

# Singlet open-shell conjugated networks generated by singular graphs: Use of Huckel-like models

*A.V.Luzanov*

SSI "Institute of Single Crystals", National Academy of Sciences of  
Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukraine

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We show how the conventional tight-binding (TB), i. e., Huckel method can be consistently extended to open-shell singlet ground states of polyradical alternant systems that correspond to singular graphs. This leads us to the open-shell TB (OS-TB) model which is presented in detail and compared here with more complicated  $\pi$ -electron approximations. In particular, the earlier introduced quasi-correlated TB (QCTB) method and its extension (EQC) are involved into assessing the accuracy of OS-TB. It is shown that commonly used bond-order matrices, as well as electron-unpairing densities are described well by OS-TB, whereas  $\pi$ -electron Green functions generally are not. At the same time, we demonstrate that the related models, QCTB and EQC, provide reasonable estimates of molecular conductance (at the Fermi energy) in polyradical conjugated networks. The obtained results may be used for a design of active molecular elements in nanoelectronics.

**Keywords:** polyradicals, electron unpairing, singular molecular graphs, long-range effects, spin correlators, molecular conductance.

**$\pi$ -Структури з відкритою оболонкою що стосуються до сингулярних графів.  
Використання хюккелеподібних моделей. А.В.Лузанов**

Досліджується, яким чином стандартний метод сильного зв'язку (ТВ), себто метод Хюккеля, можна послідовно розширити на випадок основного синглетного стану з відкритою оболонкою в полірадикальному альтернантному вуглеводні, що відповідає сингулярному графові. Це приводить до ТВ-моделі з відкритою оболонкою (OS-TB), яку в даній роботі детально описано та порівняно з більш складними  $\pi$ -електронними методами. Зокрема, для оцінки точності OS-TB залучено раніш запропонований квазі-кореляційний ТВ-метод (QCTB) та його розширення (EQC). Продемонстровано, що звичайні матриці порядків зв'язку, поруч із густиною ефективно розпарених електронів добре описуються методом OS-TB, тоді як  $\pi$ -електронні функції Гріна загалом не є задовільними. У той же час ми свідчуємо, що в полірадикальних супряжених структурах QCTB та EQC забезпечують задовільне оцінювання молекулярної провідності (з фермівською енергією). Результати, що їх отримано, можуть бути застосовані при конструюванні активних молекулярних елементів для наноелектроніки.

Исследовано, каким образом стандартный метод сильной связи (ТВ), т. е. метод Хюккеля, можно последовательно расширить на случай основного синглетного состояния с открытой оболочкой в полирадикальном альтернантном углеводороде, отвечающему сингулярному графу. Это ведет к ТВ-модели с открытой оболочкой (OS-TB), которая в данной работе подробно представлена и сравнена с более сложными  $\pi$ -электронными методами. В частности, для оценки точности OS-TB привлекается ранее предложенный квази-корреляционный ТВ-метод (QCTB) и его расширение (EQC). Продемонстрировано, что обычные матрицы порядков связи вместе с плотностью эффективно распаренных электронов

хорошо описываются методом OS-TB, тогда как  $\pi$ -электронные функции Грина вообще говоря неудовлетворительны. В то же время мы убеждаемся, что для полирадикальных сопряженных структур методы QCTB и EQC обеспечивают разумные оценки молекулярной проводимости (при фермиевской энергии). Полученные результаты могут быть использованы при конструировании активных молекулярных элементов для наноэлектроники.

## 1. Introduction

Ninety years ago E.Huckel devised a simple form of molecular orbital theory hereby inaugurating what is now known as the Huckel MO (HMO) theory of  $\pi$ -conjugated systems. Dealing with HMO we will make no fine distinction from the related term "tight-binding" (TB) model which is well known in solid state-physics. Though simple this method has served well as giving a conceptual basis for many electronic aspects of organic chemistry and organic material science.

Certainly, as such TB suffers from the known weaknesses of all one-electron semiempirical approaches. Nevertheless, even nowadays the Huckel theory remains among the useful tools for treating, say, large conjugated networks such as graphene molecules and carbon nanotubes [1–3]. That is why our own interest to TB did not subside until now. All this motivated us to look closer into paradigmatic conjugated  $\pi$ -systems, particularly of unusual non-Kekulean type, such as tetramethylenebenzene (TMB) and other diradicals. These open-shell singlet  $\pi$ -structures having extremely low-lying excited states need much more attention in light of their possible applications as active organic-molecule components in nonlinear photonics devices [4], field-effect transistors [5], molecular logical spin gates [6] etc.

Many of the mentioned radical structures can be identified with "concealed diradicals" (see [7] and the cited works therein), or widely, with concealed polyradicals. However, for our purposes, a general graph-theoretic term "singular graph" is more preferable. In fact, singular graphs appeared in [8] where graphs of this type was named "nullosungsgraf"; for further development see [9]. In terms of the conventional Huckel theory, relevant  $\pi$ -systems have at least one nonbonding MO (and at least two nonbonding MOs in the case of even alternants).

Here we will focus on TB-like models of nontrivial singlet open-shell  $\pi$ -systems such as the above mentioned TMB molecule and more complex polyradical networks. Along with the simplistic Huckel approach, we bring into play a suitable quasi-correlated TB (QCTB) scheme [10–12] and others. Thus, our aim in this paper is also to ex-

plore the quality of various Huckel-like models for singular  $\pi$ -structures. When comparing models we invoke a variety of  $\pi$ -electronic characteristics (bond orders, spin correlators and others), and study them for a number of conjugated hydrocarbons with a high singularity degree.

## 2. TB theory of alternant (bipartite) systems

For further discussion purposes, it is worthwhile to briefly recall the basic points of the conventional HMO theory in the case of alternants, that is alternant hydrocarbons (Coulson's term), or bipartites (the graph-theoretic notion). The present consideration will be confined to even alternant systems (even alternants) having even number

$$N = 2n,$$

of carbon atoms.

