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Unification of Ground-State Aromaticity Criteria –Structure, Electron Delocalization, and Energy– in the Light of the Quantum Chemical Topology

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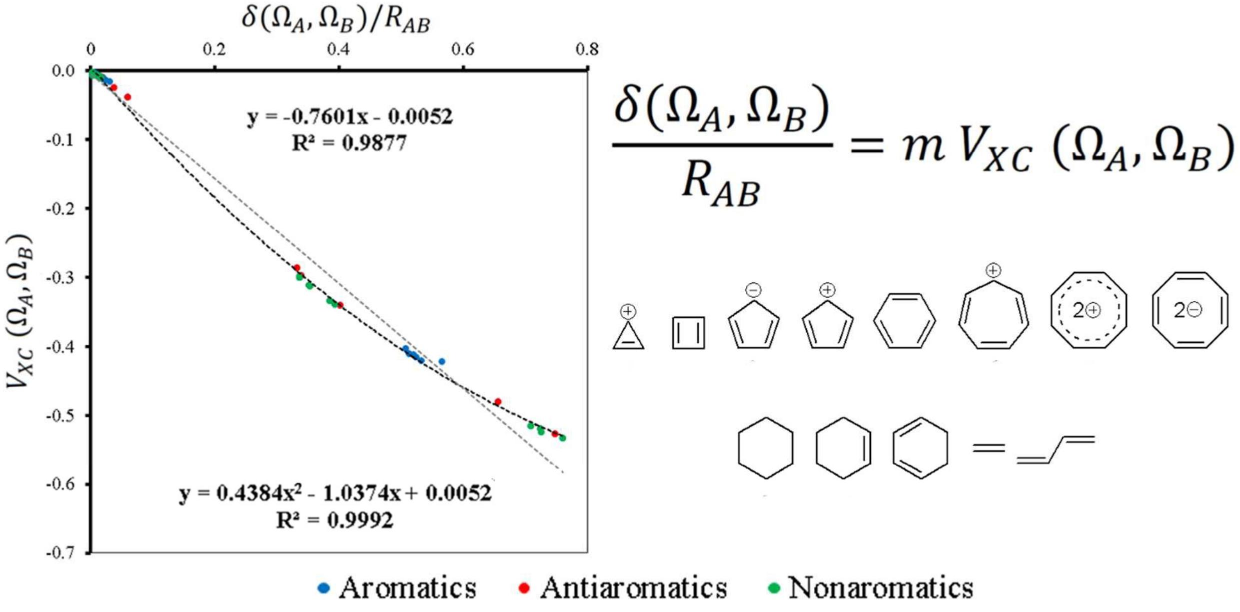
Graphical Abstract



Energy, bond length and electron delocalization are connected within the context of quantum chemical topology theories.

Abstract

In the present account we investigate a theoretical link between bond length, electron sharing, and bond energy within the context of quantum chemical topology theories. The aromatic stabilization energy, ASE, was estimated from this theoretical link without using isodesmic reactions for the first time. The ASE values obtained from our method show a meaningful correlation with the number of electrons contributing in the aromaticity. This theoretical link demonstrates that structural, electronic, and energetic criteria of aromaticity –ground-state aromaticity– belong to the same class and guarantees that they assess *the same property* as aromaticity. Theory suggests that interatomic exchange-correlation potential, obtained from the theory of Interacting Quantum Atoms (IQA), is linearly connected to the delocalization index of Quantum Theory of Atoms in Molecules (QTAIM) and bond length through a first order approximation. Our study shows that the relationship between energy-structure-electron sharing marginally deviates from the ideal linear form expected from the first order approximation. The observed deviation from linearity was attributed to a different contribution of exchange-correlation into the bond energy for the σ- and π-frameworks. Finally, we proposed two-dimensional energy-structure-based aromaticity indices in analogy to the electron sharing indices of aromaticity.

1. Introduction

The concept of aromaticity is tied with the concept of *cyclic π-electron delocalization*.[1] Chemistry pupils learn to assess aromaticity by looking for *4n+2* π-electrons as stated by Hückel rule[2] and usually keep using this golden rule for differentiating aromatic species throughout their career. Aromaticity is such a useful concept for organic chemists that any organic chemistry text book is incomplete without a chapter about "aromaticity". However, the concept of aromaticity like many other cornerstones of chemistry does not emerge from fundamental equations of quantum mechanics. Therefore, recovering the so-called aromatic stabilization energy from total electronic energy needs an *arbitrary reference state*.[3] In spite of vast efforts the physical origin of aromaticity has remained unclear beyond classical or semi-empirical models.[4,5,6]

Aromatic molecules have been conventionally classified and *identified* concerning their common properties that are non-alternating bond lengths[7] as well as kinetic and thermodynamic stability (reactivity)[8,9,10] compared with their open-chain non-aromatic counterparts. After the advent of nuclear magnetic resonance it was discovered that aromatic species sustain an electronic ring current.[11,12,13,14] Finally, in the light of the quantum chemical topology[15,16,17] theories it became possible to estimate the magnitude of the pronounced *electron delocalization* between atoms of an aromatic ring.[18,19,20]

The electron delocalization along with energetic and structural characteristics of aromatic systems can be classified as *ground-state* or *classical*[21] aromatic properties. On the other hand, ring current, which is sometimes mistakenly interpreted as "electron delocalization", is a *response* property that is *absent* in the *absence of an external magnetic field*.[22,23,24,25] Numerous studies have shown that there are correlations between the ground-state and even response-based indices of aromaticity.[26,27,28,29,30,31] Besides, in some cases aromaticity indices fail to correlate.

[32,33] Nevertheless, these studies usually do not address the physics behind success or failure of correlations.

The missing theoretical link between the electron sharing, energy and bond length has been established within the context of quantum chemical topology theories but to the best of our knowledge the concept of aromaticity has not been investigated in this context yet. In the present contribution we discuss current state of knowledge about the theoretical foundation of the ground-state aromaticity in the light of the recent advances in the field of quantum chemical topology. A main question that will be explored in the present paper is that if electron delocalization in an aromatic species provides an *extra stability* compared to a nonaromatic or antiaromatic system corresponding to aromatic stabilization energy.

