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CYCLIC AROMATICITY WITHIN HÜCKEL AND QUASI-CORRELATED HÜCKEL-LIKE MODELS

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The paper deals with quantifying aromaticity in π-electron networks by unsophisticated MO techniques. The focus is placed on local aromaticity measures associated with individual benzenoid rings. We revised the ring aromaticity index due to Cioslowski et al (2007) by including explicitly net charges and electron unpairing effects. Our previously introduced quasi-correlated tight-binding (QCTB) approximation serves here as an easily available tool for taking account of π-electron correlations. The latter crucially influence the behavior of large and even small conjugated π-structures with a nontrivial topology. Numerical applications of Hückel and QCTB models to measuring local aromaticity are reported for various structural classes (polycyclic aromatic hydrocarbons (PAHs), graphene nanoflakes, and others). We analytically investigate the aromaticity in conjugated monocycles $C_N H_N$ (neutral and charged ones). Furthermore, in the same manner several PAH structures (oligocenes, pyrene, perylene, etc.) are considered in their charged states, and the results are compared with those of related quinoid-type systems, such as p-diphenoquinodimethane. It is shown that, unlike usual PAHs, quinodimethane structures tend to increase their aromaticity in dicationic (dianionic) form. In our studies of nanographene aromaticity we find a decrease of the local aromaticity as we move to a center of graphene structures, that is in a sharp contrast to the predictions of NICS (nucleus independent chemical shift), a rather criticized approach. A particular emphasis is being put on measuring local aromaticity in highly correlated π-systems. Typical non-Kekule hydrocarbons (e.g., triangulene radical and polyradicals), are also studied within QCTB by which characteristic difficulties caused by the occurrence of many non-bonding π-MOs, are simply obviated.

Keywords: aromaticity measures, polycyclic aromatic hydrocarbons, nanographenes, Hückel MOs, open-shell systems, polyradicals, quasi-correlated tight-binding approximation.

Introduction

Aromaticity is a deep and difficult concept which raised many controversy questions of interpretation. On the one hand, the concept is treated as one "of immense practical importance" [1]; on the other hand, some researchers take it as a suspicious notion (e.g., see interesting discussions in [2,3]). Nevertheless, polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds and many others definitely reveal their aromaticity character, and the vast majority of papers were dedicated to treating this fundamental chemical notion in quantitative terms; for recent reviews and new articles see Ref. [4-14].

Several important issues still remain incompletely resolved within the theoretical approaches to aromaticity. The cyclic delocalization of π-electrons is one of them. Indeed, this delocalization is the underlying feature of PAHs, and serves as a principal characteristic of aromaticity at all. There exist many approaches to "measure" the cyclic delocalization in aromatic systems by structural [4], magnetic [15], and electronic indexes (of one sort or another) [8-13]. Unfortunately, some of them, particularly, magnetic measures, can lead to results that are not consistent with chemical expectations.

The above consideration motivates us to apply a special cyclic delocalization index which would directly reflect electronic cyclicity of benzenoid or other structural subunits. Among the existing aromaticity measures, the so-called I_{NG} index, which was introduced in Ref. [16] and investigated in Ref. [5], deserves more attention than it has received thus far. In the present paper we revive and extend the I_{NG}-approach, making improvements to it. These improvements are mainly concerned with a simplified inclusion of both electron correlation and atomic charge effects.

The essential part of our approach is an explicit incorporation of an electron-correlation factor to the resultant cyclic aromaticity index. We achieve this by invoking the recently introduced quasi-correlation tight-binding model (QCTB) [17,18]. Notice that the typical tight-binding (TB) model for

π-electrons is tantamount to the Hückel MO (HMO) method, so we will make no distinction between TB and HMO schemes. The proposed cyclic aromaticity index is easily computed within the framework of semiempirical models of TB type, and it is used here for sufficiently large PAHs and graphene nanoclusters.

Cyclic aromaticity for π-conjugated fragments

Our approach, as many others, is founded on the conventional π-electron characteristics which are named π–electron bond orders, more exactly Coulson's mobile bond orders. Like `experimental` bond orders that are used in Pozharski and Bird aromaticity scales [19,20], the Coulson bond order expresses, in relative units, the bond strength. Before giving the approach to be considered it is suitable to start with one very simple but lucid quantification scheme for the local aromaticity from Refs. [21,22].

In the above cited works, the bond-order index of aromaticity (BOIA) of the form

$$\text{BOIA} = 1 - \frac{1}{6}\sum_{a=1}^{6}(P_a - P_0)^2 \tag{1}$$

is assigned to each benzenoid rings. In Eq. (1) P_a is π–bond order of ath chemical CC bond in the given 6-atom ring, and P_0 is a reference value for the isolated benzene molecule. In practical computations based on usual Hückel and Pariser-Parr-Pople π-approximations, $P_0 = 2/3$. Slightly more complicated are the definitions of the so-called para delocalization index (PDI) [5], quantum similarity [23] and quantum fidelity [8] indexes, and several others which are also based on using bond orders.

