



## A new perspective on quantifying electron localization and delocalization in molecular systems



Dariusz W. Szczepanik\*

K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Ingerdena 3, 30-060 Cracow, Poland

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### ABSTRACT

The original method of electron density partitioning is introduced that allows one to probe electron localization and delocalization within one theoretical paradigm. The newly proposed method makes use of the age-old concept of bond-order orbitals as well as the recently developed bond-orbital projection formalism to decompose the one-electron density into density layers representing electrons localized on atoms (inner shells, lone pairs), shared between atoms (chemical bonds) and delocalized between adjacent bonds (multi-center bonding). The details of the current implementation are briefly discussed and several illustrative examples are provided.

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Our understanding of the chemical structure and reactivity is usually built up from and dependent upon such intuitive concepts as atom in molecule, chemical bond, lone pair, Lewis structure, bond covalency and ionicity, etc. [1,2]. Although the semantics of these fundamental entities is not sharply defined in modern quantum mechanics, a multitude of different formalisms has been proposed in the literature either to determine them as functions of the electron density (ED), like within the framework of the quantum theory of atoms in molecules (QTAIM) [3,4], or provide them a localized-orbital representation, like the natural bond orbital (NBO) approach does [5]. Despite great popularity and success, both these approaches have certain drawbacks that sometimes may cut back their applicability, eg. the shortcomings regarding criteria for the chemical bond to exist [6], extremely high computational cost of the localized-orbital description for large molecules with multi-center bonding, and many others. In this paper, for the first time these two methodologies are unified to provide a scheme for the exact decomposition of the one-electron density into the density layers representing electrons well-localized on atoms (EDLA), like core electrons, lone pairs and ionic bonds, and the electrons delocalized between all atoms in a molecule, (EDDA), ie. covalent bonds,

$$ED(r) = EDLA(r) + EDDA(r). \quad (1)$$

The definition of the EDDA(*r*) component is crucial for the entire method. In contrary to other approaches regarding the electron density/population distributions within physical space [7–9], here we use the Hilbert-space partitioning scheme based on the one-electron density matrix, **D**, within the basis of the natural atomic orbitals (NAO) [10],  $\{\chi_{\mu}(\mathbf{r})\}$ , but any other set of orthonormal and still well atom-assigned functions can also be used [11,12]. Here, it has to be noticed that the presented formalism is restricted to one-determinant wave functions only and thus it can be used at HF and DFT theory levels (bear in mind, however, that the Kohn–Sham determinant relies on the auxiliary set of orbitals representing non-interacting electrons and as such it provides only an approximation to the first order density matrix). The definitions given in the text are correct for closed-shell systems. The spin-resolved calculations for open-shell systems should be carried out separately for both  $\alpha$ - and  $\beta$ -spin density matrices and then, in accordance with the Gopinatham-Jug definition of the bond-covalency index [13], the resulting sum of spin-components needs to be multiplied by 2.

The construction of the EDDA(*r*) function requires solving a set of the eigenproblems for all possible Jug's matrices in the molecular system [14]. The classical Jug's matrix is determined by the off-diagonal ( $\alpha, \beta$ )-diatomic blocks of the one-electron density matrix  $\{\mathbf{D}_{\alpha\beta}\}$  [15],

$$\begin{pmatrix} \mathbf{0} & \mathbf{D}_{\alpha,\beta} \\ \mathbf{D}_{\alpha,\beta}^{\dagger} & \mathbf{0} \end{pmatrix} = \mathbf{C}_{\alpha\beta} \boldsymbol{\lambda}_{\alpha\beta} \mathbf{C}_{\alpha\beta}^{\dagger} \rightarrow |\zeta_{\alpha\beta}\rangle = |\boldsymbol{\chi}\rangle \mathbf{C}_{\alpha\beta}, \quad (2)$$

\* Tel.: +48 12 663 20 25.