2. Theoretical Background

In a series of papers Pendás et. al. introduced an energy decomposition scheme –called Interacting Quantum Atoms (IQA)– for partitioning the energy of a molecule into atomic (self) and interatomic (bond) parts in different topological subspaces **Equation 1** and **2**.[34,35,36,37]

$$E_{self}(\Omega) = T(\Omega_A) + V_{en}(\Omega_A) + V_{ee}(\Omega_A) \qquad \text{Equation 1}$$

$$E_{inter}(\Omega_A,\Omega_B) = V_{nn}(\Omega_A,\Omega_B) + V_{ee}(\Omega_A,\Omega_B) + V_{en}(\Omega_A,\Omega_B) + V_{ne}(\Omega_A,\Omega_B) \qquad \text{Equation 2}$$

In these equations T represents the kinetic energy obtained from a standard kinetic energy operator $(-\nabla^2/2)$ and V defines intra/interatomic potential energy for electron/nuclear interactions. The IQA scheme decomposes the intra- and interatomic electron-electron potential energies, $V_{ee}(\Omega_A)$ and $V_{ee}(\Omega_A,\Omega_B)$, further into Coulombic and exchange-correlation contributions. Therefore, one can cast **Equations 1** and **2** in a new form to distinguish classical and quantum mechanical components of the potential energy, **Equations 3** and **4**.

$$E_{self}(\Omega_{\mathrm{A}}) = T(\Omega_{\mathrm{A}}) + V_{Cl}(\Omega_{\mathrm{A}}) + V_{XC}(\Omega_{\mathrm{A}})$$ Equation 3

$$E_{inter}(\Omega_{\mathrm{A}},\Omega_{\mathrm{B}}) = V_{Cl}(\Omega_{\mathrm{A}},\Omega_{\mathrm{B}}) + V_{XC}(\Omega_{\mathrm{A}},\Omega_{\mathrm{B}})$$ Equation 4

In **Equations 3** and **4** V_{Cl}, the classical term, represents the sum of all Coulombic energy terms. Among all energy components obtained from the IQA analysis the formulation of the interatomic exchange-correlation term, $V_{XC}(\Omega_{\mathrm{A}},\Omega_{\mathrm{B}})$, **Equation 5**, is closely related to the formulation of the delocalization index[38,39,40,41] within the context of quantum theory of atoms in molecules, QTAIM[42], **Equation 6**.[43]

$$V_{XC}(\Omega_A,\Omega_B) = \int_{\Omega_A}\int_{\Omega_B}[\rho_2^{AB}(\boldsymbol{r_1},\boldsymbol{r_2}) - \rho_A(\boldsymbol{r_1})\rho_B(\boldsymbol{r_2})]r_{12}^{-1}d\boldsymbol{r_1}d\boldsymbol{r_2}$$ Equation 5

$$\delta(\Omega_A,\Omega_B) = -2\int_{\Omega_A}\int_{\Omega_B}[\rho_2^{AB}(\boldsymbol{r_1},\boldsymbol{r_2}) - \rho_A(\boldsymbol{r_1})\rho_B(\boldsymbol{r_2})]d\boldsymbol{r_1}d\boldsymbol{r_2}\ d\boldsymbol{r_1}d\boldsymbol{r_2}$$ Equation 6

As it has been shown by Popelier and Rafat[44] that to the first order approximation one can drive a linear equation –**Equation 7**– from **Equations 5** and **6**, in which *m* is a *universal* constant for any type of atom and R_{AB} denotes the inter-nuclear distance between the nuclei of a pair of atoms.

$$\frac{\delta(\Omega_A,\Omega_B)}{R_{AB}} = m\,V_{XC}(\Omega_A,\Omega_B)$$ Equation 7

Equation 7 is the theoretical link between the electron delocalization, energy and bond length. The QTAIM delocalization index has been employed for assessing aromaticity of planar hydrocarbons.[45,46,47,48] The relationship between the delocalization index, bond length, and the exchange-correlation potential suggests that one can recast aromaticity indices like para delocalization index, PDI,[45] and fluctuation index, FLU,[47] or even harmonic oscillator model of aromaticity, HOMA[49] in terms of energy instead of the electron sharing for the exchange-correlation energy, calibrated with respect to inter-nuclear distance, i.e., V_{XC} (Ω_A,Ω_B) R_{AB}.

In this contribution we investigate the correlation between the exchange-correlation energy and the delocalization index calibrated for bond length, **Equation 7**, to ensure validity of the first order approximation for a number of aromatic, nonaromatic, and antiaromatic hydrocarbons. In particular, we examine if aromatic species benefit from an extra stabilization resulting from the electron delocalization compared with their nonaromatic and antiaromatic counterparts. Furthermore, we discuss new aromaticity indices, which are exchange-correlation-based analogs of the electron sharing indices of aromaticity.

3. Computational Methods

Since the ground-state aromaticity and antiaromaticity are distinguishable from the energetic, electronic and structural parameters, obtained from a non-correlated level and because we are merely interested in a qualitative description of our systems, we have primarily chosen HF computational level for studying our systems. An advantage of HF over DFT methods is that the second order density matrix obtained from DFT computations suffers from an inherit inaccuracy; this can affect the magnitude of exchange-(correlation) energies. Accordingly, one cannot distinguish computational errors from DFT inherit inaccuracy. However, using HF guarantees that the second order density matrix is accurate and error in this work is limited merely to computational errors. All systems, depicted in **Figure 1**, are optimized at HF/aug-cc-pVTZ level of theory by Gaussian 09 rev D02 suite of programs.[50] All geometries correspond to local minima except planar cyclooctatetraene dication that is a second order saddle point at the studied theoretical level. The wave functions of the studied systems were further analyzed by AIMAll Version 14.06.21.[51]

