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A uniform approach to description of multicenter bonding

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A novel method of investigating the multicenter bonding patterns in molecular systems by means of the so-called Electron Density of Delocalized Bonds (EDDB) is introduced and discussed. The EDDB method combines the concept of Jug's bond-order orbitals and the indirect ("through-bridge") interaction formalism and opens up new opportunities for studying the interplay between different atomic interactions as well as their impact on both local and global resonance stabilization in systems of conjugated bonds. On several illustrative examples we demonstrate that the EDDB approach allows for reliable quantitative description of diverse multicenter delocalization phenomena (with special regard to evaluation of the aromatic stabilization in molecular systems) within the framework of a consistent theoretical paradigm.

1 Introduction

The overwhelming majority of chemical interactions in molecules can be described by a set of well localized two-center two-electron bonds (2c-2e), i.e. standard chemical bonds. Within the framework of the age-old qualitative theory of chemical bonding by Lewis and Langmuir, they represent pairs of electrons shared by two atoms so that each attains the electron configuration of the nearest noble gas ("the octet rule")^{1,2}. The development of quantum-mechanical theories of electronic structure over the decades gave rise to deeper insights into bond forming processes and provided a multitude of sophisticated tools quantifying chemical bonding patterns. One of the most well-known and resoundingly successful is the theory of Molecular Orbitals (MO)³, within which chemical bonds in diatomic species are described by linear combinations of atom-centered functions – Atomic Orbitals (AO). Admittedly, in the general case of polyatomics the molecular orbitals do not refer to well localized 2c-2e bonds anymore being usually delocalized over the whole molecule and reflecting molecular symmetry. Fortunately, in many polyatomic molecules the chemical language connected with the Lewis model can be simply adopted at the level of modern theory by introducing the doubly-occupied Localized Molecular Orbitals (LMO)⁴⁻⁷ or so-called Localized Orbitals of Bond Orders (LOBO)^{8,9}, representing core orbitals (1c-2e), lone pairs (1c-2e) and chemical bonds (2c-2e).

However, many molecules cannot be adequately described

by such localized one- or two-center orbitals and the formalism of multicenter bonding has to be utilized¹⁰⁻¹⁵. In this context, intense investigations are focused on conjugated π bonds in aromatics, chelatoaromatics and all-metal clusters, hypervalent species, boranes, molecular systems with hydrogen/dihydrogen bonds, agostic bonds, planar tetra- and pentacoordinated carbon atoms, etc. The concept of the Generalized Population Analysis (GPA)¹⁶⁻²⁰ has successfully been used to develop the entire panoply of the so-called Electron Sharing Indices (ESI)²³⁻²⁶ congeneric with the Multicenter Indices (MCI)^{21,22}, which depend on the n -order Reduced Density Matrix (n -RDM)²⁷. The MCI approach has turned out to be especially useful in evaluation of multicenter electron delocalization in aromatic species²⁸⁻³³. One should realize, however, that this multicenter descriptor is designed to deal only with local molecular cyclic units of predefined size (which opens the door to some degree of arbitrariness). As such it does not provide a comprehensive tool for description of multicenter bonding in more extended systems. Furthermore, being the RDM-derived quantities, MCIs are related to the many-orbital joint probabilities³⁴⁻⁴⁰ and so they do not correspond directly to simple electron numbers (even though different ways of normalization of MCIs have also been introduced⁴¹). Therefore they cannot take into account the influence of other multicenter interactions, depending on the choice of basis set (especially within the MO-approach involving the classical Mulliken scheme⁴²⁻⁴⁵). They also are subject to interpretative problems e.g. if one compares the degree of delocalization in cyclic units of different size (renormalization allows one to remedy this problem, but it always demands for predetermination of ring size). Moreover, for large and complex molecular systems calculations of MCIs can be difficult and time consuming, especially if extended basis sets are used.

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It has recently been argued⁴⁶ that the three-center chemical interactions are by far the most significant in detecting multicenter electron delocalization in molecular systems. Large number of studies that can be found in literature point at the relatively low importance of higher-order interactions^{47–50} in quantifying multicenter chemical bonds within the language of the population analysis, i.e. using the numbers of electrons. Herein we briefly introduce the original method of multicenter bonding analysis (with special regard to evaluation of the aromatic stabilization in molecular systems) that takes advantage of three-center delocalization⁴⁶ and does not suffer from shortcomings and limitations of the GPA-based methods. The new method is formulated within the framework of molecular orbital theory and, just like other familiar methods, e.g. the Natural Bond Order (NBO)^{7,51,52,54,55} or the Adaptive Natural Density Partitioning (AdNDP)⁵⁶ analysis, it makes use of the age-old concept of the so-called bond order orbitals, originally proposed by Jug⁸. Unlike the already existing formalisms, however, the proposed approach harnesses the power of indirect (“through-bridge”) interaction formalism^{57–62} that considerably simplifies the analysis of multicenter bonding patterns and opens up new opportunities for the investigation of the interplay between different interactions and their impact on resonance stabilization.

Our method is to some extent inspired by the method originally proposed by Bridgeman and Empson⁴⁶. However, contrary to their model which involves colored lines and triangles to describe delocalization, we use a visualization tool directly related to Electron Density (ED). Note that the new approach provides the overall picture of electron delocalization and the detailed description of delocalized electron populations in atomic resolution. It can therefore be used for quick detection of regions of increased aromaticity in very large systems as well as for quantitative studies of electron delocalization, aromatic stabilization, reactivity etc. in selected molecular fragments.

