **A**, **B** and **C** there are at least 12 possible permutations ( $6 \cdot 2$  as we can start from any atom, and run clockwise or counter-clockwise). Moreover, **B** admits three different type of structures depending on the adjacent bonds not used; for analogous reasons structure **C** admits 2. Altogether we have 12, 36 and 24 different strings for structures **A**, **B**, and **C**, respectively. To realize about the relative weight of each structure in the value of MCI we go back to Eq. (15) and see that the relative importance of CBO in *ortho* with respect to *para* is  $-2$ , as para-related CBO is negative. As a consequence **A** and **B** contribute in a positive fashion, while **C** contributes negative. Namely, in absolute value their weights to MCI are 50%, 37.5% and 12.5%. Because of the partial compensation of non-Kekulé structures, the

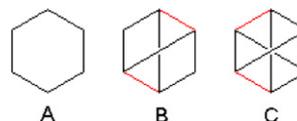


Fig. 3. All possible patterns of connectivity for benzene according to HMO calculations.

real contribution of the Kekulé structure (the only used in the calculation of  $I_{\text{ring}}$ ) is 67%; at the HF/6-311++G<sup>\*\*</sup> level this value is even higher, 89%. This is the reason for the close agreement between  $I_{\text{ring}}$  and MCI; the Kekulé structure is essentially dominant. Just on those very odd cases where non-Kekulé structures have an important weight (that does not compensate from one structure to the other) as compared to Kekulé structure, will MCI and  $I_{\text{ring}}$  significantly differ (see for instance [21]).

#### 4. Polyacenes

Benzenoid hydrocarbons are polycyclic aromatic hydrocarbons with condensed benzene rings. The  $[n]$ acenes or polyacenes are a particular kind of planar benzenoid hydrocarbons with linearly fused benzene rings (cf. Fig. 4). The highest member of the series experimentally known is heptacene ( $n = 7$ ), some derivatives of which have been recently synthesized by Anthony and coworkers [32]. Higher acenes remain unknown. These compounds show increasing reactivity with the number of rings. In fact,  $[n]$ acenes from  $n = 4$  to 6 are known to be unstable to light and air [33]. Experimentally,  $[n]$ acenes up to  $n = 7$  are found to be singlet closed-shell species [32]. However, theoretical treatments of the acene family indicate that higher acenes may have singlet open-shell ground states [34], although this point is still a matter of controversy [35]. An obvious limitation of the Hückel method is the treatment of different spin states. For this reason, in this work we discuss only the results for the singlet closed-shell state for all members of the series, being this state their ground or an excited state.

Another interesting topic of debate in  $[n]$ acenes is the evolution of aromaticity when going from the outer to the inner rings. Already for anthracene, the smallest member of the series having differentiated inner and outer rings, there is disagreement about whether the central ring is the most or the least aromatic ring. The NICS descriptor of aromaticity indicates that the local aromaticity increases steadily from the external to the central ring in  $[n]$ acenes ( $n = 4-9$ ) [36,37]. The PDI and the HOMA indices [36,37], with some exceptions, seem to point out the same trend in aromaticity when going from the outer to the inner ring, as well as the FLU index for  $n = 3, 4$  [16], the analysis of ring currents [38–41], the calculation of resonance energies [42–44], some graph theory-based descriptors [45,46], and several aromaticity indicators based on charge density

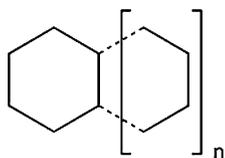


Fig. 4. Scheme of polyacenes studied, current calculations range from  $n = 1$  to  $n = 23$ .

Table 2

The most aromatic ring in polyacenes according to different aromaticity indices at the HMO level

Index	Anthracene	Polyacenes (>3 rings)
FLU	Inner	Outer
PDI	Outer	Inner
MCI	Outer	Outer
$I_{\text{ring}}$	Outer	Outer

properties derived from the Atoms-in-Molecules theory [47]. On the other hand, other different graph theory-based descriptors [45,46], together with molecular quantum similarity calculations [48], SCI and  $I_{\text{ring}}$  indices [11,12,48,49], as well as bond resonance energies [50] yield the opposite trend with outer rings more aromatic than the inner ones.