The key structural property of alternants is the absence of odd-membered cycles. As a consequence, it is always possible to divide a set of conjugated carbon atoms into two disjoint subsets ("starred" and "unstarred" sites). With this, apart from a positive energy-scaling factor, the TB Hamiltonian can be represented by a skew block diagonal matrix,  $h^{\text{TB}}$ , of the form

$$h^{\text{TB}} = - \begin{pmatrix} 0 & B \\ B^{\text{T}} & 0 \end{pmatrix}. \quad (1)$$

Here block  $B$  is  $(0,1)$  matrix with units only for nearest-neighbor atomic pairs; this  $B$  is often called biadjacency matrix. Eq. (1) was used particularly in the classical Hall work [13] where it is shown that for alternants one-electron density matrix,  $P^{\text{TB}}$ , or more precisely, the Coulson charge and bond-order matrix, can be written explicitly, as follows:

$$P^{\text{TB}} = \begin{pmatrix} I & P^{\text{TB}} \\ P^{\text{TB}} & I \end{pmatrix}, \quad P^{\text{TB}} = (BB^{\text{T}})^{-1/2}B. \quad (2)$$

This Hall representation is very profitable, making both analytic and numerical computations of alternants much more tractable. The so-called duodempotency requirement

$$(P^{\text{TB}})^2 = 2P^{\text{TB}} \quad (3)$$

is satisfied automatically, so all non-zero eigenvalues of  $P^{TB}$  are the same and equal to 2. It guarantees a one-determinant structure of the corresponding TB total wave function for singlet ground states.

As seen from Eq. (2),  $B$  is assumed to be nonsingular, that is

$$\det[B] \neq 0 \quad (4)$$

so  $\det[BB^T] = (\det[B])^2 \neq 0$ . Such alternants will be termed nonsingular, unlike the opposite case of "singular" alternants. In the latter the requirement

$$\det[B] = 0 \quad (5)$$

is obligatory, so that the occurrence of zero-energy (nonbonding) orbitals is warranted. It means that the even singular alternants have at least two non-bonding MOs (owing to Coulson-Rushbrooke alternant pairing theorem [14]). Note that the well-known cyclobutadiene molecule is only one representative example from a rich collection of singular (in TB) structures (for more detail see section 7). The distinction itself between the two cases, corresponding to Eq. (4) and Eq. (5), is essential because the occurrence of non-bonding MOs is an indication of electron instability.

### 3. Electron unpairing in singular $\pi$ -systems: QCTB theory

In singular alternants (and, in a lesser extent, in other ones) some  $\pi$ -electrons are unpaired, and this feature needs to be described at the appropriate many-electron level. However, even unsophisticated semiempirical versions can be helpful for this purpose. We will follow a simplest correlation-like scheme proposed long ago in [15]; then it is developed independently in [10, 11] in the form of the QCTB model.

The starting point of QCTB is using, instead of Eq. (1), two one-electron Hamiltonians,  $h_\alpha^{QCTB}$  and  $h_\beta^{QCTB}$  as done in the conventional "different orbitals for different spins" approaches. Only the QCTB Hamiltonians are oversimplified and taken as follows:

$$h_\alpha^{QCTB} = -\begin{pmatrix} \delta & B \\ B^T & -\delta \end{pmatrix}, \quad h_\beta^{QCTB} = -\begin{pmatrix} -\delta & B \\ B^T & \delta \end{pmatrix}, \quad (6)$$

where  $\delta$  is an orbital parameter inducing electron correlation. Thus, Eq. (6) corresponds to two TB-like topological structures described by specifically defined vertex-

weighted graphs. As to the latter ones, see, e. g., [16]. For a wide class of molecules the value of  $\delta$  may be fixed, and in our QCTB practical computations this parameter is assigned to be 7/24. Obviously, each Hamiltonian in the above equation generates its own density matrix, and it gives us two orbital projector matrices,  $\rho_\alpha$  and  $\rho_\beta$ , i. e., density matrices of spin-up and spin-down electrons, respectively.

The important result is the expression for QCTB bond order matrix  $P^{QCTB} = \rho_\alpha + \rho_\beta$ , which is of the same structure as in Eq. (2):

$$P^{QCTB} = \begin{pmatrix} I & P^{QCTB} \\ P_{QCTB}^T & I \end{pmatrix}$$

$$P_{QCTB} = (BB^T + \delta^2 I)^{-1/2} B. \quad (7)$$

Evidently, duodempotency condition (3) is not imposed on  $P^{QCTB}$ , and it reflects unpairing electron effects. Furthermore, we see that no singularity appears in  $P^{QCTB}$ , as a result of nonzero  $\delta$  in  $P_{QCTB}$ .

A more detailed information concerning electron unpairing can be suitably extracted from the the natural orbital occupation numbers (NOONs) [17], that is the  $P^{QCTB}$  eigenspectrum  $\{\lambda_j\}$ . The key quantity here is a number of effectively unpaired electrons (EUE). Denoting it by  $N_U$  (as in the basic paper [18]), we redefine the corresponding index in the transparent form [10, 11]:

$$N_U = 2N - 2 \sum_{j < n} \lambda_j \quad (8)$$

If, for instance,  $\lambda_j \equiv 2$  (as for  $P^{TB}$  from Eq. (2)) then  $N_U = 0$ , and no unpairing, of course.