2 Theoretical background

2.1 Bonding electron density

Firstly, let us express the one-electron density of closed-shell molecular systems, $\rho(\mathbf{r})$, by means of basis functions $\{\chi_\mu(\mathbf{r})\}$ and the corresponding one-electron density matrix⁶³ as follows:

$$\rho(\mathbf{r}) = \sum_{\mu,\nu} \chi_\nu^\dagger(\mathbf{r}) D_{\mu,\nu} \chi_\mu(\mathbf{r}), \quad \int \rho(\mathbf{r}) d\mathbf{r} = N. \quad (1)$$

In the basis of well atom-assigned localized orthonormal functions, e.g. Natural Atomic Orbitals (NAO)^{64,65}, one can split the spinless density matrix \mathbf{D} into diagonal and off-diagonal atomic blocks, $\mathbf{D}_{\alpha,\alpha} = \{D_{\mu,\nu} : \mu, \nu \in X_\alpha\}$ and $\mathbf{D}_{\alpha,\beta} = \{D_{\mu,\nu} :$

$\mu \in X_\alpha, \nu \in X_\beta\}$, respectively. Consequently, the overall electron population N can be straightforwardly distributed between all atoms in molecule, $\{X_\alpha\}$,

$$N = \text{tr} \mathbf{D} = \sum_{\alpha} \text{tr} \alpha \mathbf{D} = \sum_{\alpha} \text{tr} \mathbf{D}_{\alpha,\alpha} = \sum_{\alpha} N_{\alpha}. \quad (2)$$

In the case of one-determinant wavefunction the density matrix is duodempotent, i.e. $\mathbf{D} = 2^{1-k} \mathbf{D}^k$ for $k > 1$, which allows one to generalize the population analysis scheme to comprise the whole hierarchy of multicenter electron population indices^{16–20}. One of the most important among them is the Wiberg-type bond covalency index⁶⁶:

$$N_{\alpha\beta} = 2^{-1} \sum_{\mu}^{X_\alpha} \sum_{\nu}^{X_\beta} |D_{\mu,\nu}|^2, \quad (3)$$

directly referring to the concept of chemical bond order^{67–71}, deeply embedded in chemical intuition.

It has originally been pointed out by Jug⁸ that, within representation of minimal basis of atomic orbitals, the bond covalency index (3) can be simply decomposed into σ , π and higher components by solving the following eigenproblem:

$$\mathcal{D}_{\alpha\beta} = \begin{pmatrix} \mathbf{0} & \mathbf{D}_{\alpha,\beta} \\ \mathbf{D}_{\alpha,\beta}^\dagger & \mathbf{0} \end{pmatrix} = \mathcal{C}_{\alpha\beta} \lambda_{\alpha\beta} \mathcal{C}_{\alpha\beta}^\dagger. \quad (4)$$

Indeed, the subset of eigenvectors associated with positive eigenvalues of $\mathcal{D}_{\alpha\beta}$ (denoted by superscript “ b ”) gives rise to the two-center bonding orbitals (2cBO):

$$|\zeta_{\alpha\beta}^b\rangle = |\chi\rangle \mathcal{C}_{\alpha\beta}^b, \quad \text{and} \quad \sum_i (\lambda_{\alpha\beta}^b)_{i,i}^2 \equiv \sum_i N_{\alpha\beta,i} = N_{\alpha\beta}. \quad (5)$$

In the equation (5) matrix $\mathcal{C}_{\alpha\beta}^b$ constitutes an extension of the rectangular matrix $\mathcal{C}_{\alpha\beta}^b$ that expands 2cBOs in the basis of all AOs. Except that Jug’s bonding orbitals are on their own very useful in probing bonding patterns of molecular systems, they can also be used to “reconstruct” the bonding part of one-electron density, $\rho^b(\mathbf{r})$:

$$\rho^b(\mathbf{r}) = \sum_{\mu,\nu} \chi_\nu^\dagger(\mathbf{r}) \mathcal{D}_{\mu,\nu}^b \chi_\mu(\mathbf{r}), \quad \int \rho^b(\mathbf{r}) d\mathbf{r} = N^b. \quad (6)$$

Here, N^b stands for the overall number of electrons delocalized in all chemical bonds in molecule, and the bonding density matrix \mathcal{D}^b is defined as a simple sum of density-matrix layers corresponding to all possible pairs of atoms:

$$\mathcal{D}^b = 2^{-1} \sum_{\alpha} \sum_{\beta \neq \alpha} \mathcal{C}_{\alpha\beta}^b (\lambda_{\alpha\beta}^b)^2 \mathcal{C}_{\alpha\beta}^{b\dagger}. \quad (7)$$

Obviously, it follows directly from normalization condition in (6) that $\text{tr} \mathcal{D}^b = N^b$ as well as $\text{tr} \alpha \mathcal{D}^b = N_\alpha^b$ (in literature N_α^b is usually referred as a chemical valence of atom X_α).

2.2 Electron density of delocalized bonds

It has recently been argued⁷² that an eigenproblem analogous to (4) can be formulated for atomic-block off-diagonal density matrices representing indirect interactions of type $X_\alpha-X_\beta-X_\gamma$:

$$\mathcal{D}_{\alpha\beta\gamma} = \begin{pmatrix} \mathbf{0} & \mathbf{D}_{\alpha,\beta} & \mathbf{0} \\ \mathbf{D}_{\alpha,\beta}^\dagger & \mathbf{0} & \mathbf{D}_{\beta,\gamma} \\ \mathbf{0} & \mathbf{D}_{\beta,\gamma}^\dagger & \mathbf{0} \end{pmatrix} = \mathcal{C}_{\alpha\beta\gamma} \lambda_{\alpha\beta\gamma} \mathcal{C}_{\alpha\beta\gamma}^\dagger \quad (8)$$