In this work, we analyze the aromaticity of polyacenes up to 23 rings using FLU,  $I_{\text{ring}}$ , MCI and PDI at the HMO level. In general the aromaticity trend along the chain decreases or increases steadily, with the exception of PDI and FLU which reverse this trend only for the particular case of anthracene. All aromaticity indices predict anthracene outer ring to be the most aromatic, excepting for FLU, while for polyacenes of more than three rings all aromaticity indices predict the aromaticity to increase from the inner to the outer ring, excepting for PDI which gives the opposite trend. This information is collected in Table 2. As FLU in this context simply compares the adjacent electronic sharing with respect to benzene, and  $I_{\text{ring}}$  can be regarded as the geometrical mean of adjacent electron sharing, one is tempted to believe that, according to HMO, the aromaticity of rings in anthracene must be considered actually quite similar.

It is also worth to investigate at which extent the aromaticity is converged with the size of the polyacene. In Fig. 5 we have collected the trends in the convergence for the four indices, and although they reach its limit value at different number of rings annulated, the shape of the function is the

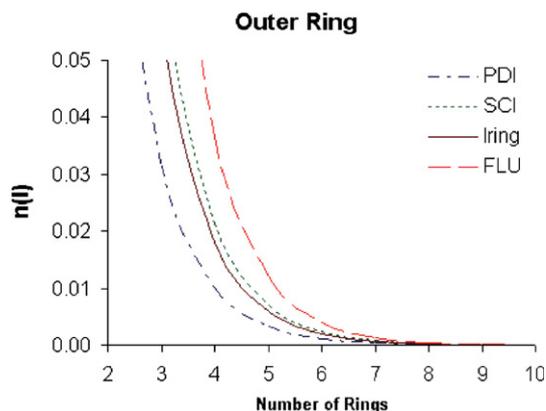


Fig. 5. Aromaticity indices for the outer ring of polyacenes normalized with respect to the difference with its limit value ( $n(I) = (I_i - I_{23})/I_{23}$ , with  $I$  being an aromaticity index.). The indices are plotted with respect to the number of rings annulated. The convergence is already achieved for  $n = 10$ .

same, indicating that the *speed of convergence* is actually the same.

## 5. Benzenoids macrocycles

In this section we will study the aromaticity of the rings of large macrocycles composed by benzenoid rings. For these macrocycles no closed-form formulas can be easily derived for CBO, and therefore, as in the case of polyacenes, we will produce numerical data to verify the convergence of the aromaticity indices with respect to the size of the macrocycle. As we increase the number of benzenoids rings in the macrocycle, we are driven towards a molecule which resembles a graphite layer. To increase the size of the macrocycle we start from benzene molecule (noted as mac-

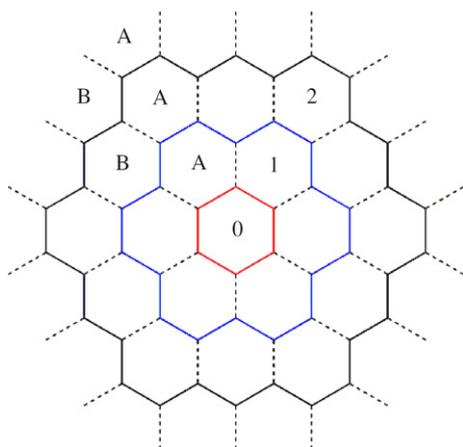


Fig. 6. Scheme of the prototype macrocycle made of benzenoid rings, notation for the crowns and the benzenoids rings is given.

rocycle[0]), and we add a benzenoid ring to each of its sides to reach coronene (macrocycle[1]), at each side of which we can add another benzenoid ring, leading to circumcoronene (macrocycle[2]) and so forth (cf. Fig. 6). Let us call *crown* to each of these layers of benzenoids rings needed to go from macrocycle[ $n$ ] to macrocycle[ $n + 1$ ]. The present HMO calculations are done for macrocycles up to 11 crowns, where convergence of aromaticity indices of inner rings is achieved.

