CROATICA CHEMICA ACTA
CCACAA **79** (3) 363–371 (2006)

ISSN-0011-1643
CCA-3101
Original Scientific Paper

Generalized Polansky Index as an Aromaticity Measure in Polycyclic Aromatic Hydrocarbons

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RECEIVED DECEMBER 6, 2005; REVISED DECEMBER 27, 2005; ACCEPTED FEBRUARY 28, 2006

Keywords
Polansky
NOEL
quantum similarity
aromaticity

In this work, the ideas of molecular quantum similarity are used to generalize the Polansky similarity index. The newly developed index gauges the aromaticity of individual benzenoid rings in polyaromatic hydrocarbons by its similarity to benzene beyond the scope of simple Hückel theory on which it was originally based. The reported generalization allows the new index to be calculated at a realistic contemporary *ab initio* level of theory, opening the possibility of its use as a new measure of aromaticity. As will be shown, the new index correlates very well not only with the original Polansky index but also with the Generalized Population Analysis based multicenter index.

INTRODUCTION

Aromaticity, despite being quite an old concept,[1–2] remains a lustrous and debated issue since there is no clear unique definition with a sound quantum chemical basis. As a result, many different quantities have been derived to express the degree of aromaticity in various molecules. A striking feature of these different measures is that some of them clearly contradict the conclusions drawn from other measures. Such divergence is naturally hard to reconcile with the unique perception of aromatic character.

Many different measures of aromaticity have already been introduced through literature. Many aspects and aromaticity related phenomena have been reviewed by Schleyer *et al.*[3] A frequently used classification of these measures divides them into structural, energetic, magnetic and reactivity based indices.[4] Structural indices are mainly based on equalization of bond lengths and on planarity of molecules.[5] Energetic indices are mainly based on the extra energetic stabilization of aromatic compounds, including various types of resonance energies, aromatic stabilization energies gauged from isodesmic reactions, *etc*. Magnetic indices are based on the special

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magnetic properties of aromatic compounds, such as chemical shifts and ring currents. In the final group, different reactivity descriptors are used to assess the degree of aromaticity,[6] using *e.g.* conceptual DFT quantities.[7] As mentioned above, different (classes of) indices can be contradictory.[8–10] An illustration is the orthogonality between aromatic stabilization energy and the NICS (Nucleus Independent Chemical Shift, a magnetic criterion)[11] values, although there may be a some correlation within limited sets of molecules.[12–14]

The contemporary situation relating to the definition of aromaticity was recently reviewed in a special issue of *Chemical Reviews*. The introduction to this issue, written by P. v. R. Schleyer,[3] clearly stressed that further efforts to characterize aromaticity and to propose new aromaticity measures and indices are still worth pursuing. In the present work, the electron density itself is used as a natural way to investigate aromaticity, rather than using structural features or quantities derived from it. To that end, molecular quantum similarity theory is used as a technique to investigate how different benzenoid rings are compared to benzene itself in different polycyclic aromatic hydrocarbons. The use of electron density, and a fortiori molecular quantum similarity theory, to assess the degree of aromaticity was previously proposed by Giambiagi *et al.*, who suggested its use to »open up new insights into the concept of aromaticity, with solid chemical and mathematical foundations«.[15] Although suggested several years ago, no in-depth report has yet been published on the application of the molecular quantum similarity theory in the context of aromaticity. This was the motivation for the present study.

Theoretical Development

The natural starting point for the present study is the important work by Derflinger and Polansky published in 1967.[16] Based on the Clar postulate[17] that individual benzenoid rings in polycyclic aromatic hydrocarbons (PAH) can be regarded as local benzene-like regions, Polansky and Derflinger proposed to characterize the aromaticity of these rings in PAH by the »similarity« to benzene itself. This similarity was characterized by the value of a certain index derived from the charge-density bond order matrix. This approach was, however, formulated only at the level of the nowadays sometimes considered outdated Hückel Molecular Orbital theory (HMO) and despite the attractiveness of this approach, no attempt has so far been reported to incorporate this aromaticity measure as such into the framework of more sophisticated contemporary computational tools. Our aim in this study is to fill this gap and to attempt a generalization of the Polansky approach so as to be applicable at the *ab initio* level of theory.