The corresponding subset of three-center bonding orbitals (3cBO), $|\zeta_{\alpha\beta\gamma}^b\rangle = |\chi\rangle \mathcal{C}_{\alpha\beta\gamma}^b$ is crucial for determining the multicenter delocalized electron density. Without going into details described in our previous paper⁷², it should be noted that the projection of 3cBOs onto the set of orthogonalized 2cBOs, $|\tilde{\zeta}_2^b\rangle \equiv (|\tilde{\zeta}_{\alpha\beta}^b\rangle, |\tilde{\zeta}_{\beta\gamma}^b\rangle)$, followed by the procedure of canceling of non-bonding and mutually phase-reversed 3cBOs, allows one to transform $\lambda_{\alpha\beta\gamma}^b$ into a diagonal matrix collecting numbers of electrons delocalized in a 3-center sense, $\lambda_{\alpha\beta\gamma}^d$. Furthermore, for any particular triatomic sequence of conjugated bonds, $X_\alpha-X_\beta-X_\gamma$, the number of electrons delocalized "through" atom X_β can be calculated straightforwardly as follows:

$$N_{\beta|\alpha\beta\gamma}^d = 2^{-1} \text{tr}(\lambda_{\alpha\beta\gamma}^d)^2 = \text{tr}_\beta[\mathcal{C}_{\alpha\beta\gamma}^b (\lambda_{\alpha\beta\gamma}^d)^2 \mathcal{C}_{\alpha\beta\gamma}^{b\dagger}] \quad (9)$$

For our purposes it is of special interest to evaluate to what degree electrons assigned to the chemical bond $X_\alpha-X_\beta$ participate in the overall delocalized electron population of 3cBOs corresponding to both subsystems of conjugated bonds, $X_\alpha-X_\beta-X_\gamma$ and $X_\gamma-X_\alpha-X_\beta$. The simplest way to get this information is to involve direct projections of 3cBOs onto the subset of orthogonalized 2cBOs corresponding to $X_\alpha-X_\beta$ as follows:

$$N_{\alpha\beta|\alpha\beta\gamma}^d = \sum_i N_{\alpha\beta,i|\alpha\beta\gamma}^d = \sum_{i,k} \left| \langle \tilde{\zeta}_{\alpha\beta,i}^b | \zeta_{\alpha\beta\gamma,k}^b \rangle \right|^2 (\lambda_{\alpha\beta\gamma}^d)_{k,k}^2, \quad (10)$$

and

$$N_{\alpha\beta|\gamma\alpha\beta}^d = \sum_i N_{\alpha\beta,i|\gamma\alpha\beta}^d = \sum_{i,k} \left| \langle \tilde{\zeta}_{\alpha\beta,i}^b | \zeta_{\gamma\alpha\beta,k}^b \rangle \right|^2 (\lambda_{\gamma\alpha\beta}^d)_{k,k}^2, \quad (11)$$

where $N_{\alpha\beta,i|\alpha\beta\gamma}^d$ and $N_{\alpha\beta,i|\gamma\alpha\beta}^d$ stand for the populations of electrons originally assigned to i th 2cBO of the bond $X_\alpha-X_\beta$ and delocalized through the corresponding atomic triplets. Obviously, electron populations from preceding equations take different values depending on the choice of atom X_γ . Therefore, to evaluate the electron population of i th 2cBO that is effectively delocalized in a three-center sense, $N_{\alpha\beta,i}^d$, it is necessary to calculate orbital populations (10–11) for each possible choice of atom X_γ covalently bonded with atom X_α

or X_β (i.e. $\gamma \neq \alpha, \beta$ and $N_{\alpha\gamma}, N_{\beta\gamma} \geq \tau^b$, where τ^b is an arbitrary threshold value). Then, we can define $N_{\alpha\beta,i}^d$ as follows:

$$N_{\alpha\beta,i}^d = \max\{N_{\alpha\beta,i|\alpha\beta\gamma}^d, N_{\alpha\beta,i|\gamma\alpha\beta}^d : \gamma \neq \alpha, \beta\}. \quad (12)$$

Thus, one can interpret $N_{\alpha\beta,i}^d$ as the highest number of electrons of bonding orbital $|\zeta_{\alpha\beta,i}^b\rangle$ that effectively participate in a three-center bonding with all other atoms in molecule. Finally, making use of equations (6–11) we can define the *Electron Density of Delocalized Bonds* (EDDB) as

$$\text{EDDB} \equiv \rho^d(\mathbf{r}) = \sum_{\mu,\nu} \chi_\nu^\dagger(\mathbf{r}) \mathcal{D}_{\mu,\nu}^d \chi_\mu(\mathbf{r}), \quad (13)$$

with the following normalization condition:

$$\int \rho^d(\mathbf{r}) d\mathbf{r} = \sum_\alpha \text{tr}_\alpha \mathcal{D}^d = \sum_\alpha N_\alpha^d = N^d. \quad (14)$$

The EDDB matrix used in above equations takes the following form:

$$\mathcal{D}^d = 2^{-1} \sum_\alpha \sum_{\beta \neq \alpha} \mathcal{B}_{\alpha\beta}^d, \quad \mathcal{B}_{\alpha\beta}^d = \mathcal{C}_{\alpha\beta}^b (\lambda_{\alpha\beta}^d)^2 \mathcal{C}_{\alpha\beta}^{b\dagger}, \quad (15)$$

where

$$\lambda_{\alpha\beta}^d = \{(N_{\alpha\beta,i}^d)^{1/2} \delta_{i,j}\}. \quad (16)$$

The $\mathcal{B}_{\alpha\beta}^d$ matrix describes this part of the electron density of the chemical bond $X_\alpha-X_\beta$ that is delocalized in a multicenter sense with all other bonds in molecular system. Thus, one can regard the EDDB matrix as assembled from density layers relating to all possible diatomic interactions in the molecule under consideration.