The suitability of HMO calculations is assessed by comparison with MCI results of Fias and Bultinck at HF/STO-3G level [51] for macrocycles where some benzenoids rings in the last crown have been added/removed. From results

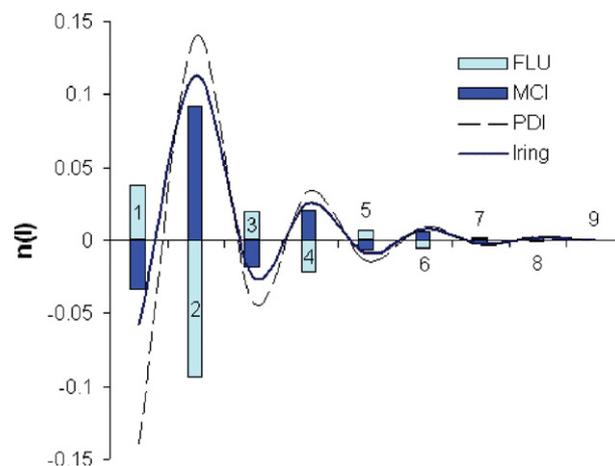


Fig. 7. Aromaticity of central benzenoid ring in benzenoid macrocycles as a function of the number of crowns. Each aromaticity index is normalized with respect to its limit value to fit the graphic ( $n(I) = (I_i - I_{11})/I_{11}$ , with  $I$  being an aromaticity index.).

Table 3  
Comparison of HF/STO-3G and HMO MCI values for a series of macrocycles

MCI	$C_{42}H_{18}$		$C_{78}H_{30}$		$C_{114}H_{30}$		$C_{186}H_{42}$		$C_{222}H_{42}$		$C_{258}H_{54}$		$C_{330}H_{54}$	
	HMO	HF	HMO	HF	HMO	HF	HMO	HF	HMO	HF	HMO	HF	HMO	HF
0	26	32	24	28	22	26	22	24	21	24	21	24	21	23
1A	16	13	19	17	19	17	20	18	20	18	20	18	20	19
2A			14	12	19	16	22	25	20	18	20	18	20	18
2B	54	61	33	39	24	28	19	17	22	25	22	24	21	23
3A			68	72	42	47	24	28	23	26	22	25	22	24
3B					17	14	19	17	20	18	20	18	20	18
4A							16	13	18	16	19	17	20	18
4B							16	13	19	16	19	17	20	18
4C					52	58	32	38	23	27	23	26	22	25
5A									41	46	16	13	18	17
5B							54	60	17	15	33	38	23	25
5C											14	12	19	17
6A													41	47
6B													17	15
6C													16	13
6D													32	38
7A											68	72		
7C													53	58
7D											53	59		

The values given are percentages with respect to benzene value at the corresponding level of theory. HF/STO-3G values are taken from Ref. [51].

of Table 3 we can immediately say that the correlation between both approaches is good, both giving the same Clar structures, and therefore, agreeing also with total  $\pi$  current density maps of Ref. [52]. Moreover, the HMO results of PDI and FLU for coronene, agree with B3LYP/6-31G\* ones available in the literature [53].