The certain drawback of the many above mentioned indexes is that they permit nonzero values even for benzenoid rings with a zero π–bond order between neighboring atoms, i.e. when no cyclic π–electron delocalization occurs (e.g., in partially hydrogenated rings). It means that the discussed indexes are not sufficiently targeted for describing the cyclic delocalization itself. It is not hard to understand that the use of arithmetic mean in Eq. (1) and related equations is the cause of such unwanted behavior. This obstacle is easily removed by replacing, in Eq. (1), the arithmetic mean by a geometrical mean. The previously cited I_{NG} index from Ref. [16] is just the measure of this type (see Eqs. (8) and (13) therein). Thus, we can start now by adopting I_{NG} index, from which we first take out its sophisticated normalization factor. It gives us a suitable quantity which will be termed the cyclic aromaticity index (CAI). The explicit expression for the given ring r is:

$$\text{CAI}[r] = [\prod_{a=1}^{6}(P_a/P_0)^2]^{1/6} = [\prod_{a=1}^{6}P_a/P_0]^{1/3} \tag{2}$$

Here we imply notations from Eq. (1), that is, all P_a in above are related to cycle r. Furthermore, in Eq. (2) the squared bond orders are, in fact, averaged over, so that we deal with the bond-orders due to Wiberg [24]. A more general is the definition of CAI for arbitrary cycle of size m:

$$\text{CAI}[r] = [\prod_{a=1}^{m}P_a/P_0]^{2/m} \tag{3}$$

It is also useful to introduce atomic aromaticity indexes (AAI) condensed to atoms. For this we will consider a cyclically connected backbone of the entire molecule without exocyclic atoms, that is a cyclic part of the whole structure. The individual values of AAI indexes will be denoted by AAI_a, with a specifying the given atom of the cyclic part. Explicitly, AAI_a are computed as follows:

$$\text{AAI}_a = (\prod_{j=1}^{3}P_{aj}/P_0)^{2/3} \tag{4}$$

Here P_{aj} is π-bond order for the $C_a C_j$ bond where atom j being adjacent to atom a, also belongs to the cyclic part. In case of the border atom a having only two neighbors, we have

$$\text{AAI}_a = \prod_{j=1}^{2}P_{aj}/P_0 \tag{4'}$$

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Moreover, by construction we adopt $AAI_a = 0$ for every exocyclic atom. The AAI set $\{AAI_a\}_{1 \leq a \leq M}$ is computed for all M atoms in the cyclic part of the molecule, and it allows one to approximately represent atomic contributions to the overall aromaticity.

As will seen in the next section, the given definitions are suitably applicable for cyclic-structure hydrocarbons (PAHs and other alternant systems). The latter, by definition, contain no odd carbon rings and heteroatoms. These are the so-called bipartite graphs in graph-theoretic terms. The remarkable fact for neutral (uncharged) alternants is that they have no π-electron net charges (a well-known consequence of the Coulson-Rushbrook pairing theorem). Otherwise, the π-electron net charges $\{q_a\}_{1 \leq a \leq M}$ appear, and they can suppress aromaticity (by increasing reactivity of polar molecules). Of course, net π- charges do not occur in the benzene molecule (within conventional π-theories). Hence, a certain charge factor, say, such as $1 - |q_a|$ for each atom a, must be additionally included into the above relations. In doing so, we imply that index a in P_a can be also treated as a number of the 'first' atom in the ath two-center bond, so q_a is the net charge on this cyclic atom. At this stage we take, instead of Eqs. (3) and (4), the following definitions:

$$CAI[r] = [\prod_{a=1}^{m} (1 - |q_a|) P_a / P_0]^{2/m} \tag{5}$$

$$AAI_a = (1 - |q_a|)^2 (\prod_{j=1}^{3} P_{aj} / P_0)^{2/3} \tag{6}$$

Obviously, all net charges and bond orders here are related to the given ring r.

Measuring cyclic aromaticity for small conjugated systems

To assess the quality and application of the proposed aromaticity measures, let us study, within the conventional Hückel approximation, several examples, mainly focusing on alternant structures. The simplest is a model case of plane annulenes, the completely conjugated monocycles $C_N H_N$ with N carbon atoms. In these model monocycles, all the AAI indexes are equal, and for the given N they will be denoted by $AAI_C[N]$. In the case of π-ions, number N will be supplied here by the superscript showing a total charge of the system. Evidently, $AAI_C[N]$ coincides with the CAI values defined in Eq. (5). For the reference benzene molecule we naturally have $AAI_C[6] = 1$. Simple computations on typical monocycles (including ions) produce the following results:

$$AAI_C[5^-] = 72(3 + \sqrt{5})/625 \approx 0.603,$$

$$AAI_C[7^+] = 324(1 + 2\cos[2\pi/7])^2 / 2401 \approx 0.681,$$

$$AAI_C[9^-] = 64(1 + 2\cos[2\pi/9] + 2\cos[4\pi/9])^2 / 729 \approx 0.728,$$

$$AAI_C[10] = 9(3 + \sqrt{5})/50 \approx 0.942,$$

$$AAI_C[\infty] = 9/\pi^2 = 0.91189....$$

Together with $AAI_C[6] = 1$, they show that in our scheme the aromaticity degree of stable monocyclic π−systems satisfying Hückel $(4n+2)$ rule, nonmonotonically varies with increasing N, and goes to the limiting value ($\approx 91\%$).

Next, in Table 1, we provided the Hückel-based characrerization of local aromaticity in the ground states of naphthalene, anthracene and others typical PAHs. The results for ring aromaticity measure, Eq. 5, are compared with σ^{arom}-indexes, that is, with our another ring aromaticity measure, defined previously in Ref. [8], Eqs. (7.3) and (7.4). In Table 1, as well as in other tables and figures, the visualization of atomic distributions $\{AAI_a\}$ is also shown. Each AAI_a value is displayed as a red circle with radius proportional to this AAI_a value. From the table we see that the "most aromatic" are outer rings of the studied systems. Judging from the data collected in Ref. [19] for linear polyacenes and related systems, this feature is not reproduced by other aromaticity scales such as NICS in Ref. [14], PDI and HOMA (the last is described in Refs. [1,4]) . At the same time, the more sophisticated scales

from Ref. [22,25] (six–center indexes etc) give the picture which is qualitatively(but not quantitatively) the same as that of our CAI scale. Interestingly enough, a similar reasonable behavior was observed as well when using the quantum fidelity measure of aromaticity from Ref. [8].