Prior to describing the basic idea of our generalization, it is worthwhile to describe briefly the original approach.[16] For this purpose, let us consider a polycyclic aromatic hydrocarbon consisting of K fused benzenoid rings and let us characterize the π electron structure of this hydrocarbon by the set of Hückel molecular orbitals φ_i expressed as a linear combination of atomic p_π orbitals χ_μ.

$$\varphi_i = \sum_{\mu} c_{\mu i}\chi_{\mu} \tag{1}$$

where the summation runs over all N atoms in the molecule.

Based on these orbitals, it is straightforward to introduce the charge density-bond order matrix (Eq. (2))

$$\boldsymbol{p}_{\mu\nu} = \sum_{i}^{occ} c_{\mu i}c^{*}_{\nu i} \tag{2}$$

This matrix, whose dimension is $N\times N$, characterizes the distribution of electron density in the whole molecule. In addition to this global information, the matrix also allows one to get information on the electron structure of any particular benzenoid ring within the molecule. Such information about the particular ring L is inherently contained in the fragment of the whole density matrix (2), involving only the atoms contributing to this ring. The basic idea of the Polansky approach to the classification of aromaticity of such a ring is based on the ingenious comparison of the fragment density matrices characterizing the benzenoid ring L in the polycyclic molecule A with the density matrix of benzene, B. Such a comparison is quantitatively expressed by the index (3):

$$P_{\mathrm{L,B}} = \frac{1}{2N_{\mathrm{L}}}\sum_{\mu\in \mathrm{L}}\sum_{\substack{\nu>\mu \\ \nu\in \mathrm{L}}} \boldsymbol{p}^{\mathrm{A}}_{\mu\nu}\boldsymbol{p}^{\mathrm{B}}_{\mu\nu} \tag{3}$$

where N_{L} is the number of atoms involved in the ring considered (6 in the case of benzenoid ring). The reason for including this parameter is to ensure proper normalization of the index so as to provide maximum similarity (identity) for the comparison of benzene with itself. In all other cases, the values will be smaller than 1 and the more the index deviates from its idealized value 1, the less similar is a given ring L to benzene and, consequently, the smaller will be its aromaticity. In this way, a simple Hückel Molecular Orbital program can be used to compute very quickly the necessary similarity measures for all benzenoid rings that will be considered in the present work.

After being reminded of the basic idea of the original Polansky approach, let us now address the problem of its generalization beyond the scope of the HMO theory. As already said above, the basic idea of the Polansky approach was to gauge the aromaticity of a given ring in PAH by its similarity to benzene itself. While in the original HMO-like approach this similarity is straightforwardly given by the index (3), the same approach cannot be straightforwardly extended to more sophisticated levels of theory. To overcome the drawback of the original approach, we found it useful to benefit from our experience with quantum molecular similarity and to attempt a generalization of the index (3) in a way that would resemble as much as possible the original approach by Polansky.

For a detailed account of molecular quantum similarity, the reader is referred to recent reviews.[18–19] For the present goals, it suffices that the similarity between two molecules, A and B, is expressed via the Molecular Quantum Similarity Measure (MQSM) as in equation (4):

$$Z_{\mathrm{A,B}} = \int [\rho_{\mathrm{A}}(\boldsymbol{r}_1)\Omega(\boldsymbol{r}_1, \boldsymbol{r}_2)\rho_{\mathrm{B}}(\boldsymbol{r}_2)]\mathrm{d}\boldsymbol{r}_1 d\boldsymbol{r}_2 \qquad (4)$$

where $\Omega(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is a positive definite operator, and $\rho_{\mathrm{A}}(\boldsymbol{r}_1)$ is the one electron density for molecule A at $\boldsymbol{r}_1$. Another quantity that describes the degree of similarity between the two molecules is the Euclidean distance:

$$d^2_{\mathrm{A,B}} = Z_{\mathrm{A,A}} + Z_{\mathrm{B,B}} - 2Z_{\mathrm{A,B}} \qquad (5)$$