E-mail address: [szczepad@chemia.uj.edu.pl](mailto:szczepad@chemia.uj.edu.pl)

URL: <http://www.chemia.uj.edu.pl/~szczepad>

and its spectrum contains positive ( $\{\lambda_{\alpha\beta}^b\}$ ), zero ( $\{\lambda_{\alpha\beta}^n\}$ ) and negative eigenvalues ( $\{\lambda_{\alpha\beta}^a\}$ ), associated with the corresponding eigenvectors representing bonding ( $\{|\zeta_{\alpha\beta}^b\rangle\}$ ), non-bonding ( $\{|\zeta_{\alpha\beta}^n\rangle\}$ ) and anti-bonding ( $\{|\zeta_{\alpha\beta}^a\rangle\}$ ) two-center bond orbitals (2cBO), respectively, i.e.

$$\lambda_{\alpha\beta} = \left( \lambda_{\alpha\beta}^b | \lambda_{\alpha\beta}^n | \lambda_{\alpha\beta}^a \right), \quad \mathcal{C}_{\alpha\beta} = \left( \mathcal{C}_{\alpha\beta}^b | \mathcal{C}_{\alpha\beta}^n | \mathcal{C}_{\alpha\beta}^a \right). \quad (3)$$

As originally pointed out by Jug [15], the sum of squared elements of the diagonal matrix  $\lambda_{\alpha\beta}^b$  is identical to the bond-order definition by Wiberg [16],  $W_{\alpha\beta}$ ,

$$W_{\alpha\beta} = \text{tr} \left( \lambda_{\alpha\beta}^b \right)^2 = \frac{1}{2} \sum_{\mu}^{\alpha} \sum_{\nu}^{\beta} |\mathbf{D}_{\alpha\beta}|_{\mu,\nu}^2. \quad (4)$$

This property (characteristic only for idempotent density matrices [17]) is used to define the quasi-metric of all bonding 2cBOs within the representation of NAOs,

$$\mathcal{S}_{\zeta}^b = \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}^b \left( \lambda_{\alpha\beta}^b \right)^2 \mathcal{C}_{\alpha\beta}^{b\dagger}, \quad (5)$$

When the summation in (5) includes only atomic pairs that represents typical covalent interactions then the trace of the  $\mathcal{S}_{\zeta}^b$  matrix can be regarded as a good approximation to the population of all shared-electron pairs in the molecular system (i.e. the population of electrons delocalized through the net of all chemical bonds). Technically, this is the case only if the highest occupied 2cBOs form a subset of the NBO-like orthonormal orbitals associated with the nearly degenerated eigenvalues  $\{(\lambda_{\alpha\beta}^b)_{\mu,\nu}\}$ . However, if one takes into account also the weak non-covalent interactions or if the multi-center bonding occurs, the 2cBOs cannot be expanded as linear combinations of the doubly-occupied molecular orbitals (MO) only. To solve this problem and give the diagonal of the  $\mathcal{S}_{\zeta}^b$  matrix a strict populational character, it is proposed to project the eigenvectors of  $\mathcal{S}_{\zeta}^b$  onto the ground-state molecular wave function or, which is fully equivalent, transform the quasi-metric (5) under the following orthogonal similarity transformation:

$$\tilde{\mathcal{S}}_{\zeta}^b = 2^{-1} \mathbf{D}^{\dagger} \mathcal{S}_{\zeta}^b \mathbf{D}, \quad N^b = \text{tr}[\tilde{\mathcal{S}}_{\zeta}^b]. \quad (6)$$

Here, one should realize that the total population of electrons delocalized between atoms in a molecule,  $N^b$ , is markedly underestimated if the bond-conjugation effect occurs [18]. This is especially important for aromatic species, in which the shared  $\pi$ -electron pairs are delocalized between more than two atomic centers and thus they cannot be exactly described by any subset of localized bond orbitals. It should be stressed, however, that in such cases the bond-order representability condition for the matrix (5) determines significant contribution of the virtual MOs to the shape of bonding 2cBOs (this property of the 2cBOs will be the subject of a separate study). If so, the complementary set of anti-bonding 2cBOs can be used to 'recover' the lacking electron population in (6). Therefore, in analogy to (5) and (6), the GS-projected quasi-metric of all anti-bonding 2cBOs within the representation of NAOs is given by

$$\tilde{\mathcal{S}}_{\zeta}^a = 2^{-1} \mathbf{D}^{\dagger} \left[ \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}^a \left( \lambda_{\alpha\beta}^a \right)^2 \mathcal{C}_{\alpha\beta}^{a\dagger} \right] \mathbf{D}. \quad (7)$$