Table 1. CAI and σ^{arom} distributions (both in %) for small π-structures at the Hückel level. AAI distributions are shown in red.

No	{CAI[r]}	{σ^{arom}[r]}	No	{CAI[r]}	{σ^{arom}[r]}
1	83 / 83	{85, 85}	4	69 / 79 79 / 69	{79, 69, 69, 79}
2	80 / 71 / 80	{83, 70, 83}	5	79 79 / 53 / 79 79	{80, 80, 48, 80, 80}
3	79 / 69 / 69 / 79	{83, 69, 69, 83}	6	72 72 / 72 61 72 / 72 72	{72, 72, 72, 56, ...}

Observe that the CAI aromaticity scale is quite different , by its nature, from the σ^{arom} scale from Ref. [8]. Indeed, σ^{arom} is produced by estimating a local energy of benzenoid cycles (a counterpart of aromaticity stabilization energy), whereas CAI is directly calculated from the corresponding ring bond orders. Nevertheless, these two scales behave very similarly in all respects.

An interesting case is the charged aromatic molecules. To be more specific, let us take the three doubly charged molecular ions (dications). For them we give, in Fig 1, the local aromaticity diagrams along with the corresponding atomic net π-charge distributions in their ground states. We observe an understandable decrease of local aromaticity for all benzenoid subunits (compare the respective CAI values in Fig. 1 and Table 1). It is natural that as a rule less charged atomic sites turn out to be the most aromatic.
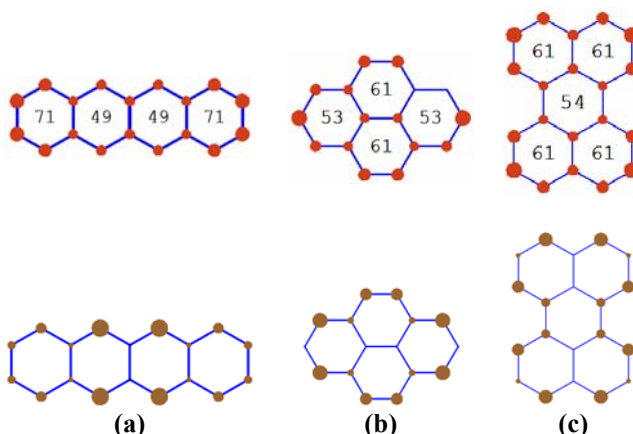

Figure 1. Dicationic states of tetracene (a), pyrene (b), and perylene (c) within HMO. Top panel: CAI (in %) and AAI distribution (in red). Bottom panel: distributions of net atomic charges (in brown).

A specific case of quinoid molecules is also worth consideration. In Fig. 2 we have displayed the data obtained for a double-quinoid structure (p-diphenoquinodimethane). When treating this hydrocarbon in its neutral form we took into account the corresponding bond-length altenation. The standard

alternation scheme of resonance integrals is used with factor 1 ± 0.125 (the upper sign is for the essentially double CC bonds, and the lower for the 'simple' CC bonds). In case of the dication, such a bond alternation was ignored because the alternation is practically absent, as follows from an analysis of the most contributing valence-bond resonance structures [8,26]. From Fig. 2 we see that the dicationic state is even more aromatic than the initial neutral state of the diquinoid (in spite of nonzero net π-charges), and it is opposite to the behavior of the PAH molecules of a similar size. This result is readily explained by the comparable analysis of valence bond schemes (for precedent cases, see Refs [8,26]). In passing, recall that cationic and anionic forms of alternants have the same π-electron density matrix, so π-aromaticity of the ionic alternant systems is indepengent of their charge sign; e.g., the aromaticity is same for dications and dianions. Notably, the similar HMO approach can be applied without difficulty to heterocyclic molecules, as our preliminary computations for several azaheterocycles show it.
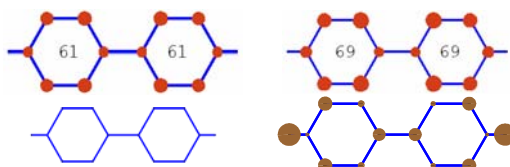

Figure 2. The neutral form (in left) and dicationic form (in right) of *p*-diphenoquinodimethane within HMO. CAI are given in %; AAI distributions are shown in red, and atomic net charge distribution in brown.

Local aromaticity for singlet open-shell and electron correlated states

Now we turn to a more refined aromaticity scale which takes into account π-electron correlation effects explicitly. In so doing we do not go essentially beyond the standard Hückel model, thus retaining the key graph-theoretic benefits of the whole approach. It becomes possible by employing the QCTB technique mentioned in the introductory section. Notice that usually high-spin electronic states (biradical and polyradical structures) are electron-correlated states in their nature, and strictly speaking, they are beyond conventional one-electron schemes. Nevertheless, for alternant systems we are able to analyze high-spin states on an equal (QCTB) footing with others. Before doing it we first sketch very briefly main points of the required formalism.

QCTB [17,18] is based on a crude description of π-electron systems by using the alternant MO (AMO) theory. The Devison-Amos model [27] (see also Ref. [28]) can be regarded as a precursor of our QCTB scheme that is but one-parametric AMO model with a fixed spin parameter δ; the last predetermines splitting of the different orbitals for different spins. The approach is consistently applicable to alternant hydrocarbons only.