Working within a single determinant method, and using the Dirac delta function as operator in (4), it is immediately seen that computation of the MQSM will require computing overlap integrals over four basis functions as:

$$Z_{\mathrm{A,B}} = \int \rho_{\mathrm{A}}(\boldsymbol{r})\rho_{\mathrm{B}}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \sum_{\nu\in \mathrm{A}} \sum_{\mu\in \mathrm{B}} \sum_{\sigma\in \mathrm{A}} \sum_{\kappa\in \mathrm{B}} D^{\mathrm{A}}_{\nu\sigma} D^{\mathrm{B}}_{\mu\kappa} S_{\mu\kappa\nu\sigma} \qquad (6)$$

Computing all these four center overlap integrals, especially for larger numbers of basis functions, becomes a very limiting step. This inspired Cioslowski *et al.*[20] to introduce a slightly different approach where the comparison of the molecules is not based on the electron densities but on first order density matrices.[21] In this Number of Overlapping Electrons (NOEL) approach, the integral (7) is introduced, which represents the similarity measure between the first order density matrix $\rho_{\mathrm{A}}(\boldsymbol{r}, \boldsymbol{r}')$ of molecule A, with the first order density matrix of molecule B $\rho_{\mathrm{B}}(\boldsymbol{r}, \boldsymbol{r}')$.

$$Z_{\mathrm{A,B}} = \int \rho_{\mathrm{A}}(\boldsymbol{r}, \boldsymbol{r}')\rho_{\mathrm{B}}(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \qquad (7)$$

As a result, the NOEL index between the two molecules A and B is given by:

$$\mathrm{NOEL}_{\mathrm{A,B}} = Z_{\mathrm{AB}} = \sum_{\mathrm{IJ}} n_{\mathrm{AI}} n_{\mathrm{BJ}} \left| \langle \chi_{\mathrm{AI}} \mid \chi_{\mathrm{BJ}} \rangle \right|^2 \qquad (8)$$

where n_{AI} is the occupation number of Molecular Orbital (MO) I in molecule A and is the natural spin orbital J of molecule B. It is immediately seen that at the HF level of theory, the self-similarity NOEL index Z_{AA} is equal to the number of electrons in a molecule. Computing the NOEL indices as in equation (8) is naturally very quick, since one needs only the MO overlap matrix between the molecules involved. This gives the NOEL index an important computational advantage over the MQSM in equation (6). Up to now, the NOEL index has been mainly used to study the similarity between benzene and a small number of substituted benzene molecules, such as aniline, nitrobenzene, *etc.* and to study the Gamma AminoButyric Acid (GABA) agonists.[20,22] Cioslowski *et al.* also noted the apparent similarity between the NOEL index and the Polansky approach, but no in-depth analysis of the performance of the NOEL index for aromaticity has been performed thus far.

Our aim in this study is to explore the above close parallel of both approaches and to demonstrate that the appropriately defined NOEL index can indeed be used as a measure of aromaticity of individual benzenoid rings of a given PAH, similarly as the original Polansky index. For this purpose, it is necessary to modify the definition of the NOEL index to make it correspond as much as possible to the intended application. This requires, first of all, specifying how to characterize the density matrix of the fragment L in a PAH.