Turn to  $P^{QCTB}$  in Eq. (7) for which the NOON spectrum is easily obtained [11]:

$$\begin{aligned} \lambda_j &= 1 + \varepsilon_j / \sqrt{\delta^2 + \varepsilon_j^2}, \\ \lambda_a &= 1 - \varepsilon_a / \sqrt{\delta^2 + \varepsilon_a^2}, \end{aligned} \quad (9)$$

where  $1 \leq j, a \leq n$  ( $n = N/2$ ), and the Huckel orbital energies  $\varepsilon_j$ , as well as  $\varepsilon_a$ , are defined as nonnegative square roots of the  $BB^T$  eigenvalues. The standard spectral resolution of matrix (7) is of the form:

$$P^{QCTB} = \sum_{1 \leq j \leq n} \lambda_j |\varphi_j\rangle \langle \varphi_j| + \sum_{1 \leq a \leq n} \lambda_a |\varphi_a\rangle \langle \varphi_a| \quad (10)$$

with  $|\varphi_j\rangle$ , and  $|\varphi_a\rangle$  being eigenkets corresponding to  $\lambda_j$  and  $\lambda_a$ , respectively; they can

be identified with occupied MOs for  $|\varphi_j\rangle$ , and virtual MOs for  $|\varphi_a\rangle$ , that is, with the  $h^{\text{TB}}$  eigenkets.

The final result (Eq. (16) in [10]) takes the explicit form:

$$N_U = N - 2 \sum_{j=1}^n \varepsilon_j / \sqrt{\delta^2 + \varepsilon_j^2}. \quad (11)$$

It is important to pay attention to the correct behaviour of Eq. (11) in a strong correlation limit. In this case, we allow  $\delta$  to be infinitive, so  $N_U \rightarrow N$ , thus meaning that all  $\pi$ -electrons are unpaired as should be for the strong Mott-like transition. As we will see below, Eq. (11) and related ones also provide a consistent way for understanding singular alternants at the Huckel level.

#### 4. QCTB and open-shell Huckel limit

Previously, QCTB was sporadically applied to singular alternants [9, 19]. Now we elucidate in more detail the respective EUE issue. Let us consider the EUE density matrix  $D_U$  which is also a fundamental object in the problem [18]. It is appropriate to define  $D_U$  by the spectral decomposition (Eq. (6.41) in [11]):

$$D_U = \sum_{1 \leq j \leq n} (2 - \lambda_j) |\varphi_j\rangle \langle \varphi_j| + \sum_{1 \leq a \leq n} \lambda_a |\varphi_a\rangle \langle \varphi_a|. \quad (12)$$

This matrix can be understood as a hole-particle density matrix. In the case of  $D_U^{\text{QCTB}}$  the corresponding NOONs are taken from Eq. (9).

Now we concentrate on our main case of interest. Let the given singular even-alternant system have even number, say  $r = 2m$  of nonbonding MOs; evidently, in even-alternant molecules the singularity starts with  $r \geq 2$ . This number  $r$  will be termed the singularity rank of the  $\pi$ -structure in question. It is permissible to assign the first  $m$  nonbonding MOs to the occupied MOs, and the rest to the unoccupied ones. Then,  $r = 2m$  NOONs in Eq. (9) are equal to 1, and Eq. (12) can be specified as follows:

$$D_U = \rho_O + \sum_{1 \leq j \leq n-m} (2 - \lambda_j) |\varphi_j\rangle \langle \varphi_j| + \sum_{m+1 \leq a \leq n} \lambda_a |\varphi_a\rangle \langle \varphi_a|. \quad (13)$$

Here  $\rho_O$  is a projector on the subset of nonbonding MOs:

$$\rho_O = \sum_{1 \leq j \leq m} |\varphi_{n-m+j}\rangle \langle \varphi_{n-m+j}| + \sum_{1 \leq a \leq m} |\varphi_a\rangle \langle \varphi_a|, \quad (14)$$

$$\rho_O = (\rho_O)^2, \quad \text{Tr} \rho_O = r,$$

that is,  $\rho_O$  is a projector on MOs of the open shell subsystem. Naturally, computing  $N_U$  by Eq. (11) we find that within QCTB the EUE number

$$N_U \geq 2m = r,$$

and it corresponds to the expected result that the singular alternants are polyradicals, as earlier stated by Longuet-Higgins [20] in qualitative terms of the classic TB model.

At this point we consider the "Huckel" limit when  $\delta \rightarrow 0$  in Eq. (13). We find immediately that  $D_U$  is simply  $\rho_O$ , so we can write

$$D_U^{\text{TB}} = \rho_O. \quad (15)$$

The same limit in Eq. (10) leads to the correctly defined full bond-order matrix  $2\rho_{cl} + \rho_O$  where we introduce the closed sub-shell projector

$$\rho_{cl} = \sum_{1 \leq j \leq n-m} |\varphi_j\rangle \langle \varphi_j|.$$

The approach based on the above Huckel limit to the open-shell  $\pi$ -system will be termed the open-shell TB (OS-TB) model. Hence, the charge and bond-order density matrix for OS-TB is evidently defined as follows:

$$P^{\text{OS-TB}} = 2\rho_{cl} + \rho_O, \quad (16)$$

and  $D_U^{\text{OS-TB}} = \rho_O$ . Clearly,  $P^{\text{OS-TB}}$  cannot be directly obtained by Eq. (2) if dealing with singular alternants. In particular, the duodempotency relation, Eq. (3), is no longer valid because

$$(P^{\text{OS-TB}})^2 + \rho_O = 2P^{\text{OS-TB}}.$$

In doing so, the respective EUE index  $N_U^{\text{OS-TB}} = r$ , thus reflecting electron correlation effects. The latter are simplistically included in our scheme as a result of the special Huckel-limit for singular strongly correlated systems. Evidently, Eq. (16) matches up with a singlet state in which  $r$  unpaired electrons occupy  $r$  nonbonding Huckel MOs. Strictly speaking, high-order electron correlation models should be employed when treating these open-shell many-electron problems. Nevertheless, we may obtain rather reasonable results just retaining

the Huckel framework of the above described OS-TB approach. In particular, we can introduce the local  $D_U$  densities, that is a set

$$\partial_{1 \leq \mu \leq N} \quad (17)$$

of diagonal matrix elements  $(D_U)_{\mu\mu} \equiv \partial_\mu$  in  $\pi$ -AO basis (the EUE atomic distribution). They give a sensible picture even though  $\partial_\mu$  are computed at the OS-TB level.