First, we write down the QCTB energy spectrum:

$$\varepsilon_i^{\mathrm{QCTB}} = -\sqrt{\delta^2 + \varepsilon_i^2}, \quad \bar{\varepsilon}_i^{\mathrm{QCTB}} = \sqrt{\delta^2 + \varepsilon_i^2}, \tag{7}$$

where $1 \le i \le n$, and sets $\{\varepsilon_i^{\mathrm{QCTB}}\}$ and $\{\bar{\varepsilon}_i^{\mathrm{QCTB}}\}$ are related to occupied and virtual MOs, respectively. In Eq. (7), a set $\{\varepsilon_i\}$ of nonnegative Hückel orbital energies (graph spectrum) is produced by the square root of the eigenvalues of B^+B, with B being a submatrix of the full topological matrix (adjacency matrix). The latter allows the standard block-matrix representation:

$$h_{\mathrm{top}} = -\begin{pmatrix} 0 & B \\ B^+ & 0 \end{pmatrix} \tag{8}$$

Nowadays the Hückel (graph) spectrum can be quickly computed for multi-thousand atom systems even by laptops (to say nothing of the fact that the graph spectrum is easily available for many polymer structures with translation symmetry).

An important result of electron correlations is the occurrence of effectively unpaired electrons (EUE) in formally closed-shell singlet molecules (see review [17] and references therein). The main entity of the EUE formalism is EUE density matrix, D^{U} [29] (or D^{eff} in Ref. [17]). It describes, in particular, how unpairing electrons are distributed over the entire molecule. The respective EUE densi-

ties, which are condensed to atoms, constitute a set of the EUE atomic indexes, $\{D_a^U\}_{1 \leq a \leq M}$, and the latter will serve us as the key instrument to incorporate electron correlation effects into the aromaticity measurement. In Appendix A we show in detail that QCTB also provides a generally correct account of the EUE properties of π-conjugated radicals and polyradicals. Interestingly, quite recently in Ref. [30] a special analysis of the QCTB bond orders was proposed, which aimed to describe bond alternation effects in terms of implicit spin–spin repulsion forces [31].

We now suggest that local aromaticity must incorporate not only a benzenoid similarity of the ring bond orders, but also a change of the electron unpairing in the rings. To be consistent, we must take account of a small electron unpairing in the benzene molecule itself. Let us denote by D_0^U the EUE atomic π-density in the isolated benzene molecule. Then, for the given atom a, factor $1 - \left| D_a^U - D_0^U \right|$ can be used when accounting for a diminution of aromaticity due to electron unpairing. Hence, we have the resultant definition of the ring aromaticity at the QCTB level:

$$\mathrm{CAI}[r] = [\prod_{a=1}^{m} (1 - \left| D_a^U - D_0^U \right|)(1 - |q_a|)P_a / P_0 \;]^{2/m}. \tag{9}$$

The respective atomic delocalization index is

$$\mathrm{AAI}_a = [(1 - \left| D_a^U - D_0^U \right|)(1 - |q_a|)]^2 \, (\prod_{j=1}^{3} P_{aj} / P_0)^{2/3}, \tag{10}$$

with the corresponding change in the case of atom a having two neighboring atoms [see Eq. (4')]. Here the computations are performed with using the QCTB matrix P given in Eq. (A1).

Applying QCTB to the benzene π-shell, we find the reference value

$$D_0^U = (3 - 2/\sqrt{1+\delta^2} - 2/\sqrt{4+\delta^2})/3 \tag{11}$$

needed for Eqs. (9) and (10) [for the derivation see Appendix A]. Furthermore, in Eqs. (9) and (10) the HMO reference value $P_0 = 2/3$ is also replaced by the respective QCTB value of the form
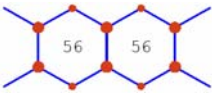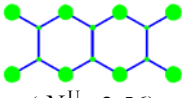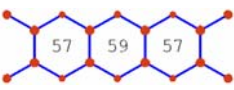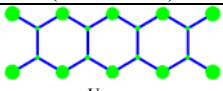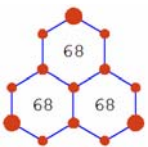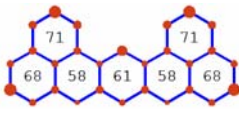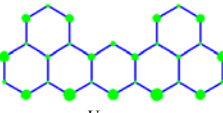
$$P_0 = (1/\sqrt{1+\delta^2} + 2/\sqrt{4+\delta^2})/3. \tag{12}$$

Taken together, Eqs. (9) - (12) give a complete set of relations for computing the local aromaticity indexes within QCTB. In our practical computations, splitting parameter δ was taken as previously in Refs. [17,18]: $\delta = 7/24$.

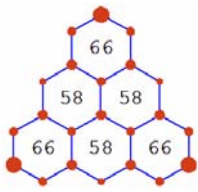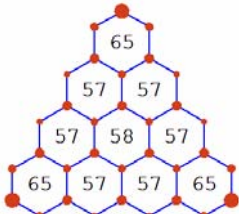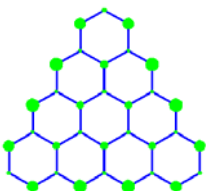Let us now consider pertinent examples that illustrate the introduced QCTB aromaticity measures. We take several tetramethylene-based aromatic diradicals and other radical structures with the phenalenic motif (Table 2). These and closely related systems are frequently discussed in literature [32-35]. The case of tetramethylenic radicals (structures **7** and **8** in the table) is of particular interest because the singlet-state diradicals of this type belong to the class of the so-called non-Kekulé conjugated molecules (no classical valence formula with alternating single and double bonds). It means that, strictly speaking, they cannot be treated by the simple TB π-model. For such diradicals the conventional Hückel model leads, in practice, to charge symmetry breaking solutions due to a degeneration of frontier MOs. In other words, the singlet biradicals are the open-shell systems which require sufficiently advanced electron-correlation models. But in QCTB owing to splitting different orbitals for different spins one can easily manage these open-shell problems, thus providing resulting symmetry-correct solutions.

