Localization-Delocalization Matrices (LDMs) and Electron Density-Weighted Adjacency Matrices (EDWAMs): A Bridge between the Quantum Theory of Atoms in Molecules and Chemical Graph Theory

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The quantum theory of atoms in molecules (QTAIM) [1] defines localization and delocalization indices (LIs ($\Lambda(\Omega)$), and DIs ($\delta(\Omega,\Omega')$)) in terms of the double integral of the Fermi hole density over a single atomic basin or over two basins, respectively [2]. These indices, arranged in a "*localization-delocalization matrix* (LDM, or **ζ**-matrix)", can be treated by the tools of chemical graph theory [3-6] to extract graph invariants, *e.g.* eigenvalues or matrix distances from a given reference, for use into QSAR [7-15]. The LDM is defined [7]:

$$\zeta \equiv \begin{bmatrix} \Lambda(\Omega_1) & \delta(\Omega_1,\Omega_2)/2 & \cdots & \delta(\Omega_1,\Omega_n)/2 \\ \delta(\Omega_2,\Omega_1)/2 & \Lambda(\Omega_2) & \cdots & \delta(\Omega_2,\Omega_n)/2 \\ \vdots & \vdots & \ddots & \vdots \\ \delta(\Omega_n,\Omega_1)/2 & \delta(\Omega_n,\Omega_2)/2 & \cdots & \Lambda(\Omega_n) \end{bmatrix}_{n\times n} \begin{matrix} = N(\Omega_1) \\ = N(\Omega_2) \\ \vdots \\ = N(\Omega_n) \end{matrix} \Bigg\} \sum_{i=1}^{n} N(\Omega_i) = N$$

$$\sum_{\text{column}} \underbrace{N(\Omega_1) \quad N(\Omega_2) \quad \cdots \quad N(\Omega_n)}_{\sum_{\text{row}}} \qquad tr(\zeta) = N_{\text{loc}}$$

$$\sum_{i=1}^{n} N(\Omega_i) = N$$

The example in Fig. 1 shows the correlation between the matrix distance of the diagonal-suppressed LDM (DM) of partial molecular graphs with pK_a of a series of benzoic acids.

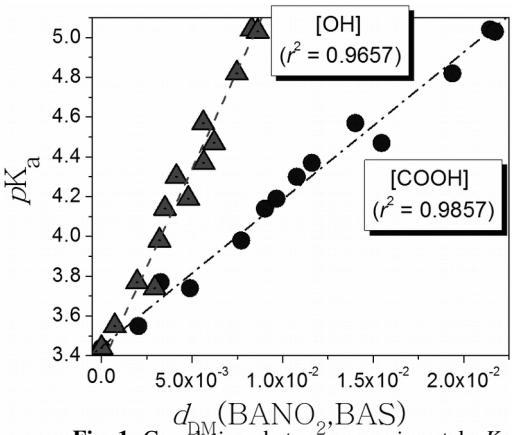

Fig. 1. Correlations between experimental pK_a and Frobenius distance of the partial delocalization matrices (DMs) from the most acidic molecule in the group (*p*-nitrobenzoic acid, or BA–NO_2). The partial DMs for the least steep plot include the atoms of the –COOH group while those of the steepest plot include the –OH group only. (From Ref. [12]).

A matrix representative of the QTAIM molecular graph can also by constructed by inserting the electron density at the bond critical point ($\rho_{\mathbf{BCP}}$) as the matrix element common between two bonded atoms. This matrix, termed "*electron density-weighted adjacency matrix* (EDWAM)" [7], is accessible from X-ray diffraction experiments, unlike the LDM. These matrix representatives of molecules provide the basis for robust empirical correlations and predictions of properties including pK_a's, λ_{max}'s, aromaticity of rings in polycyclic aromatic hydrocarbons, corrosion inhibition efficiencies, log *P*'s, log IC50%, and provide a tool for assessing the quality of basis sets in electronic structure calculations. The same tools developed for LDMs are straightforwardly extendable to the "*Interacting Quantum Atoms* (IQA)" energy components [16].

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