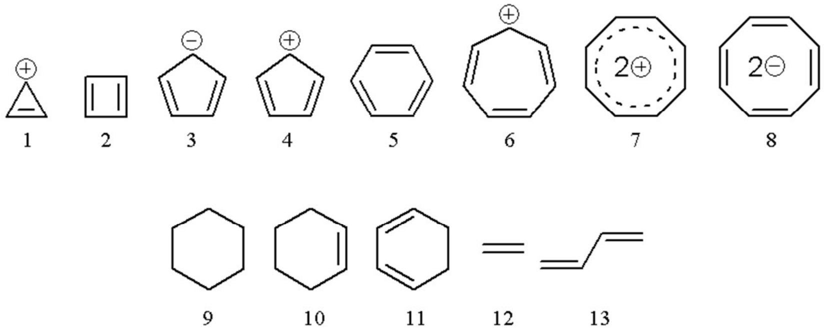


Fig 1. Lewis presentation of molecular structures of the model systems studied in the present account.

The pure contributions of the σ-frameworks in the exchange energy and delocalization index were determined by removing electrons from π-molecular orbitals of molecules with $D_{nh/d}$ point groups and cyclopentadienyl cation (C_{2v}). The difference between the delocalization index and exchange energy of the σ-frameworks and those of the molecules denotes the contribution of π-framework and σ-π overlap in the delocalization index and exchange energy. Hereafter we refer to this term as π-contribution but the readers must keep in mind that a part of this contribution results from the overlap between σ and π frameworks. High symmetry and lack of heteroatoms guarantees that removing π-electrons does not alter position of inter-atomic surfaces (IASs); therefore, the relative contributions of the π- and σ-frameworks in delocalization index and the exchange-correlation energy remain legitimate for individual atoms. We should warn that removing electrons from systems with low symmetry, e.g., cyclohexene or 1,3-cyclohexadiene, or having heteroatoms with π-electrons, such as pyridine, may cause unexpected errors due to displacement of IASs. Nevertheless, separating the effect of individual orbitals in AIM properties would be more reliable if developers of AIM software packages decided to add an orbital-based AIM analysis to their products. Correlations between the interatomic exchange energy, $V_X(\Omega_A,\Omega_B)$ and $\delta(\Omega_A,\Omega_B)/R_{AB}$ values were studied by CurveExpert software.[52] It is worth emphasizing that **Equation 7** is valid for all types of atoms and at DFT levels by inclusion of correlation as well. Interested reader may check the validity of this equation for systems containing heteroatoms elsewhere.[53] Aside from HF computations, Aromatic Stabilization Energies (ASE) obtained from **Equation 7** (discussed in Section 4.2.) are also computed at B3LYP/aug-cc-PVTZ computational level to make sure that inclusion of correlation does not affect the ASE values. To do so, all geometries were fully optimized at the DFT level and the DFT wavefunction was analyzed.

4. Results and Discussion

4.1. Exchange-correlation potential *versus* delocalization index; how they correlate?

Validity of the **Equation 7**, as an approximate connection between **Equations 5** and **6** can be evaluated by plotting the interatomic exchange energy versus the delocalization indices between all carbon atoms of the rings among our model systems, **Figure 2**. A linear equation with high correlation coefficient ($r^2 = 0.9877$) and low standard error ($s = 0.0223$) can be fitted into the data. The intercept of the line is quite close to zero as it is expected from **Equation 7**. Scrutinizing the interatomic exchange energy and the delocalization indices for carbon-carbon bonds (1,2 interactions) reveals that the *aromatic bonds* are quite similar among different aromatic molecules. The $V_X(\Omega_A,\Omega_B)$ and the delocalization indices for these species falls between that of double and single bonds with higher and lower $V_X(\Omega_A,\Omega_B)$ and $\delta(\Omega_A,\Omega_B)/R_{AB}$ values, respectively. The $V_X(\Omega_A,\Omega_B)$ and $\delta(\Omega_A,\Omega_B)/R_{AB}$ values for antiaromatic systems is similar to those of nonaromatics, which makes them easy to distinguish from aromatics. This explains the success of the electron sharing indices like FLU for distinguishing between aromatics and anti/nonaromatics.

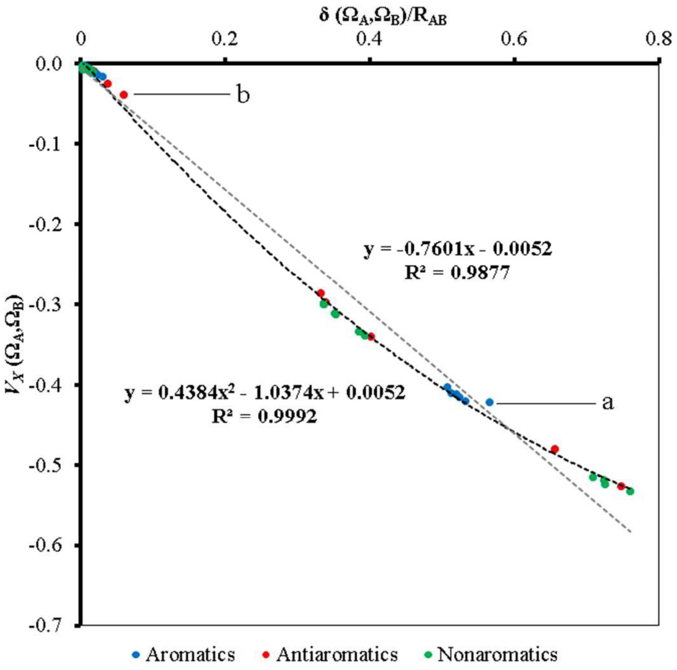


Fig 2. Plot of the interatomic exchange energy versus the delocalization indices, calibrated for the inter-nuclear distances (bond lengths), between all atoms in the model systems of **Figure 1**; all values are in atomic units. Points *a* and *b* in the plot represent values related to 1,2 interaction in cyclopropenyl cation and 1,3 interaction in the cyclobutadiene, respectively. All quantities are presented in atomic units.