What should be noticed is that, in the case of planar molecules/molecular fragments, the EDDB can also be strictly dissected into the "in-plane" and "out-of-plane" EDDB-layers or the density layers corresponding to respective symmetry components,

$$\text{EDDB} = \text{EDDB}_\sigma + \text{EDDB}_\pi + \dots, \quad (17)$$

by solving the corresponding eigenproblem of the density matrix (15). Strict separation of the symmetry components σ and π of the EDDB follows mainly from the facts that degeneration within the spectrum of eigenvalues of the EDDB matrix practically never occurs (in contrast to the ED matrix). It has to be stressed, however, that the exact separation of higher symmetry components may be not always possible (e.g., a dissection of σ and δ bonding contributions is not necessarily possible in an exact way⁵³).

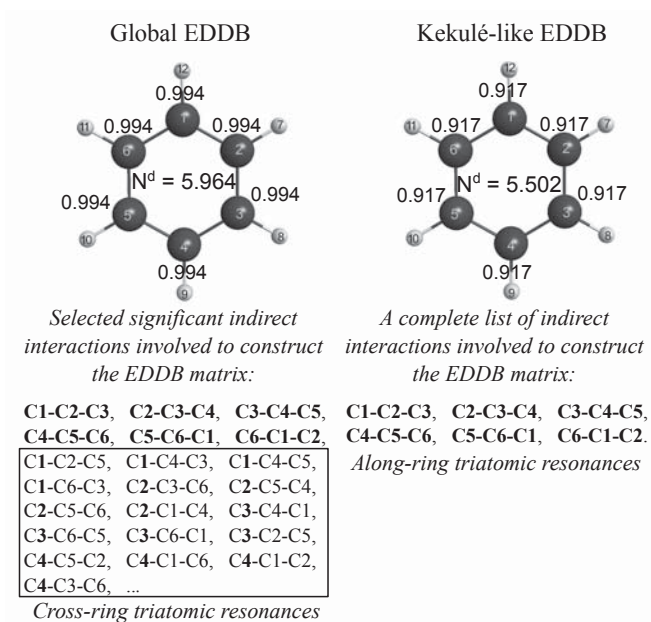


Fig. 1 Global and local ("Kekuléan") EDDB-populations N^d and N_C^d (alongside atoms); contributions from hydrogen atoms are neglected. Method: B3LYP/6-31G*/NAO, equilibrium geometry.

2.3 Global and local character of EDDB-populations

First we would like to stress that the outlined scheme of the EDDB construction is far more efficient than "multicenter scanning" techniques available in other formalisms⁵⁴⁻⁵⁶, especially in the case of highly accurate wavefunctions of large-size molecular systems. In our method the multicenter bonding density is reconstructed by means of two-atomic fragments and regards only local resonance triatomic hybrids, $X_\alpha-X_\beta-X_\gamma$ and $X_\gamma-X_\alpha-X_\beta$, representing the corresponding indirect interactions ("X $_\alpha$ with X $_\gamma$ through X $_\beta$ " and "X $_\gamma$ with X $_\beta$ through X $_\alpha$ ", respectively).

It should be emphasized that the use of such indirect interaction formalism allows one to investigate the influence of particular chemical interactions and their mutual coupling on the effectiveness of multicenter bonding in particular molecular fragment by "enabling" or "disabling" the appropriate subspace of interacting atoms X $_\gamma$ for each two-atomic density layer. Therefore, beyond a routine study of multicenter bonds and aromatic stabilization, the EDDB method provides precise and valuable information about the coupling between two adjacent rings in polycyclic aromatics, the impact of cross-ring interactions on the effectiveness of along-ring multicenter delocalization, etc. The latter is clearly illustrated in Figure 1 with the benzene molecule used as an example. Even a cursory look at global (including delocalized electron contributions from all possible triatomic resonance hybrids)

and Kekulé-like EDDB-populations allows one to draw the conclusion that local resonances between cross-ring interactions (mainly Dewar's *para* carbon-carbon bonds) and along-ring carbon-carbon bonds contribute noticeably to the global EDDB (up to 8% of the overall delocalized electron population assigned to carbon atoms). Therefore their influence on the electron delocalization within such a 6-member molecular cyclic unit should not be neglected, especially in accurate calculations. Indeed, it is well known that the cross-ring interactions are more important in benzenoid-like units in which the *para*-delocalization effect was the basis of methods such as the PDI^{28,73-75}.

3 Several illustrative examples

To demonstrate the performance of the EDDB approach, several illustrative examples are presented and briefly discussed. All the *ab initio* calculations were performed using Gamess^{76,77} and Gaussian⁷⁸ packages at the DFT level with the B3LYP/CAM-B3LYP⁸⁷⁻⁸⁹ exchange-correlation functional as well as two correlation-consistent basis sets: cc-pVDZ and aug-cc-pVTZ⁹⁰. All electron population descriptors introduced in the text were calculated within the NAO-representation^{64,65} obtained from the NBO6 software⁹¹ by means of several computer scripts originally developed by the first author; ED and EDDB contour maps were obtained using visualization programs Molden⁷⁹ and MacMolPlt⁸⁰ with a number of manually prepared special input files.