In the present paper, we will also exemplify the use of one modified version of QCTB given in [19, 21]. We term this version as the extended quasi-correlated (EQC) approximation. Within EQC we work with the improved Hamiltonians of the type given in Eq. (6). Namely,

$$h_\alpha^{EQC} = - \begin{pmatrix} \delta & B^{eff} \\ (B^{eff})^+ & -\delta \end{pmatrix}, \quad (18)$$

$$h_\beta^{EQC} = - \begin{pmatrix} -\delta & B^{eff} \\ (B^{eff})^+ & \delta \end{pmatrix}.$$

In this case the TB biajacency matrix  $B$  with elements  $B_{\mu\nu}$  is replaced with the extended one of the form

$$B^{eff} = \|B_{\mu\nu}^{eff}\|, \quad B_{\mu\nu}^{eff} = (\beta_0 B_{\mu\nu} - \gamma_{\mu\nu} P_{\mu\nu} / 2) / |\beta_0^{eff}|,$$

where  $\beta_0$  is the standard hopping (resonance) integral for CC bond ( $-2.4$  eV as usual);  $\gamma_{\mu\nu}$  are standard two-center two-electron integrals between  $\pi$ -AOs of starred and unstarred sites. The recalibrated resonance integral  $\beta_0^{eff}$  is given previously in [19]:

$$\beta_0^{eff} = \beta_0 - \gamma_{1,2} / 2$$

( $\gamma_{1,2}$  is the Coulomb integral for  $\pi$ -bond). Furthermore,  $P_{\mu\nu}$  in Eq. (18) are the corresponding elements  $(p_{TB})_{\mu\nu}$  of  $P^{TB}$  in Eq. (2) or those of  $P^{OS-TB}$  (in the case of singular systems). Importantly, by using EQC we roughly but simply take into account long-range electronic effects which can be crucial for a number of physical problems, such as molecular conductance (see section 8).

### 5. Computations of charge and spin correlations in open-shell structures

At the current stage, we must construct open-shell density matrices. While doing this, an orbital degeneracy of frontier MOs must be taken into a proper account. As usually, the two-electron density matrices are predominantly needed to directly de-

scribe interelectron interaction effects. When examining our specific open-shell problem we can draw from the quantum-chemistry experience of working with analogous states within the canonical Hartree-Fock theory. The results from [22, 23] concerning the Roothaan open-shell theory [24] are particularly helpful for this purpose.

We will use notations  $\Gamma_1^{open}(1)$  for one-electron and  $\Gamma_2^{open}(1,2)$  for two-electron density matrices of the open-shell subsystem. Based on an open-shell part of the well-known Roothaan average energy functional (e. g., see Eq. (1) in [23]) we easily extract the needed formulas for the studied open shell with  $r$  electrons in  $r$  MOs. Clearly,  $\Gamma_1^{open}(1)$  is but the same matrix as in Eq. (15):

$$\Gamma_1^{open}(1) = \rho_O, \quad (19)$$

$\Gamma_2^{open}$  is computed as follows:

$$\Gamma_2^{open}(1,2) = \frac{1}{2}(a - \frac{b}{2} P_{12}^0) \rho_O(1) \rho_O(2) \quad (20)$$

with  $a$  and  $b$  being Roothaan's coupling parameters, and  $P_{12}^0$  the spinless transposition operator. The full (involving all subshells) density matrices, one-electron matrix  $\Gamma_1$ , that is  $P$ , and two-electron  $\Gamma_2$ , are also gotten from the Roothaan energy functional. They are of the form

$$\Gamma_1^{OS-TB} = 2\rho_{cl} + \rho_O, \quad (21)$$

$$\Gamma_2^{OS-TB} = \frac{1}{2}(2 - P_{12}^0)[\rho_{cl}(1)\rho_{cl}(2) + \rho_{cl}(1)\rho_O(2) + \rho_O(1)\rho_{cl}(2)] + \Gamma_2^{open}(1,2). \quad (22)$$

According to [22, 23], in our case the coupling parameters are

$$a = \frac{2s(s+1)/r + r^2 - r/2 - 2}{r^2 - 1},$$

$$b = \frac{4s(s+1) + r^2 - 2r - 2}{r^2 - 1}.$$

Incidentally, we cite a less transparent analysis from [25] where one can find expressions for  $a$  and  $b$  that are actually the same as those in the earlier works [22, 23].

Let us proceed to the applications we present now at the formal level (specific examples will be given later). We turn to the correlation functions (correlators) for charge and spin. Such correlators come, each in its own way, to generalized bond orders and bond indexes, as known long ago [26, 27]. The charge correlators will be con-

sidered first, following [28] where the main pertinent references are given.

Within the adopted  $\pi$ -electron theory, one of the basic is the two-center generalized bond index  $K_{\mu,\nu}^{bond}$ , where  $\mu$  and  $\nu$  are related to the given  $\pi$ -centers of the studied conjugated molecule ( $1 \leq \mu, \nu \leq N$ ). The bond index is defined via matrix elements of the full density matrices  $\Gamma_1$  and  $\Gamma_2$

$$K_{\mu,\nu}^{bond} = -2[\Gamma_2(1,2) - \Gamma_1(1)\Gamma_1(2)]_{\mu\nu,\mu\nu}, \quad (23)$$

where subscript  $\mu\nu$ ,  $\mu\nu$  signifies the diagonal element of the corresponding two-electron matrices. The two-center spin correlator  $K_{\mu,\nu}^{spin}$  can be also computed through the same matrices  $\Gamma_1$  and  $\Gamma_2$  [29]:

$$K_{\mu,\nu}^{spin} = \frac{3}{4}(\Gamma_1)_{\mu\mu}\delta_{\mu\nu} - \frac{1}{2}[(\Gamma_2)_{\mu\nu,\mu\nu} + 2(\Gamma_2)_{\mu\nu,\nu\mu}]. \quad (24)$$