Inspecting various types of curves that can be empirically fitted to the plot of $V_X(\Omega_A,\Omega_B)$ versus $\delta(\Omega_A,\Omega_B)/R_{AB}$ shows that a second order polynomial curve improves both the correlation coefficient ($r^2 = 0.9992$) and standard error ($s = 0.0057$) significantly. The curve reveals that the interatomic exchange energy for single –and to some extent aromatic bonds– has a *negative* *deviation* from what that is expected on the basis of **Equation 7**. On the other hand, $V_X(\Omega_A,\Omega_B)$ for double bonds has a positive deviation from linearity. The deviations might be explained with the fact that in single (σ) bonds electrons are more confined between two nuclei; therefore, they are closer in space and the exchange-correlation plays a more substantial role for reducing the energy compared with the relatively free electrons of π-bonds. The position of points representing aromatic bonds in **Figure 2** suggests that these bonds have more in common with ordinary single bonds than double bonds from an energetic point of view.

It is worth noting that two points in **Figure 2** have a positive deviation from the rest of the points on the polynomial curve. These points belong to two highly strained molecules, cyclopropenyl cation and cyclobutadiene. We hypothesize that the deviation might originate from the effect of strain on the interatomic exchange-(correlation) energy. However, validation of the hypothesis needs further studies.

The validity of **Equation 7** for the σ- and π-electrons of the model systems can be assessed on the basis of **Figure 3**. Linear equations with small intercepts, standard error (0.0045 and 0.0057 for σ- and π-densities, respectively), and high correlation coefficient can be fitted into the plots of the exchange energy versus the delocalization index for both the σ- and π-electron densities. A quadratic polynomial improves the correlation coefficient and standard error (0.0034 for both the σ- and π-densities) for the plots of the $V_X(\Omega_A,\Omega_B)$ versus $\delta(\Omega_A,\Omega_B)/R_{AB}$. However, concerning the correlation coefficients and curvatures of the polynomial fits one may conclude that the σ-electron delocalization satisfies **Equation 7** (first order approximation) more precisely compared to the π-delocalization. Furthermore, the slope of the linear equation is steeper for the σ-densities; suggesting that the delocalization of the σ-electrons is more effective in lowering the exchange energy compared with that of the π-electrons. Different slopes for the plots of V_X

(Ω_A,Ω_B) versus $\delta(\Omega_A,\Omega_B)/R_{AB}$ of the σ- and π-electrons might explain the observed curvature in **Figure 2**.

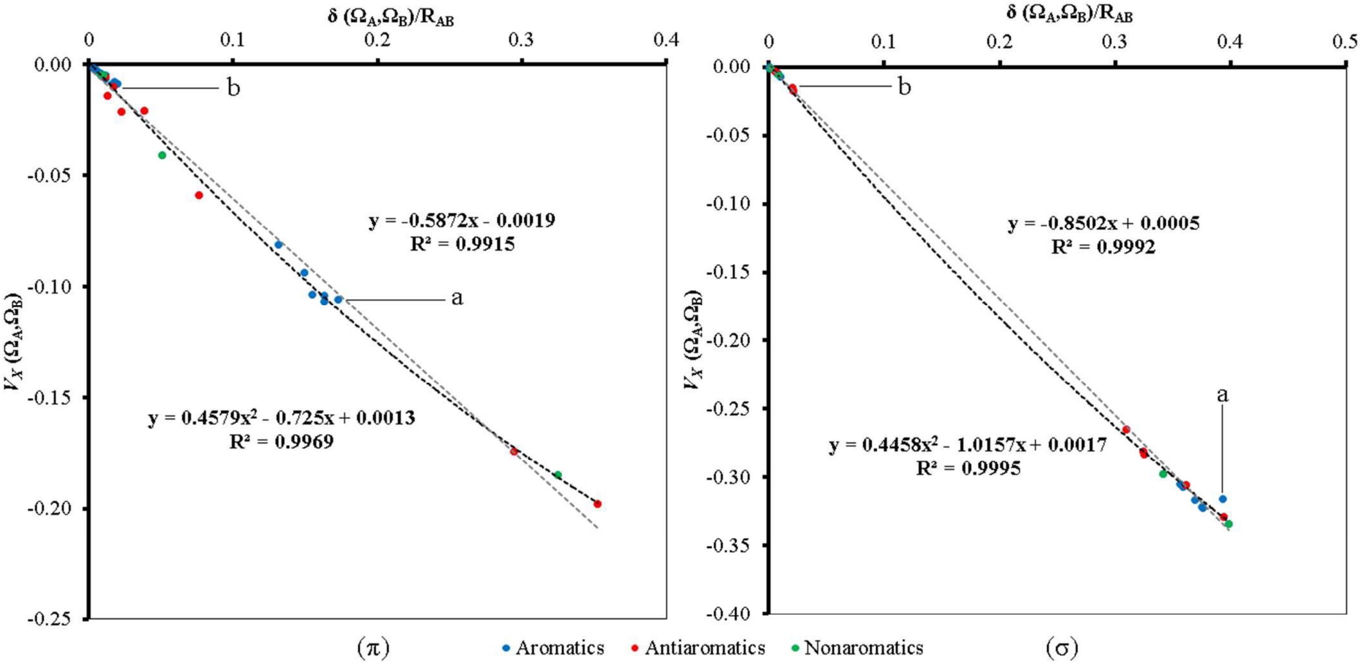


Fig 3. Plots of the interatomic exchange energy versus the delocalization indices, calibrated for the inter-nuclear distances (bond lengths), presented for the π- and σ-frameworks of our model systems. In the figure the data for molecules 1 to 8 and 13 are presented. The rest of systems are not shown due to the risk of changes in the position of their IASs. Points *a* and *b* on the plots refer to cyclopropenyl cation and cyclobutadiene, respectively. All quantities are presented in atomic units.