It has to be emphasized that the use of the representation of natural atomic orbitals is crucial for the EDDB-based population analysis since the NAO-based populations automatically satisfy Pauli constraints. Furthermore, the stability of the weighted orthogonalization procedure used in the construction of NAOs^{65,81,82} automatically insures appropriate convergence profiles and numerical stability of atomic charges and bond orders with respect to basis set enlargement^{64,65,83}. This contrasts sharply with electron populations and the corresponding multicenter indices obtained within the framework of Mulliken's population analysis scheme, which are known to exhibit unphysical negative values and numerical instabilities when the extended basis sets are used⁸⁴⁻⁸⁶.

3.1 Simple aromatic hydrocarbons

Figure 2 presents isosurfaces of ED and EDDB with the corresponding electron populations, global (black numbers) and the Kekulé-like (bold burgundy numbers), for the following simple aromatic hydrocarbons (AH): cyclopropenyl cation (C₃H₃⁺), cyclobutadienyl dication (C₄H₄²⁺), cyclopentadienyl anion (C₅H₅⁻), benzene (C₆H₆) and cycloheptatrienyl cation (C₇H₇⁺); the calculations were performed at the CAM-B3LYP/aug-cc-pVTZ/NAO theory level and at $\tau_b = 0.001$

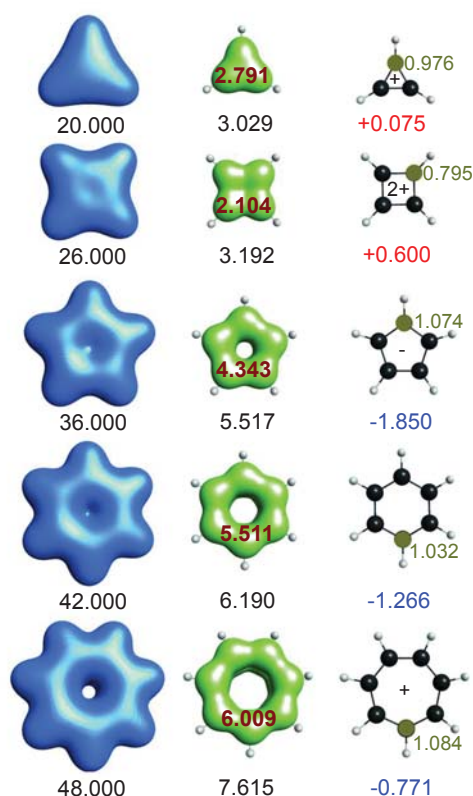


Fig. 2 Isosurfaces of ED (blue) and EDDB (green), generated at $\tau_b = 0.001$ (bonding threshold) and $\tau_p = 0.015$ (isosurface values), with the corresponding electron populations N^d (second column), global (black numbers) and the Kekulé-like (bold burgundy numbers), populations N_C^d (colored numbers alongside atoms) and natural atomic charges (colored numbers below molecule) for several simple AHs. Method: CAM-B3LYP/aug-cc-pVTZ/NAO, equilibrium geometries.

(bonding threshold) and $\tau_p = 0.015$ (isosurface values). In the last column formal charges of ions (inscribed in molecular rings), total natural atomic charges of all carbon atoms as well as atomic populations of delocalized electrons obtained from equation (14) are displayed. It should be noticed that, in contrast to the example presented in Figure 1, in Figures 2,3 and 5 the sum of all EDDB populations assigned to carbon atoms slightly differs from total EDDB populations reported below each structure. This is mainly due to very minor but noticeable contribution of hydrogen atoms to multicenter bonding (usually 0.01 – 0.03e per atom).

It is evident even from a cursory analysis of numbers in Figure 2 that, to a greater or lesser extent, populations N^d differ from the expected Hückel's numbers: "2" for C3H3+, C4H4+ and "6" for C5H5-, C6H6, C7H7+. Essentially, there are three reasons for these discrepancies: (1) N^d counts for

electrons from both, π - as well as σ -delocalization, (2) the cross-ring interactions between carbon atoms and (3) C–H bonds of charged AHs are much more polarized revealing tendency to somewhat overgenerous accumulation of electrons on carbon atoms (it follows directly from comparison of total atomic charges of all carbon atoms and formal charges of molecules in Figure 2). A more detailed discussion of these points can be found in our previous paper⁷². It is worth noticing that, as follows directly from analysis of along-ring EDDB-populations (bold burgundy numbers inscribed in cyclic structures), resonances between along-ring (Kekulé-like) and cross-ring (Dewar-like) atomic interactions are particularly important in charged aromatic hydrocarbons. Preliminary results of more insightful analysis indicate that, contrary to the *para*- π -delocalization effect observed in the benzene molecule, in other charged AHs also the *meta*- π -delocalization as well as σ -delocalizations (including even hydrogen atoms) play an important role.

3.2 Polycyclic aromatic hydrocarbons

Isosurfaces of EDDB, $EDDB_\pi$ and ED_π with the corresponding electron populations for selected polycyclic aromatic hydrocarbons (Figures 3 and 4) were calculated using the B3LYP/cc-pVDZ/NAO method (equilibrium geometries) at $\tau_b = 0.001$ and $\tau_p = 0.015$. Black numbers denote global populations while bold burgundy numbers refer to populations of electrons delocalized only along each cyclic unit. Second columns presents atomic populations N_α^d (colored numbers near atoms); resonance energies (Figure 4) for ED_π were calculated at the Hückel Molecular Orbital (HMO) theory level^{92–95}.