Using Eqs. (21) and (22) we directly find the needed indexes:

$$K_{\mu,\nu}^{bond}[\text{OS-TB}] = 4[|(\rho_{cl})_{\mu\nu}|^2 + |(\rho_{cl})_{\mu\nu}(\rho_O)_{\mu\nu}| + b|(\rho_O)_{\mu\mu}|^2 - 2(a-1)(\rho_O)_{\mu\mu}(\rho_O)_{\nu\nu}], \quad (25)$$

$$K_{\mu,\nu}^{spin}[\text{OS-TB}] = \frac{3}{4}(\Gamma_1^{\text{OS-TB}})_{\mu\mu}\delta_{\mu,\nu} - \frac{1}{2}|(\rho_{cl})_{\mu\nu}|^2 - \frac{3}{2}(\rho_{cl})_{\mu\nu}(\rho_O)_{\mu\nu} - \frac{a-b}{4}(\rho_O)_{\mu\mu}(\rho_O)_{\nu\nu} - \frac{4a-b}{8}|(\rho_O)_{\mu\nu}|^2. \quad (26)$$

The respective QCTB expressions can be written in the form known in the unrestricted Hartree-Fock method ([30], Eq. 5). A more suitable is the working formula:

$$K_{\mu,\nu}^{spin}[\text{QCTB}] = \frac{3}{4}[(\Gamma_1^{\text{QCTB}})_{\mu\mu}\delta_{\mu,\nu} - \frac{1}{2}|(\Gamma_1^{\text{QCTB}})_{\mu\nu}|^2] + \frac{1}{8}[(Q_1^{\text{QCTB}})_{\mu\mu}(Q_1^{\text{QCTB}})_{\nu\nu} + |(Q_1^{\text{QCTB}})_{\mu\nu}|^2], \quad (27)$$

where  $\Gamma_1^{\text{QCTB}} = \rho_\alpha + \rho_\beta$ , and  $Q_1^{\text{QCTB}} = \rho_\alpha - \rho_\beta$ .

## 6. TMB: a case study of $\pi$ -electron singularity

### 6.1 One-electron characteristics

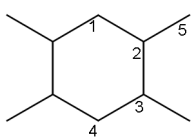
Here we will start the examination of selected singular networks by presenting the case study that demonstrates the possibilities of main approximations, OS-TB, QCTB, and EQC in comparison with the "exact"  $\pi$ -model. By the exact  $\pi$ -model we

mean the full configurational interaction (FCI) description of  $\pi$ -shells treated by the conventional Pariser-Parr-Pople Hamiltonian. The traditional  $\pi$ -parametrization is employed here as in previous our  $\pi$ -electron computations ( $\gamma_{\mu\nu}$  due to Ohno etc.).

To begin with, we present in Table 1 the basic one-electron  $\pi$ -characteristics that are usual bond-orders  $P_{\mu\nu}$  for the nearest neighbor pairs ( $\mu, \nu$ ) in the different models of TMB. We see that all the models are capable to well reproduce the FCI values of chemical  $\pi$ -bond orders. This expresses a well-known ability of  $\pi$ -electron theories to reflect primarily the molecular topology (adjacency) which in some way is incorporated in any correctly defined  $\pi$ -electron Hamiltonian. However, notice that QCTB predicts the  $\pi$ -electron bond-order structure markedly better than OS-TB. In Table 1 we included a long-range bond order,  $P_{1,4}$  because the long-range bond orders are in fact a measure of electron delocalization [31]. We see that even approximate  $P_{1,4}$  values do not deviate significantly from the respective FCI value.

For open-shell systems, particularly important is their characterization by one-electron EUE indexes  $N_U$  and  $\partial_\mu$  defined in section 4. For TMB we find that  $N_U$  takes values 2.0, 2.29 and 2.5 in OS-TB, QCTB and FCI, respectively, and all the values obviously reflect a diradical nature of the singlet ground state of TMB; but QCTB and EQC produces the result more close to the FCI one. The EUE distribution (17) at the OS-TB level is easily found by using Dewar's nonbonding MO method:  $\partial_1 = \partial_5 = 1/3$ ,  $\partial_2 = 0$  (for Dewar's method, see [32]). However, there is fine differences between the OS-TB and rest distributions: in the latter  $\partial_2 \neq 0$ , and  $\partial_1 \neq \partial_5$ . For instance, in FCI we obtain  $\partial_1 = 0.371$ ,  $\partial_5 = 0.376$ , and  $\partial_2 = 0.065$ ; QCTB and EQC give sufficiently close values. In a whole, more than 1/3 of the  $N_U$

Table 1.  $\pi$ -electron bond orders  $P_{\mu\nu}$  in TMB within OS-TB, QCTB, EQC, and FCI

TMB structure	$\mu, \nu$	$P_{\mu\nu}^{\text{OS-TB}}$	$P_{\mu\nu}^{\text{QCTB}}$	$P_{\mu\nu}^{\text{EQC}}$	$P_{\mu\nu}^{\text{FCI}}$
	1,2	0.555	0.546	0.531	0.520
	2,3	0.362	0.372	0.333	0.351
	2,5	0.725	0.695	0.719	0.681
	1,4	-0.185	-0.177	-0.184	-0.172
	1,5	-0.185	-0.177	-0.184	-0.172

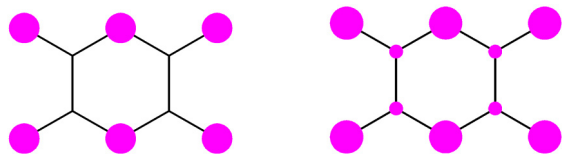


Fig. 1. Distribution of effectively unpaired electrons (in magenta) for the TMB "diradical" within the OS-TB (left) and FCI (right) schemes.

full value can be assigned to the two central atoms of the benzenoid ring. Thus, as seen in Fig. 1, it is difficult to identify TMB with a classical diradical system having two clearly defined radical centers.