The $V_X(\Omega_A,\Omega_B)$ and $\delta(\Omega_A,\Omega_B)/R_{AB}$ values for σ- and π-electrons were computed individually to inspect the origin of the observed deviation from **Equation 7**, **Figure 3**. The plot of exchange energy versus the calibrated delocalization index in dissected electron density curves (**Figure 3**) demonstrates that the observed deviation of the $V_X(\Omega_A,\Omega_B)$ and $\delta(\Omega_A,\Omega_B)/R_{AB}$ values for cyclopropenyl cation in **Figure 1** mainly originates from its σ-framework. This suggests that the effect of the strain is mainly reflected in the σ-electron density but does not affect the π-system. On the other hand, a similar trend was not observed for the 1,3 interaction in cyclobutadiene.

Nevertheless, the physical origins of deviations for these species need more careful examination before drawing a certain conclusion, which is beyond the main purpose of the present study.

To conclude from this section we state that **Equation 7** is a useful theoretical tool that ensures the legitimacy of application of electron sharing indices for assessing aromaticity and connects the delocalization index and bond length to the energy, the key property of aromatic species.

4.2. Aromatic stabilization energy from Equation 7

The ASE is a quantity that has been obtained by comparing aromatic systems with their alternate hydrocarbon counterparts or non-cyclic systems.[3] The magnitude of ASE varies by variation of the reference systems that are employed as the nonaromatic. The negative deviation of the interatomic exchange energy for the "π-electrons" of aromatic bonds from **Equation 7** compared to their nonaromatic/antiaromatic counterparts suggest that one may obtain ASE on the basis of **Equation 7** for the π-framework. In order to estimate the ASE for our *aromatic* model systems $V_X(\Omega_A,\Omega_B)$ for 1,2 π-interactions (bonds) were plotted versus $\delta(\Omega_A,\Omega_B)/R_{AB}$. Similarly, $V_X(\Omega_A,\Omega_B)$ for 1,2 π-interactions (bonds) versus $\delta(\Omega_A,\Omega_B)/R_{AB}$ were plotted for *nonaromatic* and *antiaromatic* species. **Equation 7** with an intercept of zero was fitted to each plot to obtain the slope (*1/m*) for the aromatic and alternate hydrocarbons, **Figure 4**.

According to **Figure 4** the slope of the plot of $V_X(\Omega_A,\Omega_B)$ versus $\delta(\Omega_A,\Omega_B)/R_{AB}$ for 1,2 *aromatic* interactions is more negative (-0.6375) compared to that of *nonaromatic/antiaromatic* species (-0.5768). Replacing the $\delta(\Omega_A,\Omega_B)/R_{AB}$ values from aromatic systems into the equation obtained from the plot of alternate hydrocarbons represents a hypothetical interatomic exchange energy for aromatic systems assuming that they behave as alternate hydrocarbons. The difference between the real $V_X(\Omega_A,\Omega_B)$ and the values obtained from a slope of -0.5768 provides an estimate of ASE for a single bond. Multiplication of bond values in the number of bonds can provide an estimate of ASE for a molecule, **Table 1**. Here we must emphasis that the obtained ASEs are defined merely on the basis of exchange energies and for the π-electrons so here we present them by $ASE_{X\pi}$ to distinguish them from ordinary ASE values.

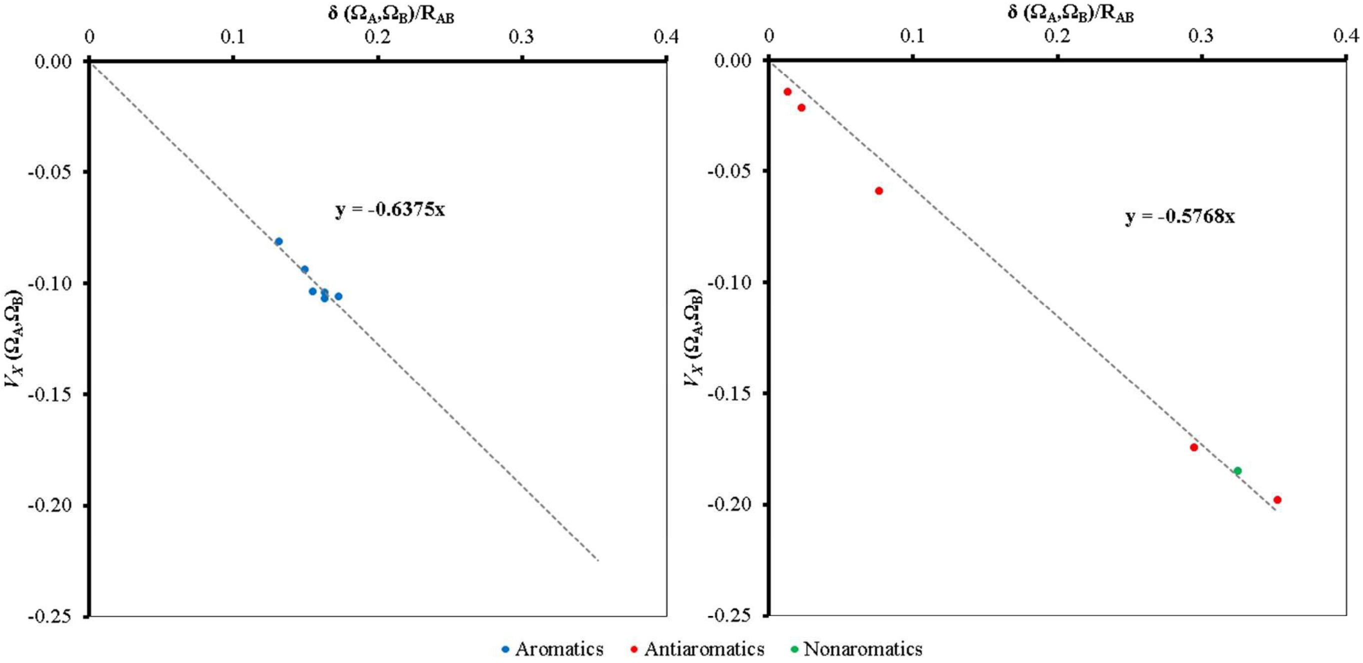


Fig 4. Plots of the interatomic exchange energy versus the delocalization indices, calibrated for the inter-nuclear distances (bond lengths), presented for the π-frameworks of aromatics and antiaromatic/nonaromatic systems separately. In the figure the data for 1,2 interactions (bonds) are presented. Equation 7 is fitted to the data assuming the intercept is zero. The slope for aromatics is more negative compared to the slope of antiaromatic/nonaromatic species. All quantities are presented in atomic units.