Figure 3 clearly shows that in several cases even qualitative analysis of EDDB contours enables one to predict the relative aromatic stabilization of respective cyclic units that is in agreement with the common knowledge about the reactivity of these species. In particular, it is evident from comparing $EDDB$ s and the corresponding global populations for anthracene and phenanthrene molecules that multicenter electron delocalization is more effective by about 0.5e in the latter one. Accordingly, resonance energies (Figure 4a) for these molecules are 3.60eV and 3.95eV, respectively. Quantitative analysis of EDDB-based populations of electrons delocalized only along each cyclic unit (bold burgundy numbers) leads to the conclusion that the most highly resonance-stabilized rings are: the middle one in anthracene and two side rings in phenanthrene. In-depth study reveals that 8 atoms in the anthracene terminal rings and 2 atoms in the phenanthrene middle ring have significantly lower values of N_α^d , which means that their contributions to multicenter bonding in both molecules are of minor importance. Consequently, in the anthracene molecule the electrophilic aromatic substitution usually involves only the

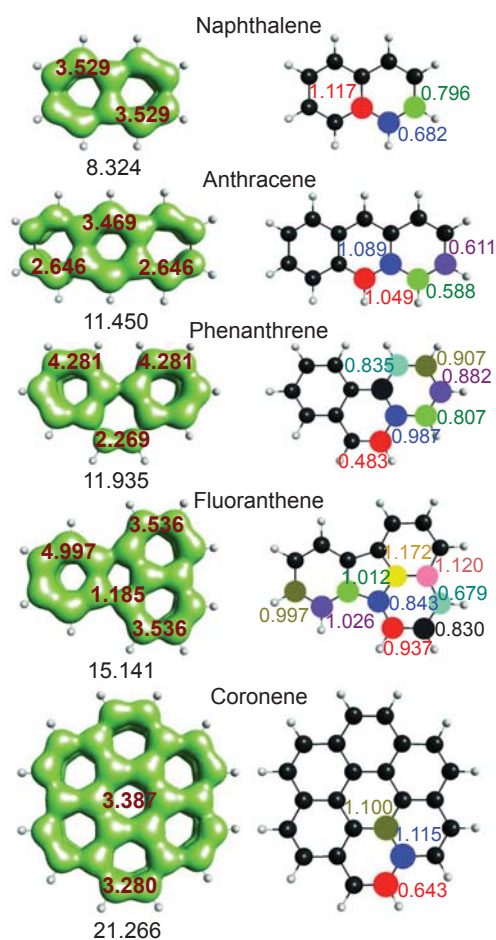


Fig. 3 Isosurfaces of EDDB, generated at $\tau_b = 0.001$ (bonding threshold) and $\tau_p = 0.015$ (isosurface values), with the corresponding electron populations N^d (first column), global (black numbers) and the Kekulé-like (bold burgundy numbers), populations N_C^d (second column) for several simple PAHs. Method: B3LYP/cc-pVDZ/NAO, equilibrium geometries.

inner ring (two equivalent atoms with $N_\alpha^d = 1.049$) while in the phenanthrene molecule it prefers four atoms of outer rings (with $N_\alpha^d = 0.882$ and $N_\alpha^d = 0.907$). However, it should be stressed that, in general, local aromaticity is not simply related to reactivity since the effectiveness of delocalization in a particular molecular fragment says nothing about the HOMO-LUMO gap or the stability of the transition state (e.g., the Diels-Alder reactions always take place in the central ring of anthracene molecule in spite of fact that it is more resonance-stabilized cyclic unit than the terminal benzenoids). Nevertheless, the relative aromaticity of the central and external rings in anthracene is still a matter of controversy in literature⁹⁶.

Another important conclusion can be drawn from the anal-

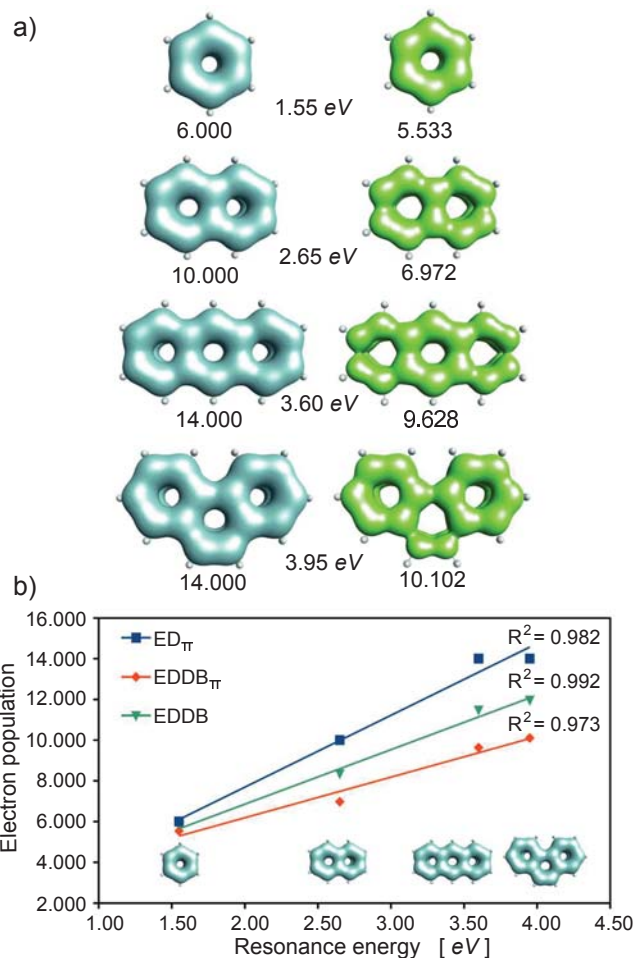


Fig. 4 a) Isosurfaces of ED_π (left column) and $EDDB_\pi$, generated at $\tau_b = 0.001$ (bonding threshold) and $\tau_p = 0.010$ (isosurface values), with the corresponding electron populations N^π and $N^{d,\pi}$ and the HMO resonance energies for benzene and several small PAHs. b) Correlations between resonance energies and the overall populations N^π (ED_π), $N^{d,\pi}$ ($EDDB_\pi$) and N^d ($EDDB$). Method: B3LYP/cc-pVDZ/NAO, equilibrium geometries.