For macrocycles[ $n$ ] the different aromaticity indices essentially agree at which  $n$  the aromaticity of the inner rings converge to a certain value. Indeed, in Fig. 7 one can see the convergence of the central benzenoid ring of the macrocycle, and how all indices coincide on an alternated pattern of aromaticity as the size of the macrocycle increases. Yet another proof that all indices convergence similarly with the size of the macrocycle is that for  $n > 5$  all reproduce the same aromaticity for rings 1A and 2A. However, as it comes to the general aromaticity distribution of the rings in macrocycle, some indices provide rather different results. One value which presents some controversy is  $nA$  for a particular macrocycle[ $n$ ]. NICS calculations [54] attribute a low aromaticity value to  $nA$ , as our current PDI and FLU calculations,<sup>4</sup> whereas, according to  $I_{\text{ring}}$  and MCI,  $nA$  is the most aromatic benzenoid ring in the macrocycle. Indeed,  $nA$  is the only exception in the aromaticity trend along the radii (i.e. when going from 1A to  $nA$ , cf. Fig. 6), which follows roughly the same alternated pattern for FLU,  $I_{\text{ring}}$ , MCI and PDI. Moreover, in a given crown or layer, when going from A to Z (being Z the last non-equivalent ring moving counterclockwise/clockwise within an angle of  $\pi/6$ )  $I_{\text{ring}}$  and MCI find a decrease of aromaticity, whereas FLU and PDI find a sudden increase of aromaticity from A to B, a smooth increase to a maximum value, which afterwards decreases as we move counterclockwise/clockwise. The latter is in reasonable agreement with NICS results, when also the sudden increase from A to B is found, though the maximum is reached in the last non-equivalent benzenoid ring, as we follow counterclockwise/clockwise [54].

In this line, recently some authors [55] have studied the series  $n = 0-5$  with the NICS and the HOMA measures of aromaticity, and have found a good correlation between NICS indices and the Clar sextet structures corresponding to the macrocycles. If we take the rings with a  $\pi$ -sextet in the Clar structures as the most aromatic rings of each crown, all indices show with a reasonable agreement all Clar sextets, with the exception of MCI and  $I_{\text{ring}}$  for the last crown. However, the only index that recognizes all Clar sextets as the most aromatic rings with respect to the rest of the rings in the macrocycle is FLU.

In all macrocycles the trends for  $I_{\text{ring}}$  and MCI are exactly the same, whereas FLU and PDI exhibit a similar behavior, especially for  $n > 5$  macrocycles. As compared with the NICS values available in the literature, FLU reproduces the closest trends.

## 6. Conclusions

In this paper we have reviewed some electronically based aromaticity indices at the Hückel molecular orbital (HMO) method. It has been proved a good agreement between HMO and first principles calculations for a variety of conjugated polyenes. It is fair noticing that due to HMO limitations the study has been restricted to aromatic molecules, as antiaromatic molecules are not recognized as such from the electron distribution picture which arises from HMO calculations.

Several interesting results have been put forward. First it is demonstrated that to correctly account for ring size effects of aromaticity  $\text{FLU}^{1/2}/n$  should be used instead of FLU. Our results also show a general agreement for large linear polyacenes, with the exception of PDI. On the other hand, FLU shows the opposite aromaticity trend of anthracene rings as compared to other indices, which prompt us to believe that actually the aromaticity of these rings is quite similar. It is also worth noticing that for all calculations  $I_{\text{ring}}$  and MCI always report the same trends, with no exception.

Because of their reduced computational expense, we have been able to address large carbon macrocycles, with an increasing number of benzenoids rings to emulate the situation of a graphite layer. Our results, in concordance with some *ab initio* calculations available in the literature, show how all indices give a qualitative agreement of the limit where inner rings are surrounded by enough benzenoid rings to show convergence in aromaticity measures. According to our MCI,  $I_{\text{ring}}$  and PDI values the aromaticity of the six-membered rings in the graphite layer is 20%, 24% and 31% of that of benzene, respectively. Unlike the  $I_{\text{ring}}$  and MCI indices, the PDI and FLU indices perform reasonable well identifying the Clar structures, with the outstanding success of FLU which recognizes all sextets as the most aromatic rings in the macrocycle.

## Note added in proof

Very recently have appeared a paper [56] which does an extensive review on the Hückel Theory, and it is worth to mention in this context.

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<sup>4</sup> See supporting information for PDI, FLU and  $I_{\text{ring}}$  values of the macrocycles studied.

## Appendix A. Supplementary data

An excel file containing the values of FLU,  $I_{\text{ring}}$ , MCI and PDI of polyacenes of Section 4 and macrocycles of Section 5 is given as supporting material.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.theochem.2007.01.015](https://doi.org/10.1016/j.theochem.2007.01.015).

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