To ensure that the observed trends of ASE values are valid at a DFT level by inclusion of correlation effect too, the same computations were performed at B3LYP/aug-cc-pVTZ computational level. The slopes, obtained regarding **Equation 7**, for aromatics and alternate hydrocarbons are -0.6310 and -0.5603, respectively. The ASE values of DFT level are also listed in **Table 1** under $ASE_{XC\pi}$ column.

Table 1. Estimated exchange-based aromatic stabilization energy ($ASE_{X\pi}$ and $ASE_{XC\pi}$ for HF and DFT levels, respectively) values on the basis of **Equation 7**. In the table $V(\Omega_A,\Omega_B)_{Hyp}$ and $\Delta V(\Omega_A,\Omega_B)$ represent hypothetical interatomic exchange energy obtained from assuming aromatic systems to be like an alternate hydrocarbon and the difference between hypothetical $V(\Omega_A,\Omega_B)_{Hyp}$ and real values $V(\Omega_A,\Omega_B)$, respectively. Both quantities are presented in atomic units. $ASE_{X\pi}$ values are presented in kcal/mol units. Nπ denotes number of π-electrons in each system. Please note that values obtained at HF and DFT levels have X and XC subscripts referring to exchange-only (obtained from HF) and exchange-correlation (from DFT) energies.

Molecules	$V_X(\Omega_A,\Omega_B)_{Hyp}$	$V_{XC}(\Omega_A,\Omega_B)_{Hyp}$	$\Delta V_X(\Omega_A,\Omega_B)$	$\Delta V_{XC}(\Omega_A,\Omega_B)$	$ASE_{X\pi}$	$ASE_{XC\pi}$	Nπ
Cyclopropenyl cation	0.0992	0.0953	0.0064	0.0074	12.0	13.9	2
Cyclopentadienyl anion	0.0940	0.0900	0.0124	0.0136	38.8	42.7	6
Benzene	0.0938	0.0906	0.0102	0.0118	38.4	44.6	6
Cycloheptatrienyl cation	0.0858	0.0830	0.0076	0.0094	33.2	41.5	6
Cyclooctatetraene dication	0.0754	0.0729	0.0058	0.0076	28.9	38.4	6
Cyclooctatetraene dianion	0.0890	0.0851	0.0142	0.0155	71.1	77.8	10

Estimated ASEs values show a reasonable trend as the values for 2π-electron aromatic cyclopropenyl cation is almost one third of that of 6π-electron species. The 10π-electron cyclooctatetraene dianion shows an enhanced ASE compared to those of 2π- and 6π-electron species as it is more than five times greater than that of cyclopropenyl cation. This trend was previously observed for ring current strength of these species.[22] ASE values computed at B3LYP/aug-cc-pVTZ level are relatively larger for each compound compared with the values obtained at HF/aug-cc-pVTZ level.

Aside from that, the values obtained from HF and DFT computations are slightly different among 6π-electron species. Inclusion of correlation at the DFT level increases the ASE of benzene slightly more than that of cyclopentadienyl anion while at the HF level the ASE values decrease regularly by increasing the ring size. Finally, it is worth noting that obtained ASE_{π} values are in good agreement with ASE values available in literature estimated from various methods.[3,26,54,55]

4.3. Proposals for two-dimensional energy-structure-based aromaticity indices

The direct link between energy, bond length, and the delocalization suggest that besides ASE$_{X\pi}$, other aromaticity indices can be developed on the basis of exchange –or exchange-correlation for DFT levels– energy and structure. Although, studying performance of such indices is of interest of aromaticity community, here we just introduce new opportunities but leave testing each index for a separated work in future on a larger group of systems.

An index similar to PDI can be defined on the basis of the exchange-correlation energy, calibrated for the internuclear distances, i.e. $V_{XC}(\Omega_A,\Omega_B)$**.**R$_{AB}$. We name this index para exchange-correlation index, **pXCI**, and expect that it correlates well with the electron sharing index PDI on the basis of **Equation 7** and correlations observed in section 4.1. Validity of pXCI should be tested for a group of 6-membered ring systems however it is beyond the goal of the present work.

Another possibility for an energy-based aromaticity index is using the definition of FLU[47] index. Such an index can measure fluctuation of the exchange-correlation energy between pairs of atoms in a molecule and link it to the aromaticity. The XC$_{FLU}$ can be computed according to **Equation 8** for either hydrocarbons or heterocyclic systems.

$$XC_{FLU} = \frac{1}{n}\sum_{\Omega_A-\Omega_B}^{ring}\left\{\left[\frac{V_{XC}(\Omega_A,\Omega_B)R_{AB}}{V_{XC}(\Omega_B,\Omega_A)R_{BA}}\right]^{\delta}\left[\frac{V_{XC}(\Omega_A,\Omega_B)R_{AB}-V_{XC}^{ref}(\Omega_A,\Omega_B)R_{AB}}{V_{XC}^{ref}(\Omega_A,\Omega_B)R_{AB}}\right]\right\}^{2} \qquad \text{Equation 8}$$

Where δ is either 1 or –1 and defined in a way that $\left[\frac{V_{XC}(\Omega_A,\Omega_B)R_{AB}}{V_{XC}(\Omega_B,\Omega_A)R_{BA}}\right]^{\delta}$ remains always equal or greater than unity; this term will deviate from one significantly for heterocycles having polarized bonds. Similar to the original FLU index, XC_{FLU} will be zero for a totally aromatic system but larger for systems with lesser degrees of aromaticity or non/antiaromatics.