ysis of the EDDB and the corresponding population numbers referring to electrons delocalized along particular ring (bold burgundy numbers) in the case of fluoranthene molecule (Figure 3). As follows from these numbers, only the benzenoid-like cyclic units are found to be aromatic, and, what is more important, the whole molecule can be regarded as built up from the naphthalene unit ($3.536e$ per ring compared to $3.529e$ per ring in a separate naphthalene molecule) being cross-linked to the benzene unit ($4.997e$ compared to $5.295e$ in a separate benzene molecule). Indeed, it is well-known that application of the Hückel rules sometimes leads to the conclusion that particular polycyclic compounds (e.g. fluoranthene or pyrene) should be anti-aromatic, which disagrees with their

known chemical properties. The examination of such PAHs as conjugated cyclic polyenes which are internally cross-linked and/or linked to other cyclic polyenes was historically the first commonly accepted solution for this problem⁹⁷.

An insightful investigation of possible resonance structures of the coronene molecule indicates that, according to the well-known Clar's rule^{98,99}, the center benzenoid is less aromatic than external rings. This evidently contradicts the delocalization pattern that follows from the EDDB-based population analysis; the latter accords to some extent with the picture of coronene proposed by Popov et al¹⁰⁰. As a matter of fact, analysis of EDDBs of all PAHs larger than naphthalene allows for the conclusion that the Clar's rule is fulfilled only for species having a single unambiguous Clar structure (the same conclusion has been drawn previously by G. Portella et al.¹⁰¹). Moreover, it follows from a comprehensive analysis of larger group of PAHs that at the level of Hückel MO method local aromaticities of overwhelming majority of species satisfy the Clar's rule regardless of the number of equivalent Clar structures per each molecule^{22,101}. One should realize, however, that the HMO method is only a crude approximation that assumes the same idealized geometries for benzenoids and does not take into account any σ -delocalizations. This, in our opinion, is more than enough to cast doubt on the relative resonance stability of cyclic units in coronene predicted by the Clar's rule.

Note that qualitative analysis of the π -layer of electron density (1), ED_{π} , must not necessarily lead to the same conclusions as the analysis of $EDDB_{\pi}$ itself. Comparison of ED_{π} and $EDDB_{\pi}$ contours for several simple aromatic hydrocarbons (Figure 4a) shows that not the entire π -electron population is delocalized along aromatic rings, as one might expect. In fact, the effectiveness of π -delocalization varies between 70% (PAHs) and 92% (benzene). It should be stressed here that this result has been obtained from the first principles and is free from any arbitrariness and references to any idealized system. Moreover, as follows directly from analysis of π -electron populations and their correlations with the corresponding resonance energies (Figure 4b), the ED_{π} -populations fail in predicting of relative aromatic stabilization of iso- π -electronic systems and only the EDDB- and $EDDB_{\pi}$ -populations are able to reliably evaluate global aromaticity of all molecules.

3.3 δ -aromaticity and atypical aromatics

Multicenter delocalized electron density contours and the corresponding atomic populations can be very helpful in probing molecular systems with electron delocalization involving d-block transition metals. Figure 5 presents populations and isosurfaces of EDDBs for porphine dianion (Por^{2-}), cobalt(II) porphine complex (Co-Por) as well as maltol complexes with vanadyl dication ($\text{VO}(\text{Ma})_2$) and aluminium ($\text{Al}(\text{Ma})_3$). Cal-

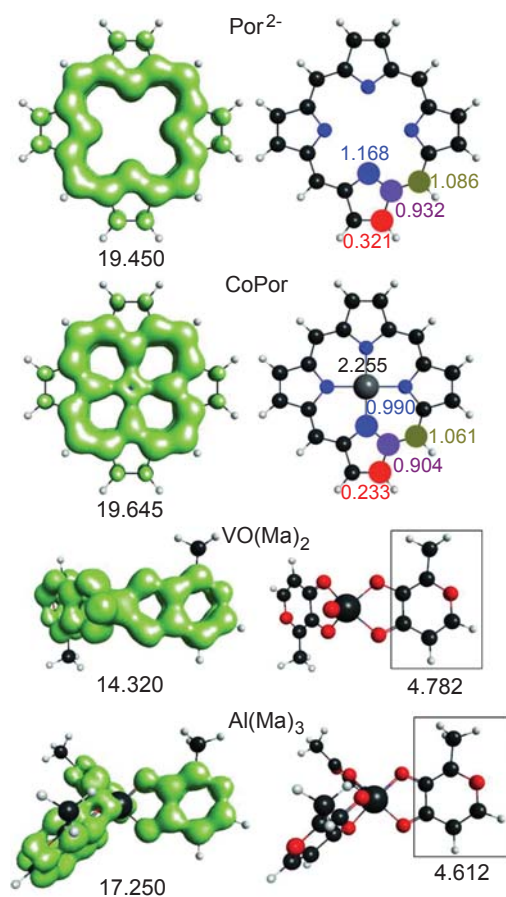


Fig. 5 Isosurfaces of EDDB, generated at $\tau_b = 0.001$ (bonding threshold) and $\tau_p = 0.015$ (isosurface values), with the corresponding electron populations N^d (first column) and constituent atomic/fragment populations (second column) for porphine dianion, cobalt(II) porphine complex, vanadyl(IV) and aluminium maltol complexes. Method: B3LYP/cc-pVDZ/NAO, equilibrium geometries.