As a result, for the singlet open-shell systems we obtain a large amount of EUE ($N^U \geq 2$) as well as a significant spreading of EUE over the whole molecule (see the last column in Table 2). Because of that the ring aromaticities are reduced, especially for tetramethylenic radicals. It is also worth noting that atomic local aromaticity indexes AAI_a are rather marked even for sites with nonnull values of D_a^U. Furthermore, the AAI_a values can be treated as the chemical stability (passivity) index of the given atom a in respect to substitution and/or radical attack in the molecule of question. So, $1/\mathrm{AAI}_a$ might be used as conditional atomic reactivity indexes (in the benzene units) but further discussion of this is beyond of scope of the paper.

Table 2. Aromaticity and effectively unpaired electrons in open-shell π-structures with spin value S at the QCTB level. Distributions $\{CAI[r]\}$ are displayed in %; AAI indexes are shown in red, and atomic EUE distributions $\{D_a^U\}$ in green.

No	S	$\{CAI[r]\}$	$\{D_a^U\}$
7	0		(N^U =2.56)
8	0		(N^U =2.91)
9	1/2		(N^U =1.31)
10	1		(N^U =2.74)
11	1		(N^U =2.50)
12	3/2		(N^U =3.75)

We call attention to the fact that it is typical that polyradials with large EUE degree (e.g,. the last system in Table 2) actually remain sufficiently aromatic. Possibly, this internal stability of the aromatic radicals is responsible for the fact that the here treated open-shell structures are quite realistic. More than that, the ingenious experimentalists succeeded recently to synthesize the related high-spin radical structures at last. These are a derivative of 1,14:11,12-dibenzopentacene and triangulene (structures **10** and **11** in Table 2) [36,37].

Large graphene-like molecules

In this section we present the aromaticity characterization of graphene nanoflakes of different structural types (Figs. 3 and 4). The first system, C_{154}, Fig. 3 is related to the periacene - type nanographenes which we discussed previously in Refs [14,17,18]. The second (C_{192}) is the antidote structure taken from Ref. [38]. The third, C_{426}, Fig. 4, has triangular zigzag graphene subunits as building blocks. As a system with the compensated topological frustration it was proposed in Ref. [39] for future spintronics applications. In Ref. [18] we examined the EUE properties of this C_{426}, named in Ref. [39] 'Kekulean logic gate structure' (KLGS).
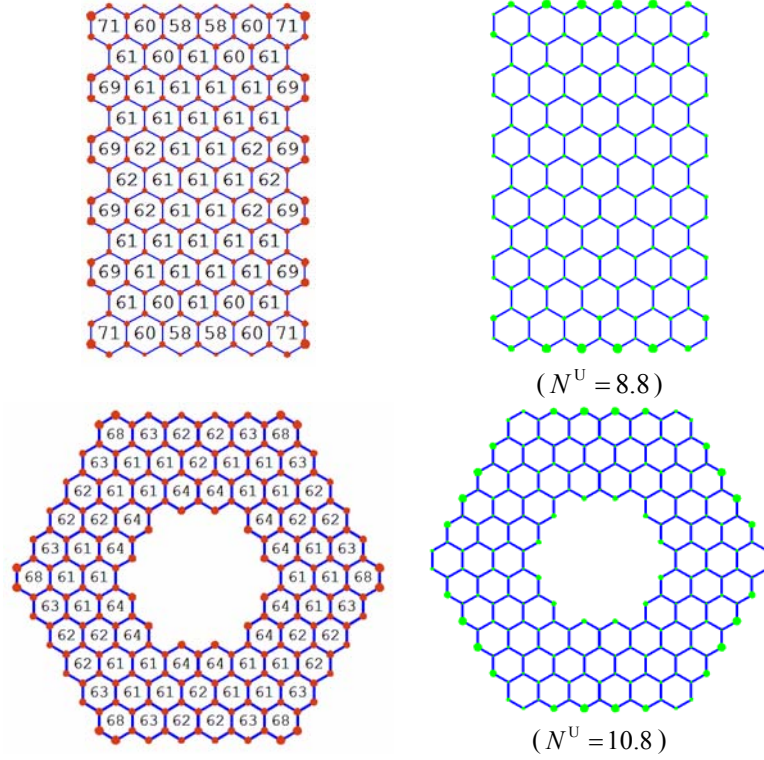
Figure 3. Local aromaticity and effectively unpaired electrons in nanoflakes C_{154} and C_{192} at the QCTB level. The left panel: CAI (in %) and AAI (in red). The right panel: EUE distributions (in green).
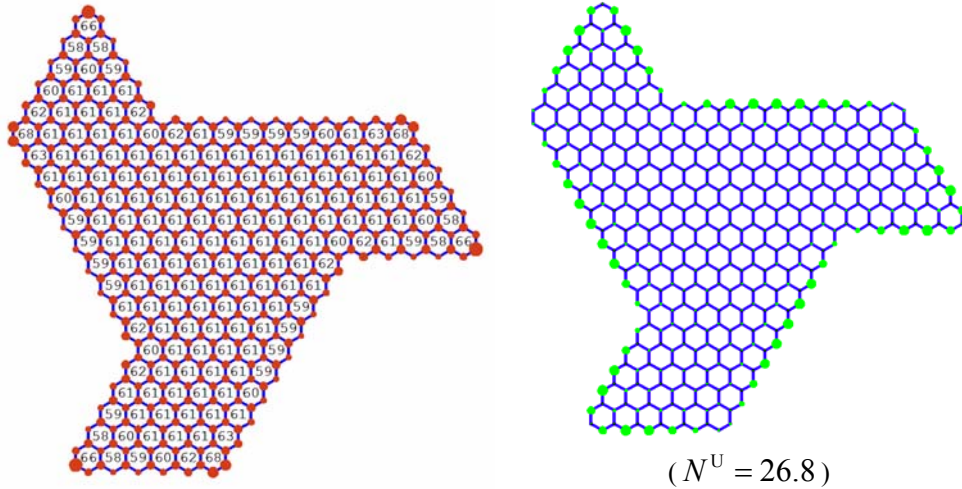