5. Conclusions and Prospects

In the present work we studied the connection between the energy, structure, and electron sharing within the light of quantum chemical topology approaches, QTAIM and IQA theories. The delocalization index defined within the context of QTAIM theory is connected to the interatomic exchange-correlation energy of the IQA energy decomposition scheme and bond length, **Equation 7**.[44] The most important consequence of the presence of such theoretical link is unification of three main classes of aromaticity indices that are known as ground-state aromaticity indices. Aromatic stabilization energies obtained from **Equation 7** in section **4.2.** demonstrate validity of the proposed unification.

Examining the validity of **Equation 7** for a number of aromatic, nonaromatic and antiaromatic compounds suggests that although linear correlation expected from **Equation 7** is reasonably accurate, the relationship between energy, electron sharing, and bond length resembles more a quadratic polynomial, **Figure 2**. Examining **Equation 7** for σ- and π-electrons separately shows that the equation has different slopes for different molecular orbital subsets. This observation suggests that the electron delocalization among σ-electrons reduces exchange-correlation energy more effectively compared with the electron delocalization among π-electrons. Such a different behavior for σ- and π-electrons is not expected on the basis of **Equation 7**. Accordingly, the theoretical link between energy, electron sharing and structure can be improved more by linking **Equations 5** and **6** through higher order approximations.

It is demonstrated that aromatic stabilization energy can be recovered via **Equation 7** by comparing the difference between plots of $V_X(\Omega_A,\Omega_B)$ versus $\delta(\Omega_A,\Omega_B)/R_{AB}$ for π-electrons of aromatic bonds and those of alternating hydrocarbons. Recovering ASE via **Equation 7** suggests that aromatic stabilization energy originates from exchange energy.

It is worth mentioning that *two-dimensional* structure/energy-based aromaticity indices similar to PDI and FLU can be established on the basis of exchange-correlation potential and bond-length on the basis of **Equation 7** and correlations presented in **Figures 2** and **3**. Here we name them para-exchange-correlation index, **pXCI**, and exchange-correlation fluctuation index, XC_{FLU}. Application of these indices will be discussed later in a separated work.

Finally, we should emphasis that although the connection between ground-state aromaticity criteria is established within the light of the quantum chemical topology theories, a link between these criteria and the *magnetic* criterion of aromaticity is still missing beyond empirical correlations and needs further investigations.

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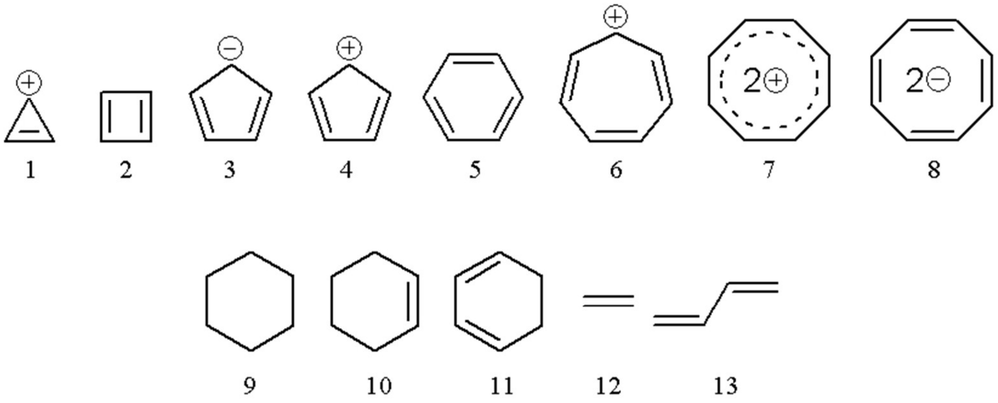

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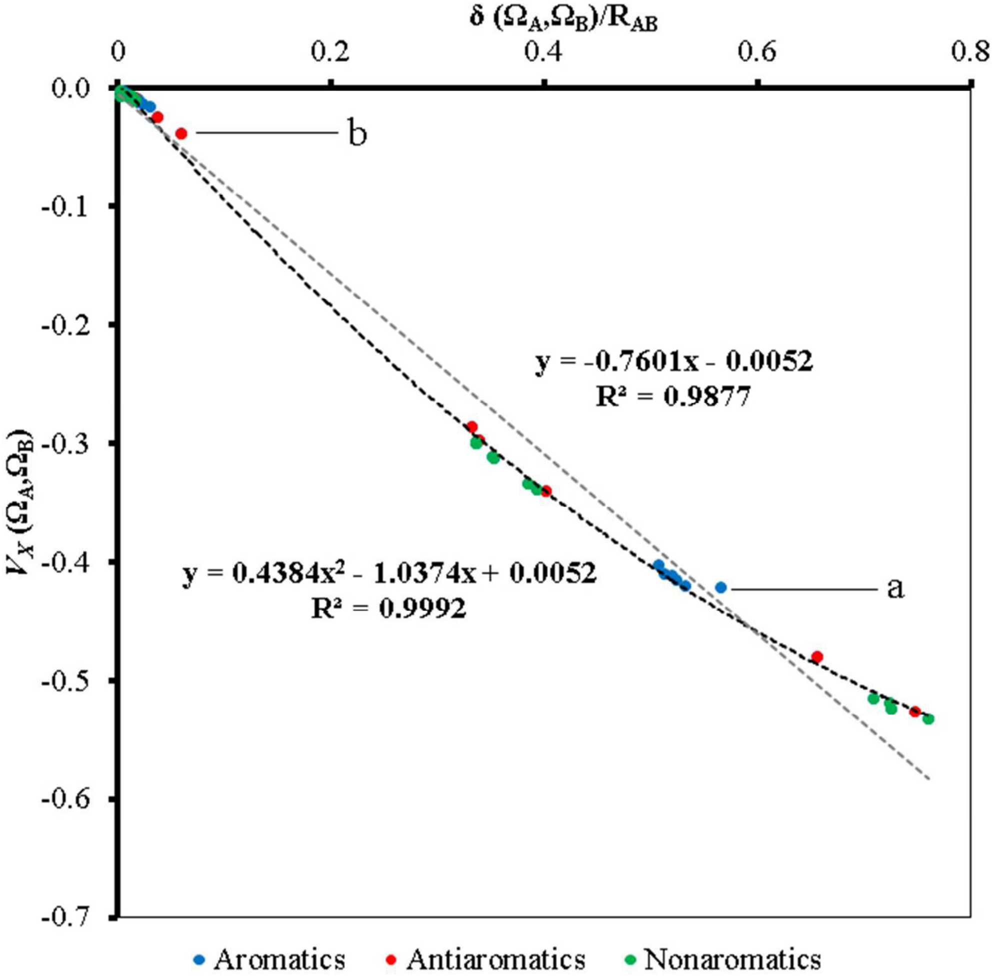