culations were performed using the B3LYP/cc-pVDZ/NAO method (equilibrium geometries) at $\tau_b = 0.001$ and $\tau_p = 0.015$; the last column presents atomic populations N_{α}^d or the total number of electrons delocalized over particular molecular fragment. Comparing porphine with its cobalt complex it is clear that the central atom participates in electron delocalization. Quantitative analysis exhibits some outflow of delocalized electron population from the ring due to the presence of cobalt atom (bridging character of the central atom). This back-donation arises only within systems with d-electron central atoms. For the next two examples in Figure 5, $\text{VO}(\text{Ma})_2$ and $\text{Al}(\text{Ma})_3$, the total number of electrons delocalized over the maltol unit is greater in the former case for about $0.2e$, which is in agreement with the well-known facts about the

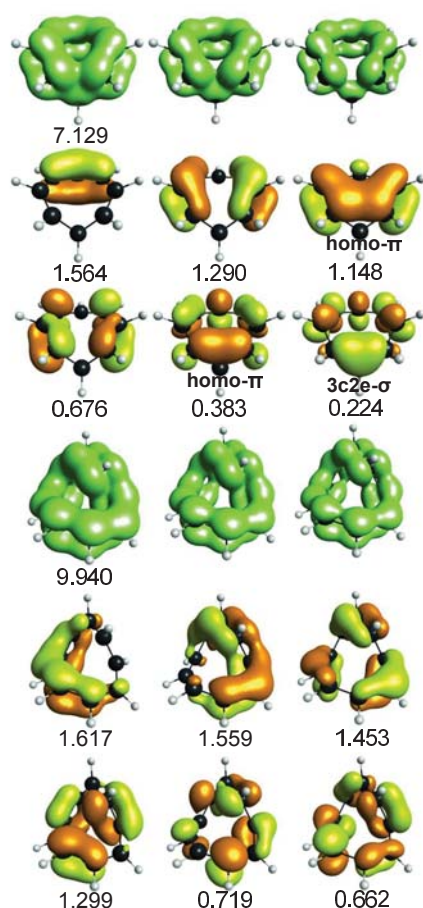


Fig. 6 Isosurfaces of EDDB, generated at $\tau_b = 0.001$ (bonding threshold) and three different isosurface values, $\tau_p = 0.010, 0.015, 0.020$, respectively, with the corresponding electron populations N^d for homotropylium cation and cyclononatetraenyl cation. Additionally, the most highly occupied EDDB-derived natural orbitals (generated at $\tau_b = 0.001$ and $\tau_p = 0.015$) and the corresponding occupation numbers are displayed. Method: B3LYP/cc-pVDZ/NAO, equilibrium geometries.

resonance stabilization of maltol in its chelatoaromatic complexes^{102,103}.

Sometimes, especially in the case of non-planar and atypical aromatic molecules, natural orbitals that diagonalize the EDDB matrix can give additional insight into the electronic structure of the studied systems. Figure 6 shows isosurfaces of EDDB, calculated using the B3LYP/cc-pVDZ/NAO method (equilibrium geometries) at three different values of density, $\tau_p = 0.010, 0.015, 0.020$, with the corresponding electron populations for homotropylium cation and cyclononatetraenyl cation. Additionally, the most highly occupied natural

orbitals of EDDB matrix selected for both structures are presented ($\tau_b = 0.001$ and $\tau_p = 0.015$). The analysis of eigenvectors and eigenvalues of the EDDB matrix for homotropylium cation indicates that, beside the evident π -homoconjugation, some residual σ -delocalization through the methylene carbon atom exists; this is a new result that might have important implications for the origins of homoaromatic stabilization effects¹⁰⁴. In turn, solving the eigenproblem of the EDDB matrix for cyclononatetraenyl cation gives rise to the well-known Möbius-like orbitals¹⁰⁵.

4 Conclusions

To summarize, there are several important features that set the newly proposed method apart from other measures of multicenter delocalization in aromatic rings. (1) Universality – the EDDB-based populations can be easily calculated for planar and non-planar molecular rings and therefore they can be successfully used for study of a wide range of aromatic species including both the Hückel- and Möbius-type aromatics¹⁰⁶, homoaromatics¹⁰⁴ and even non-cyclic aromatic molecules¹⁰⁷. (2) Intuitiveness and interpretative simplicity – quantifying multicenter bonds involves the language of the first-order population analysis. (3) Lack of arbitrariness connected with the necessity of predefining the size of molecular cyclic units (like in the MCI-based techniques) when constructing the EDDB. (4) Ability for strict separation of σ and π components of multicenter delocalization and investigation of their mutual interplay. (5) Local, semi-local or global character of the populations of multicenter delocalized electrons, depending on the strategy of the EDDB matrix construction.

The main purpose of this paper was to introduce the new theoretical approach, describe computational details and briefly demonstrate its performance on several representative aromatic species. A comprehensive comparison of EDDB-based delocalization descriptors with a multitude of aromatic stabilization measures based on structural, thermodynamic and magnetic criteria of aromaticity has already been performed and the corresponding paper is currently under preparation. The examples presented in this work show that the electron density of delocalized bonds is a powerful tool in searching and probing electron delocalization in systems of conjugated chemical bonds.

The EDDB definition introduced in this paper involves the spin-less density matrix and as such it is appropriate for both closed- and open-shell one-determinant wavefunctions. On the basis of several previous investigations^{18,39,71}, in the nearest future we plan to generalize the method to cover also multi-determinant wavefunctions of both, ground- and excited-state molecular systems.

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