Figure 4. Local aromaticity and effectively unpaired electrons in the KLGS nanogaphene C_{426}. The left panel: CAI (in %) together with AAI distribution (in red). The right panel: EUE distribution (in green) at the QCTB level.

For the periacene molecule C_{154} we observe a higher aromaticity at armchair edges (along the long axis of the molecule), and it is in agreement with the results of Refs. [11,14,40] for related structures in alternative considerations. Concurrently, in our approach the local aromaticity decreases as we move to the center of graphene structures, and this behavior contradicts the NICS (nucleus independent chemical shift) predictions discussed in [11]. The analysis of the rest structures and other systems (not reported here) draws the above conclusion that aromaticity is decreased in the inner core of the graphene clusters. As to the cited NICS predictions we only remark that it may be strongly doubted whether NICS can provide a reliable description of the relative aromaticity at all [6,41,42].

Whilst this paper was in preparation a new analysis of π-electron aromaticity was reported [43], and one of the Referees kindly informed the author about this work. The cited paper motivated us to provide in Appendix B a supplementary example which elucidates peculiarities of using bond orders in π-theories.

Conclusion

Summing up, we would like to stress once more that aromaticity must be regarded as one of the most important chemical paradigms. It unites fundamental aspects of electronic and structural behavior of various conjugated systems – from small molecules to large nanoclusters.

As to the practical side, it may be worthwhile to keep in mind a quotation from Ref. [44]: "As a concept, aromaticity is not directly accessible experimentally, but its consequences are.". For instance, the stability of π-conjugated networks is directly connected with aromaticity, and in our paper we have just faced such a situation in section 4. At the same time, we must not forget about "the many guises of aromaticity" [45].

It the present paper we have revised the so-called ring indexes of aromaticity earlier defined by Cioslowski et al in Ref. [16] (see also Ref [46]). We stressed upon the cyclic delocalization as an underlying characteristic of aromaticity, and used an appropriate term "the cyclic aromaticity" from Ref. [47] . Starting from the simple Hückel model we incorporated net charge and electron correlation effects into the ring aromaticity indexes, while retaining a simplicity of the whole approach. It allowed us to investigate, in an elementary way, the large open-shell systems which are electronically of biradicaloid or polyradical nature (sections 4 and 5). The atomic aromaticity indexes (10) per se also deserve attention when chemical reactivity rather than benzenoid or total aromaticity is the main focus. Our experience in working with the proposed aromaticity measures, Eqs. (9) and (10), suggests that after a small modification their usage can be extended to more sophisticated methods. In particular, the generalized bond order indexes which are based on the cumulant analysis of the two-electron density matrix (see, e.g [48]) should be used for bona-fide many-electron approaches. Seemingly, also realistic would be the perspective to treat, in the same manner, heteroaromatic polymers, nanotubes and other quasiconjugated networks.

Acknowledgement

Appendix A. Effective unpaired electrons within QCTB

Below we briefly outline the procedure for determining EUE density matrix D^{U} within QCTB. Starting from our initial work [49], the QCTB scheme was applied only to the closed-shell singlet states of alternant hydrocarbons. Now, following Ref. [18], we extend the consideration, and show that QCTB is also applicable for analyzing aromaticity in high-spin ground states of alternanant diradicals/polyradicals. Notice also that in general the key idea of QCTB was in fact contained in Ref. [27] (which remained unknown to us for a long time). For π-polymer structures, a related approach was elaborated in Ref. [50] and many others Tyutulkov's papers.

We refer the reader for details of QCTB to review [17], and begin with the explicit representation of the ordinary density matrix (charge and bond order matrix), P, at the QCTB level:

$$P = I - h_{\mathrm{top}}(h_{\mathrm{top}}^2 + \delta^2 I)^{-1/2}. \tag{A1}$$

The basic matrix of the EUE theory is the density matrix D^{odd} defined in Ref. [51]. It describes a deviation of P from its one-determinant pattern. More exactly, D^{odd} is a duodempotency deviation matrix, that is $D^{\mathrm{odd}} = 2P - P^2$. Within QCTB this matrix allows the explicit representation:

$$D^{\mathrm{odd}} = \delta^2 (h_{\mathrm{top}}^2 + \delta^2 I)^{-1} \tag{A2}$$

(see Ref. [18], Appendix D). From it the useful expression for D^{U} is derived to be

$$D^{\mathrm{U}} = I - (I - D^{\mathrm{odd}})^{1/2}. \tag{A3}$$

The above result provides a consistent EUE characterization within the hole-particle approach [38] which for the ground state is equivalent to the EUE theory given in Ref. [29]. By using a spectral resolution of matrix h_{top}, Eq. (8), we obtain the working expression for atomic densities of the unpaired electrons, that is diagonal matrix elements ($D_a^{\mathrm{U}} \equiv D_{aa}^{\mathrm{U}}$):

$$D_a^{\mathrm{U}} = \sum_{j=1}^{M} |C_{aj}|^2 [1 - |\varepsilon_j| (\delta^2 + \varepsilon_j^2)^{-1/2}], \tag{A4}$$

with C_{aj} being atomic expansion coefficients for the jth Hückel MO of energy ε_j. In doing so, the total number of unpaired electrons, which by definition is $N^{\mathrm{U}} = \mathrm{Tr}\, D^{\mathrm{U}}$, can be presented as the spectral sum:

$$N^{\mathrm{U}} = \sum_{i=1}^{M} (1 - |\varepsilon_j| / \sqrt{\delta^2 + \varepsilon_j^2}). \tag{A5}$$