### 6.2 Two-electron characteristics

Spin and charge correlators which are described in section 5, provide an additional information for interpreting open-shell structures. The computed data for the TMB selected spin correlators are tabulated in Table 2. The first three lines of this Table show diagonal (local) spin correlators  $K_{\mu\mu}^{spin}$ . According to [33], they are closely related to an ionic valence character  $\iota_{\mu} = 1 - 4K_{\mu\mu}^{spin}/3$  (ionity index) of the given atom in molecule. We have  $K_{\mu\mu}^{spin} = 3/8 = 0.375$  in usual correlation-free  $\pi$ -models of alternants. Then,  $\iota_{\mu} = 0.5$  which is a typical value for MO approximations. Ionity indices tend to be diminished owing to electron correlation effects, and at the QCTB, EQC, and FCI levels it is clearly manifested by all carbon atoms in TMB, particularly by the exocyclic atoms ( $\iota_5$ [FCI]). The effect, however, is too weak at the OS-TB level.

Among the two-center indices, the long-range correlators are firstly interesting. Indeed, for the TMB first-order neighboring (chemically bonded) atoms, typical correlators are negative (antiferromagnetic coupling) whereas  $K_{\mu\nu}^{spin} > 0$  for the second-order neighboring atoms (ferromagnetic coupling); e.g.,  $K_{1,5}^{spin}$ [FCI] = 0.1. More to the point, this electron correlation effect is found to be feeble within OS-TB; besides,  $K_{\mu\nu}^{spin}$ [TB] = 0 for any atomic pair of starred or unstarred atoms.

Now turn to generalized bond indices  $K_{\mu\nu}^{bond}$  (Table 3). Such indexes are also sensitive to accounting for electron correlation effects, as seen from the Table where we observe that the  $K_{1,3}^{bond}$  value becomes even negative at the OS-TB level. We see that the generalized bond indices are described by QS-

Table 2.  $\pi$ -electron spin correlators  $K_{\mu\nu}^{spin}$  for TMB within OS-TB, QCTB, EQC, and FCI

$\mu, \nu$	OS-TB	QCTB	EQC	FCI
1,1	0.361	0.453	0.473	0.513
2,2	0.375	0.390	0.397	0.447
5,5	0.361	0.486	0.478	0.563
1,2	-0.115	-0.135	-0.137	-0.178
1,4	-0.041	-0.064	-0.078	-0.161
2,5	-0.197	-0.209	-0.226	-0.297
1,5	0.014	0.071	0.076	0.101
3,5	0.	0.028	0.032	0.059

Table 3.  $\pi$ -electron bond indexes  $K_{\mu\nu}^{bond}$  for TMB within OS-TB, QCTB, EQC, and FCI

$\mu, \nu$	OS-TB	QCTB	EQC	FCI
1,2	0.309	0.298	0.282	0.271
1,4	0.182	0.031	0.034	0.029
2,3	0.131	0.138	0.111	0.163
2,5	0.525	0.483	0.517	0.392
1,5	-0.037	0.074	0.068	0.038
3,5	0.	0.005	0.002	0.012

TB even worse than spin correlators, whereas for the same quantities the satisfactory results are obtained by QCTB and EQC.

Based on the above obtained generalized bond indexes we can estimate an aromaticity measure of the single benzenoid ring of TMB. In doing so, we use the approach proposed in [34] for quantifying local aromaticity with accounting for cyclic delocalization as well as electron correlation. The respective cyclic aromaticity index (CAI) for 6-rings can be defined as follows:

$$\text{CAI} = \left[ \prod_{a=1}^6 (1 - |\partial_a - \partial_0|) K_a^{bond} / K_0^{bond} \right]^{1/6}, \quad (28)$$

where  $K_a^{bond}$  is the bond index of the  $a$ th CC-bond in the given benzenoid ring, and  $K_0^{bond}$  is the corresponding value for the isolated benzene ring;  $\partial_a$  and  $\partial_0$  are related to the EUE densities of respective carbon atoms ( $\partial_0$  is the EUE reference value for benzene molecule). Unlike [34], in which the squared bond orders (as simplified bond indexes) are employed, we apply now, for each model, the more consistent

Table 4. Singularity rank  $r$  for chain-like structures with antiaromatic motif, and the FCI singlet-triplet energy gap  $\lambda_1^{S \rightarrow T} \equiv \lambda_1^{S \rightarrow T} [u = 1]$  (in eV) for the respective monomer subunits

Chain structure	$r$	$\lambda_1^{S \rightarrow T}$
	$\begin{cases} u+1 \text{ for odd } u \\ u \text{ for even } u \end{cases}$	0.339
	$\begin{cases} u+1 \text{ for odd } u \\ u \text{ for even } u \end{cases}$	0.438
	$\begin{cases} u+1 \text{ for odd } u \\ u \text{ for even } u \end{cases}$	0.306
	$2u$	0.113
	$2u$	0.360

$K_{\mu\nu}^{bond}$  values based on Eq. (23). The computations in all the schemes give a rather low value of the local aromaticity (in %): CAI[FCI] = 48, and CAI[QCTB] = 45, CAI{QS-TB} = 46.

### 7. Chain-like singular $\pi$ -electron networks

Before considering the obtained results, some points concerning singular networks should be outlined. We will use the term "high-order singularity" for alternant  $\pi$ -systems with  $r > 2$  (recall that singularity rank  $r$  is the null space dimension of  $h^{TB}$ ). In the prior works [19, 35], non-Kekulean chain-like structures were mainly treated. Now we consider less trivial chain-like singular alternants of Kekule type (Table 4). Seemingly, most of these polyradicals with an antiaromatic motif were not discussed previously, while the respective monomeric units were explored in many works starting from [36]. Only oligomeric cyclobutadienes (the first class of structures in Table 4) were earlier treated in [37] by the  $\pi$ -electron extended Hartree-Fock method. For completeness, we also give in Table 4 the reference data for singlet-triplet splitting  $\lambda_1^{S \rightarrow T}$  at the  $\pi$ -FCI level; the comparison with

other approaches will be given elsewhere. For all structures in the Table,  $\lambda_1^{S \rightarrow T} > 0$  in concordance with the Lieb-Ovchinnikov rule [38] concerning the ground state spin of bipartite organic  $\pi$ -radicals.