Then, the entrywise sum of the matrices (6) and (7) gives rise to the NAO-based density matrix of the EDDA( $r$ ) function, and hence

$$\text{EDDA}(r) = \sum_{\mu,\nu} \chi_{\mu}^{\dagger}(r) \mathcal{D}_{\mu,\nu}^{\text{DA}} \chi_{\nu}(r), \quad \mathcal{D}^{\text{DA}} = \tilde{\mathcal{S}}_{\zeta}^b + \tilde{\mathcal{S}}_{\zeta}^a, \quad (8)$$

The corresponding total population of electrons delocalized between atoms in a molecule can be easily partitioned into atomic contributions:

$$\mathcal{N}^{\text{DA}} = \sum_{\alpha} \text{tr}_{\alpha} \mathcal{D}^{\text{DA}} = \sum_{\alpha} \mathcal{N}_{\alpha}^{\text{DA}}. \quad (9)$$

In accordance with Eq. (1), the density layer representing electrons well-localized on atomic centers, EDLA( $r$ ), can be straightforwardly obtain by the subtraction of EDDA( $r$ ) from the one-electron density, ED( $r$ ). But, furthermore, as shown very recently by the author [14,19], the EDDA( $r$ ) layer can be regarded as a sum of two components representing electron density of localized and delocalized bonds, EDLB( $r$ ) and EDDB( $r$ ), respectively. The latter is determined through the bond-orbital projection technique, which, alongside involving the subset of appropriately orthogonalized [20] 2cBOs, requires also their three-center counterparts [21] to represent all the possible bond-conjugations in the molecular system. Thus, taking into account additional step of the EDDA( $r$ ) decomposition, the electron density can be partitioned as follows:

$$\text{ED}(r) = \text{EDLA}(r) + \text{EDLB}(r) + \text{EDDB}(r). \quad (10)$$

To illustrate how the newly proposed ED-partitioning procedure works in practice, it has been used to probe the electronic structure of the valence shells of benzene, s-triazine and borazine, calculated at the B3LYP/6-311++G\*\* theory level, as well as the anthracene molecule calculated using the CAM-B3LYP/6-311+G\*\* method. The quantum-chemical software including Firefly [22], MultiWFN [23] and Molden [24] has been used to perform computations and visualize the results. The EDDB( $r$ ) density layers have been dissected into  $\sigma$  and  $\pi$  components to provide a more detail description of the bond-conjugation effects [18].

The results, as presented in Fig. 1, clearly shows that the EDLA( $r$ ) function easily copes with detection of lone-pairs in s-triazine as well as regions of highly localized electrons due to charge polarization (borazine, but also to a small extent the benzene molecule). However, in contrast to the expectations dependent upon the qualitative model of bonding by Lewis, in the case of borazine the six  $\pi$ -electrons do not form a typical aromatic ring but tend to remain as unhybridized electron-pairs centered on nitrogen atoms. This fact explains remarkable electron localization on nitrogen atoms, but also rationalizes significantly less effective multi-center delocalization quantified by the EDDB $_{\pi}$  component, which is in full agreement with findings by other researchers [25]. In turn, the effectiveness of  $\pi$ -delocalization in both benzene and s-triazine is very high, but still slightly lower than expected for an ideal aromatic 6 $\pi$ -electron system. Here, the reason is that the cross-ring interactions, which are particularly important for *para*-related atoms, are reluctant to conjugate with the covalent bonds along molecular ring, remaining weak but well-localized 'bonds' in nature. Although this fact has already been noticed in the literature [19], no comprehensive research has been reported so far regarding the influence of cross-ring interactions on the effectiveness of bond-conjugation in aromatics. Here, it should be mentioned that the *para*-delocalization effect is the basis of the very popular aromaticity index by Poater et.al. (PDI) [26]. Since it has been reported that in some cases this descriptor is not suitable for the description of local aromaticity due to overestimation of the contribution of Dewar's resonance structure to the electron delocalization [27], a comparative study of PDI with EDLB and EDDB components of the electron density seem to be even more strongly justified. In contrast to the  $\pi$ -type bonds, which have a much higher tendency to conjugation in the unsaturated species, the  $\sigma$ -bonding represents rather typical localized two-center bonds in all three molecular systems. Again, the EDDB $_{\sigma}$ ( $r$ ) function reaffirms this fact setting the magnitude of  $\sigma$ -delocalization up to about 5% of total population of  $\sigma$ -electrons.

The newly proposed ED-partitioning scheme can also be very useful in rationalizing the electronic structure of polycyclic systems with conjugated  $\pi$ -bonds. In particular, it is well-known that

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