With this, we have identity $N^{\mathrm{U}} = \sum_{a=1}^{M} D_a^{\mathrm{U}}$. Interestingly, Eqs. (A4) and (A5) can be directly extended to nonalternant systems too, but this possibility requires additional testing.

We infer from Eq. (A5) that arbitrary alternant polyradical has indeed a high N^{U} value for any δ, namely,

$$N^{\mathrm{U}} \geq n_* - n_0, \tag{A6}$$

where we use notation, n_* and n_0, for the corresponding numbers of starred and unstarred π-centers. Really, it is well known that $n_* - n_0$ is just a number of zero-energy MOs (more exactly, of nonbonding MOs), and condition $n_* > n_0$ provides existence and stability of radical/polyradical states as the ground states of these π-structures [52]. Turning to Eq. (5) we realize that for such structures at least, $n_* - n_0$ terms in Eq. (A5) are equal to 1; other terms are certainly nonnegative, and this leads to inequality (A6). If we recall the known Ovchinnikov-Lieb rule for the ground-state spin, S, of the alternant (bipartite) networks [53,54], then (A6) can be rewritten as follows:

$$N^{\mathrm{U}} \geq 2S,$$

where N^{U} at the QCTB level is determined by Eq. (A5). We see that the elementary expression (A5) affords a correct EUE picture by using only a Hückel-like framework.

Let us take, as a simple example, the benzene molecule for which the orbital energy spectrum $\{\varepsilon_j\}$ is well known:

$$\{\varepsilon_j\} = \{-2, -1, -1, 1, 1, 2\}.$$

Substituting these values into Eq. (A.5), we find $N^{\mathrm{U}} = 2(3 - 2/\sqrt{1+\delta^2} - 2/\sqrt{4+\delta^2})$. Due to symmetry we have $N^{\mathrm{U}} = 6 D_0^{\mathrm{U}}$, where D_0^{U} is the EUE atomic density for carbon atom in the benzene molecule. It gives Eq. (11) for D_0^{U}, that is the reference value needed for computing QCTB aromaticity indexes by Eqs. (9) and (10). Moreover, with somewhat more work, we obtain from Eq. (A1) the explicit expression (12) for the reference bond order P_0.

Appendix B. Which bond orders are preferable for aromaticity measures

This appendix is appropriate to be added in a general context of the aromaticity analysis which draws on the bond order theory. We recall that there are at least two key definitions used for π-electron bond orders (if ignoring the experimental bond orders mentioned in section 2). The most popular and most consistent is the definition based on one-electron density matrix theory. In its simplest MO realization this leads to the well-known classical bond orders due to Coulson. These ones and their QCTB counterparts are employed in the present work. Another definition of π-bond orders is due to Pauling

and Ruedenberg [55]. Let us denote the Pauling-Ruedenberg bond order matrix by $P^{\text{P-R}}$. Then for 'nonsingular' ($\text{Det}[h_{\text{top}}] \neq 0$) benzenoid systems, $P^{\text{P-R}}$ can be obtained as an inverse of the Huckel Hamiltonian matrix [56]:

$$P^{\text{P-R}} = h_{\text{top}}^{-1}. \tag{B1}$$

This elegant relation was analyzed and used in many papers. It is also suitable to be applied when discussing local aromaticity in the spirit of the recent works [43,57,58]. However, there is one unpleasant disadvantage with $P^{\text{P-R}}$. It turns out that one can encounter the cases when $P^{\text{P-R}}_{\mu\nu} = 0$ even for chemically bonded carbon atoms $_{(\mu,\nu)}$! The specific perylene example having $P^{\text{P-R}}_{\mu\nu} = 0$ was mentioned in Ref. [59] (for the related critique of $P^{\text{P-R}}$ see also Ref. [60]). Moreover, it is possible to find large classes of PAHs where the Pauling-Ruedenberg theory predicts such unnatural zero-valued π-bond orders for chemical C-C bonds. For instance, the well-known periacene structures, such as C_{154} in Fig. (1), represent just such a class of molecules. We see that using Pauling bond orders is not generally wholly satisfactory procedure, and it warns us to be cautious when analyzing local aromaticity by the technique from Refs. [43].

Nevertheless, it would be interesting to compare the results of Randić and Balaban with ours. As a preliminary study, let us take the specific example of a double peropyrene molecule given in the cited work. This system termed here as diperopyrene is dislayed in Fig. 5. The molecule has no anomal zero Pauling bond orders, and apparently, the results from Ref. [43] should be resonable in this case. An interesting point in papers [43,58] is taking into account the so-called migrating Clar sextets when forming local benzenoid aromaticity. For various aspects of the Clar theory the reader is also referred to Refs. [11,61-63].
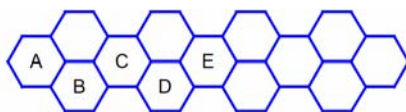

Figure 5. Ring labels for diperopyrene.