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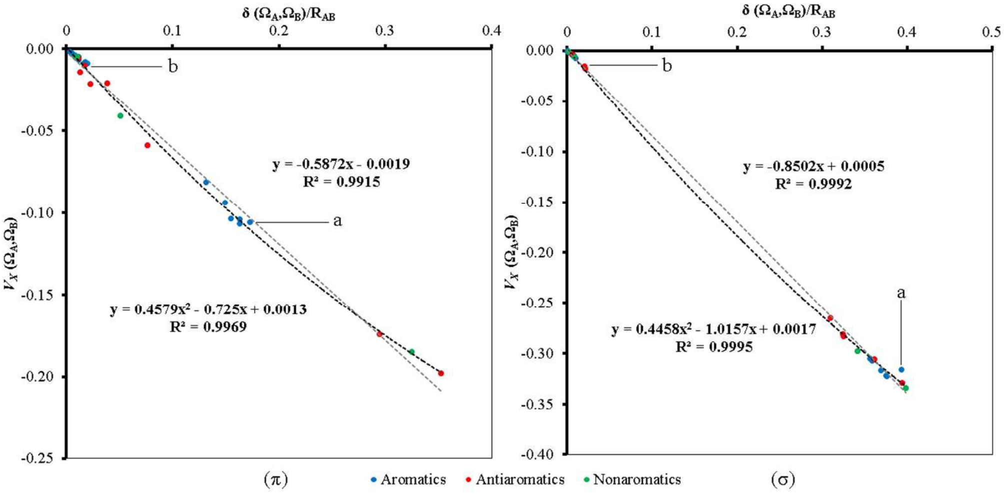

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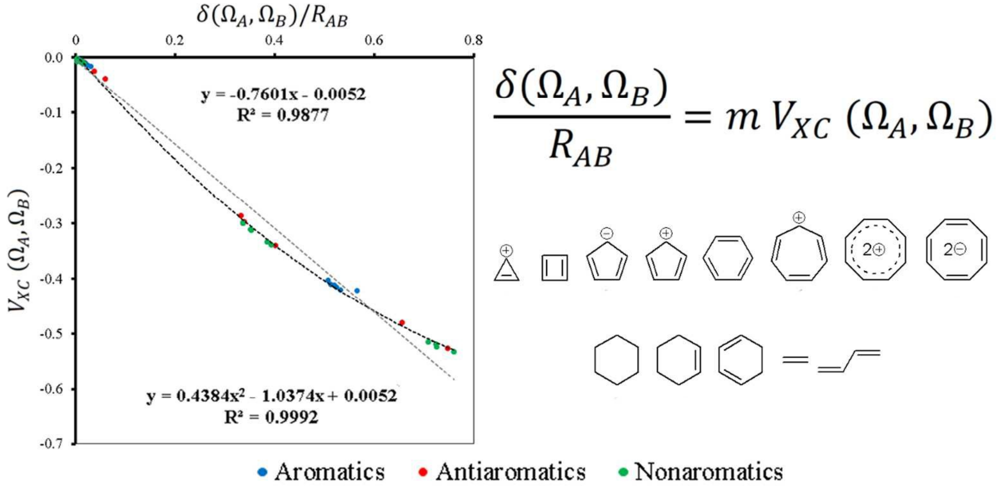

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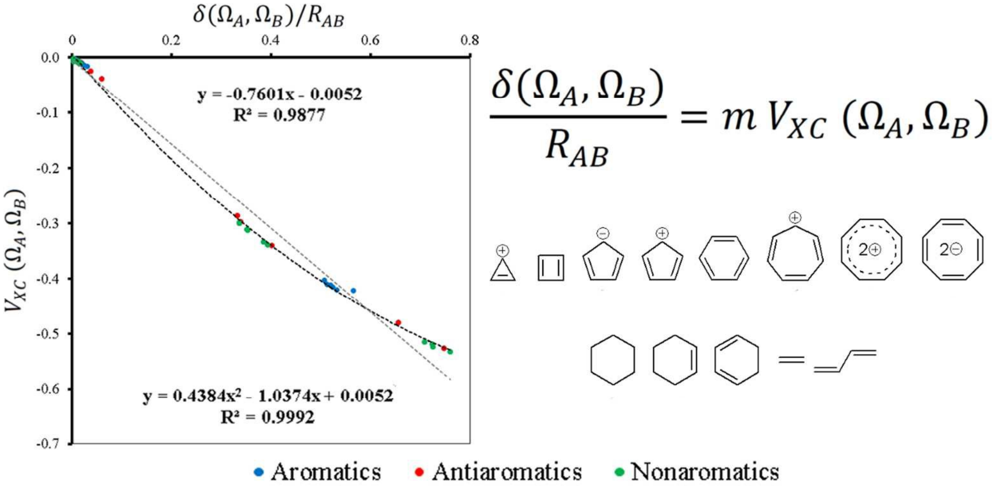

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