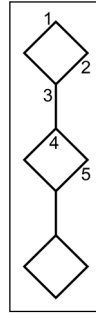
Let us focus here on the ground-state open-shell singlet tetraradical ( $r = 4$ ) of the tri(cyclobutadienyl) molecule ( $u = 3$  for the first structural class in Table 4). For this system we give in Table 5 the computed local squared spin  $K_{\mu\nu}^{spin}$  and local unpairing indexes  $\partial_\mu$ . Looking at the table we see again that the local squared spins are poorly reproduced by OS-TB, whereas the unpairing indexes are reasonably estimated by the same model. For instance, unpairing electrons are primarily localized on the external sites (positions 1, 2, and 5), as the FCI theory supports this to be true. At the same time, the both indexes,  $K_{\mu\nu}^{spin}$  and  $\partial_\mu$ , are satisfactorily predicted by the uncomplicated QCTB scheme.

### 8. Application to one-electron Green's function

Another attractive possibility for applications of  $\pi$ -electron TB models is their use in estimating electrical conductance across molecular junctions [39, 40]. We will follow our recent works [19, 35] where, compared



Table 5. Local squared spin  $K_{\mu\nu}^{spin}$  and local unpairing indexes  $\partial_\mu$  obtained for the  $\pi$ -system of tri(cyclobutadienyl) within OS-TB, QCTB and FCI models



$\mu$	$K_{\mu\mu}^{spin}$			$\partial_\mu$		
	OS-TB	QCTB	FCI	OS-TB	QCTB	FCI
1	0.371	0.440	0.521	0.222	0.254	0.289
2	0.356	0.501	0.561	0.500	0.508	0.528
3	0.371	0.428	0.494	0.222	0.244	0.291
4	0.375	0.399	0.466	0.000	0.042	0.109
5	0.352	0.519	0.566	0.556	0.560	0.586

to TB, more advanced QCTB and half-projected Hartree-Fock  $\pi$ -models were elaborated for these purposes. As known from the theory of single-molecule conductance [39], the Green function (GF) method is a standard tool for solving appropriate problems. Let us denote by  $G_0^{TB}$  the TB approximation of the one-electron retarded Green's function at the Fermi energy  $E_F$ . Then,

$$G_0^{TB} = G_0^{OS-TB} = (i0^+ - h^{TB})^{-1} \quad (29)$$

(in TB with the Hamiltonian (1)  $E_F = 0$ ). As shown in [35], the occurrence of imaginary infinitesimal  $i0^+$  guarantees, in concordance with Sokhotsky's formula, a correct behavior of the GF real part for singular  $h^{TB}$  matrices. Namely, for the singular systems, the GF real part is obtained as a pseudoinverse of  $h^{TB}$  (see Eqs.(12) and (13) in [35]). Computations of GF at the QCTB level are also elementary by Eq. (6) of the same paper:

$$G_0^{QCTB} = \frac{-h^{TB}}{\delta^2 + (h^{TB})^2}. \quad (30)$$

In the Huckel limit  $\delta \rightarrow 0$  we automatically produce the correct result for  $G_0^{TB}$  that is equivalent to using Eq. (29). Likewise, in EQC we have

$$G_0^{EQC} = \frac{-h^{EQC}}{\delta^2 + (h^{EQC})^2}. \quad (31)$$

where  $h^{EQC} = \begin{pmatrix} 0 & B^{EQC} \\ (B^{EQC})^+ & 0 \end{pmatrix}$ . Notice that Eqs. (29)–(31) additionally allow us to use them for systems lacking the bipartite symmetry (e.g., nonalternant hydrocarbons), but their study is beyond of scope of the present paper.

Now we turn to our singular structures, By computing specific examples, we will estimate the accuracy of model Green's matrices

$G_0^{TB}$ ,  $G_0^{QCTB}$ , and  $G_0^{EQC}$ . The results are compared with those of the corresponding "exact" Green's matrix  $G_0^{FCI}$ . We will exploit the following deviation measure,  $s^X$ , of the given  $G_0^X$  from ( $X$  is TB, QCTB or EQC):

$$s^X = \|G_0^X - G_0^{FCI}\|/\sqrt{N} \quad (32)$$

(in fact,  $N$  is equal to the used AO basis size). The results for the first three members of oligomeric cyclobutadienyl (CBD) series are presented in Table 6. As expected, the EQC which accounts for long-range interaction effects, provides the best results for GF. Less satisfactory are the results in QCTB; and more worse are the TB results. As our experience has shown, this observation is typical. Among the  $\pi$ -models we deal with here, EQC seems to be most reliable for large systems. So, we can use EQC for an approximate estimation of inaccuracy of TB and QCTB for large-size structures (Table 7). We observe from the table that QCTB is naturally more accurate than OS-TB; the inaccuracy measures are markedly larger for even members of the oligomeric series (that is for even  $q$ -CBD in Table 7). Analogous results are obtained for other singular-structure series from Table 4.