The obtained results are given in Table 3. In this table, the data from Fig. 7 in Ref. [43] are presented in the rescaled form (by factor 1/3) for making them comparable with ours. By inspecting the table one can conclude that the used aromaticity scales are all qualitatively similar; e. g., the local aromaticity value of the central ring in diperopyrene is lesser than all other values. Concurrently, we observe certain quantitative differences between the results of Ref.[43] and ours. In particular, in the Randić-Balaban approach, we have a seemingly too large aromaticity measure in the terminal rings, and a too low one in the central ring. Notice that the electron correlation at the QCTB level slightly enhances the local aromaticity. At last, again turn attention to the fact that energetic aromaticity indexes $\sigma^{\text{arom}}[r]$ from Ref. [8], and the QCTB aromaticity measures by Eq. (9) are very similar.

Table 3. Rescaled ring indexes from Ref. [43], local energy indexes σ^{arom}, and aromaticity indexes CAI for benzenoid rings of diperopyrene at the TB and QCTB levels. Rings A, B,… are shown in Fig. 5; all values are in %.

Method	Cycles				
	A	B	C	D	E
Ref. [43]	89	72	63	80	48
CAI [TB]	72	67	56	69	55
σ^{arom}, Ref. [8]	79	71	57	73	67
CAI [QCTB]	76	71	58	72	58

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А.В. Лузанов. Циклическая ароматичность в методе Хюккеля и в квазикорреляционном хюккелеобразном подходе.

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В статье рассматривается количественное мероопределение ароматичности π-электронных структур простыми схемами МО. Делается акцент на мерах локальной ароматичности, которую приписывают отдельным бензольным кольцам структуры. Модифицируется индекс циклической ароматичности по методу Cioslowski и сотр. (2007), где теперь учитываются остаточные заряды и эффекты электронного распаривания. Прежнее наше квазикорреляционное приближение сильной связи (QCTB) служит здесь в качестве подходящей модели, которая весьма простым образом включает эффекты π-электронных корреляций. Последние могут критично влиять на поведение больших и даже малых сопряженных молекул с нетривиальной топологией. Представлены применения моделей Хюккеля и QCTB для локальной ароматичности в разнообразных структурных классах полициклических ароматических углеводородов (ПАУ), наночастиц графена и т.п. Аналитически исследована мера ароматичности в сопряженных моноциклах $C_N H_N$ (нейтральных и заряженных). Кроме того, в тех же схемах изучено несколько ПАУ-структур (олигоцены, пирен, перилен и пр.) в их заряженных состояниях и проведено сравнение со структурами хиноидного типа, как в *п*-дифенохинодиметане. Показано, что в отличие от обычных ПАУ, хинодиметаны увеличивают ароматичность в дикатионной (дианионной) форме. Изучая нанографены, мы фиксируем понижение их локальной ароматичности по мере перехода к центру структуры, что вовсе не отвечает результатам NICS-метода (независимый от ядра химический сдвиг), впрочем, метода довольно спорного. В работе делается особенный акцент на оценке локальной ароматичности в сильно коррелированных π-электронных системах. Типичные некекулевские углеводороды (например, триангуленовый радикал и полирадикалы) также изучены с помощью QCTB, где с легкостью обходятся характерные трудности, обусловленные наличием большого числа несвязывающих МО.

Ключевые слова: меры ароматичности, полициклические ароматические углеводороды, нанографены, хюккелевские МО, системы с открытой оболочкой, полирадикалы, квазикорреляционное приближение сильной связи.

А.В. Лузанов. Циклічна ароматичність за методом Хюккеля та квазікореляційним хюккелеподібним наближенням.

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У статті розглядається кількісне міровизначення ароматичності π-електронних структур невибагливими методами МО. Акцентується на мірах локальної ароматичності, що пов'язуються з окремими бензольними кільцями. Модифіковано індекс циклічної ароматичності Cioslowski та співроб. (2007), в якому наразі враховано наявні остаточні заряди та ефекти електронного розпарювання. Попереднє наше квазікореляційне наближення сильного зв'язку (QCTB) слугую тут за придатну модель, котра у вельми простий спосіб враховує ефекти π-електронних кореляцій. Останні спроможні критично впливати на поведінку великих та навіть малих супряжених структур з нетривіальною топологією. Зроблено чисельні застосування моделей Хюккеля та QCTB до локальної ароматичності у різноманітних структурних класах (поліцикличних ароматичних углеводнів (ПАУ), графенових наночастинок тощо). Аналітично досліджено ароматичну міру в супряжених моноциклах $C_N H_N$ (нейтральних та заряджених). Крім цього, за тими же схемами розглянуто декілька ПАУ-структур (олігоцени, пірен, перилен тощо.) у заряджених станах; їх порівняно із структурами за хіноїдним типом, як у *п*-дифенохінодиметані. Продемонстровано, що на відміну від звичайних ПАУ, хінодиметани збільшують ароматичність у дикатіонній (дианіонній) формі. Досліджуючи нанографени, ми знаходимо зниження їх локальної ароматичності, коли просуваємось до центру структури, що зовсім не відповідає результатам за NICS-методом (незалежний від ядер хімічний зсув), який взагалі є доволі спірним. В роботі робиться особливий акцент на оцінювання локальної ароматичності в сильно корельованих π-елетронних системах. Типові некекулівські вуглеводні (наприклад, тріангуленовий радикал та полірадикали) також вивчено за допомогою QCTB, який з легкістю оминає характерні ускладнення, котрі пов'язано із значною кількістю незв'язуючих МО.

Ключові слова: міри ароматичності, поліцикличні ароматичні вуглеводні, нанографени, хюккелівські МО, системи з відкритою оболонкою, полірадикали, квазікореляційне наближення сильного зв'язку.