We will also analyze GF in terms of the GF distance correlators. It should be noted

Table 6. The Green's function deviation  $s^{OS-TB}$ ,  $s^{QCTB}$ , and  $s^{EQC}$  in respect to  $G_0^{FCI}$  for the short CBD molecules

Method	1-CBD	2-CBD	3-CBD
OS-TB	0.109	0.532	0.236
QCTB	0.116	0.265	0.172
EQC	0.025	0.114	0.078

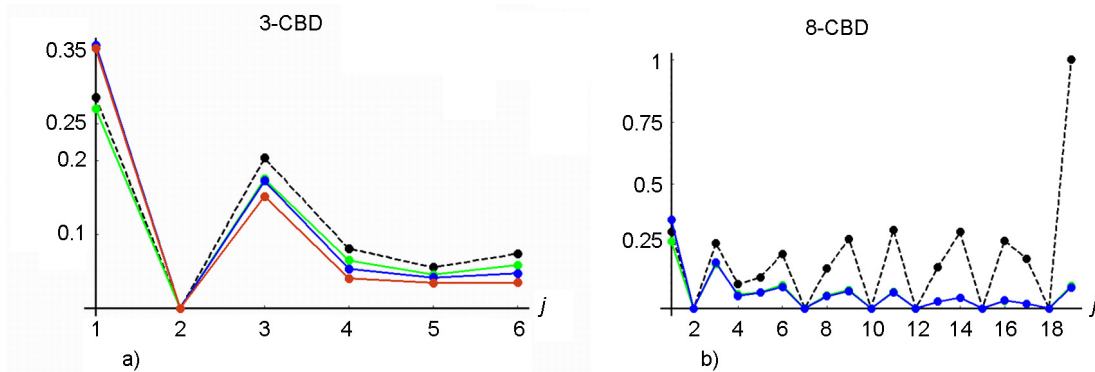


Fig. 2. Distance correlator  $K_j^G$  in 3-CBD at the FCI (red), EQC (blue), QCTB (green), and TB (dashed black) levels, and for 8-CBD at the EQC, QCTB, and TB levels.

that there is a difficult problem about the long-range behavior of GF in conjugated networks. Recently, unusual results are reported concerning the increase of electron transport in long molecular systems treated within TB and density functional models [41–43]. The systematic study of this issue for singular structures will be given elsewhere, and here we present preliminary results and their analysis in terms of the distance correlators defined in [21].

For the given intersite distance  $jL_{CC}$  ( $j$  is an integer, and  $L_{CC}$  is the C=C bond length) we define the GF distance correlator  $K_j^G$  as an average absolute value of the GF matrix elements  $G_{\mu\nu}$  taken for all sites  $\mu$  and  $\nu$  situated from each other at the distance  $jL_{CC}$  (with a small interval window). The computations thus performed give a dependence of  $K_j^G$  as a function of integer  $j$  (i. e., a discrete distance in units of  $L_{CC}$ ). In Fig. 2 we show such dependences for 3-CBD and 8-CBD molecules (in this case, the FCI computation is available only for the short 3-CBD molecule, and the results are also given in Fig. 2, left panel).

The obtained dependencies are rather generic, and similar results are detected for the other structures from Table 4. We see that, if neglecting oscillations, the  $K_j^G$  values at the EQC and QCTB levels tends to diminish with increase of distance  $j$ . At the same time, TB can prescribe a wrong abnormal behavior of GF, as it is the case of 8-CBD on Fig. 2.

Stress that both the discussed systems in Fig. 2 are of high-order singularity with singularity rank  $r = 4$  and  $r = 8$ , respectively. From the viewpoint of the above cited works they should be effective conductors, but it is not the case, as the exact  $\pi$ -model FCI (see the left panel in Fig. 2)

Table 7. The Green’s function deviations,  $s^{QS-TB}$  and  $s^{QCTB}$ , in respect to  $G_0^{EQC}$  for several oligomeric molecules  $q$ -CBD where  $q = 3 \div 9$

$q$	3	4	5	6	7	8	9
OS-TB	0.177	0.760	0.294	1.058	0.422	1.322	0.549
QCTB	0.142	0.170	0.152	0.178	0.154	0.195	0.155

demonstrates this. As to oscillations in these plots, we interpret them as a natural consequence of the known selection rule, valid for GF in bipartite  $\pi$ -networks. According to the general  $\pi$ -electron theorem from [44],  $G_{\mu\nu} = 0$  if both  $\mu$  and  $\nu$  simultaneously belong to starred (or unstarred) sites. So, for certain values of  $j$ , many site pairs ( $\mu, \nu$ ) follow this rule what causes  $K_j^G = 0$  or yields a significant diminution of the resulting  $K_j^G$ .

Recall that according to customary theories of molecular electron transport [39], the GF squared matrix element  $|G_0^X|^2$  ( $X = TB$  etc.) provides, apart from a factor of proportionality, an estimate of zero-bias molecular conductance (at the zero-temperature). Thus, we can conclude that among the used one-electron schemes, EQC yields more reliable results. Concurrently, a preliminary study shows that far from zero-bias point the approximate conductance spectra for polyradicals can show poor results, but further calculations are needed to make a more definite inference.

## 9. Conclusion

In this paper, we have dealt with singular strongly correlated  $\pi$ -electron structures. To simply treat them we have proposed the OS-TB model that consistently extends the conventional Huckel (TB)

$\pi$ -approximation to singlet polyradicals having multiple degenerate frontier MOs. It allowed us, in particular, to incorporate into the analysis of this Huckel-like model the characteristics taken from the theory of effectively unpaired electrons. We compare the OS-TB approach with the previously given QCTB and EQC models, and show a reasonable behavior of the unpaired electron density in OS-TB, as well that of usual one-electron properties of polyradicals.

At the same time, OS-TB gives a poor description of two-electron quantities, e. g., spin correlators. It is also shown that for  $\pi$ -electron Green functions, QCTB and EQC provide clearly better results than OS-TB. Simultaneously, QCTB and EQC are carried out almost as easily as OS-TB is. Therefore, we can conclude that  $\pi$ -electron structure of conjugated polyradicals is recommended to be studied by OS-TB only for elementary one-electron characteristics and related indexes (e.g., aromaticity indexes based on bond orders). More sophisticated problems, particularly those of single-molecule conductance, are beyond the possibilities of TB and OS-TB models. In this relation, the better models, QCTB and especially the very recent approach EQC [21], require further attention and development.

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