Several techniques could be proposed to do this, for example the Hirshfeld[23] procedure or the Atoms-In-Molecules (AIM) approaches.[24–26] Although both are attractive schemes, they require substantial computational effort and are quite hard to use for the molecules that are presently used. Instead, we introduce an efficient procedure in which the fragment densities are obtained using Mulliken projection operators.[27–28] Using this approach, the carbon C_6 (denoted L) backbone fragment density matrices for a benzenoid ring in a molecule M can be obtained through the following projection operator:

$$\Pi_{\mathrm{L}} = \sum_{\nu\in \mathrm{L}} \sum_{\mu} S^{-1}_{\nu\mu} |\nu\rangle\langle\mu| \qquad (9)$$

The summation, on the one hand, runs only over the basis functions on the benzenoid ring L and, on the other hand, all basis functions μ, located everywhere in the molecule. This allows us, within a single determinant wave function, as in Hartree-Fock and formally DFT, to obtain fragment density matrices in the molecule M, expressed as:

$$\rho^{\mathrm{M}}_{\mathrm{L}}(\boldsymbol{r}, \boldsymbol{r}') = \Pi_{\mathrm{L}}\rho^{\mathrm{M}}(\boldsymbol{r}, \boldsymbol{r}') =$$

$$\left[\sum_{\nu\in \mathrm{L}} \sum_{\mu} S^{-1}_{\nu\mu} |\nu(\boldsymbol{r})\rangle\langle\mu(\boldsymbol{r}')| \right] \sum_{\sigma\lambda} D^{\mathrm{M}}_{\lambda\sigma} |\lambda(\boldsymbol{r})\rangle\langle\sigma(\boldsymbol{r}')| \qquad (10)$$

where $\boldsymbol{D}^{\mathrm{M}}$ is the charge and bond order matrix of molecule M. The fragment density matrix then becomes:

$$\rho^{\mathrm{M}}_{\mathrm{L}}(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\nu\in \mathrm{L}} \sum_{\sigma} D^{\mathrm{M}}_{\nu\sigma} |\nu(\boldsymbol{r})\rangle\langle\sigma(\boldsymbol{r}')| \qquad (11)$$

Using the above projection for both benzenoid ring fragments L and for the benzene carbon ring itself, the NOEL index $Z_{\mathrm{L,B}}$ between two fragments can be obtained by the application of projector Π_{L} on the density matrix of the first molecule and Π_{B} for the C_6 ring in benzene. It then becomes clear that the similarity between the C_6 ring in the benzenoid ring L in molecule A, and that in benzene, B, is given by:

$$\mathrm{NOEL}_{\mathrm{L,B}} = Z_{\mathrm{L,B}} = \sum_{\mathrm{IJ}} n_{\mathrm{AI}} n_{\mathrm{BJ}} \left\langle \Pi_{\mathrm{L}} \chi_{\mathrm{AI}} \middle| \Pi_{\mathrm{B}}\, \chi_{\mathrm{BJ}} \right\rangle \left\langle \chi_{\mathrm{AI}} \middle| \chi_{\mathrm{BJ}} \right\rangle \qquad (12)$$

Equation (12) allows a very efficient calculation of the similarity between the benzenoid ring L in the PAH and the pure benzene ring and it is also worth noting that it can be straightforwardly used also at the correlated post-Hartree-Fock level of theory. In connection with Eq. (12), it is also interesting to note that for planar molecules considered in the present work, we can also distinguish between the σ and π density of the rings, so that separate σ and π components of the NOEL indices can be calculated as well. Such an additional partitioning can be especially useful just in our case, since it is widely recognized that the phenomenon of aromaticity is closely linked to the existence of delocalized π bonding.

Application to Polycyclic Aromatic Benzenoid Hydrocarbons

The algorithm described above was applied to a set of polycyclic aromatic benzenoid ring containing hydrocarbons (Table I). This set comprises molecules from previous studies of Giambiagi *et al.*[15] and Polansky *et al.*[20] and adds several more molecules.

TABLE I. Molecules contained in the studied set of PAH's. Roman numbers refer to the different symmetry-unique rings in the molecules

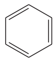
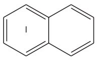
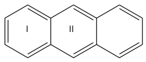
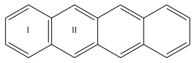
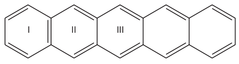
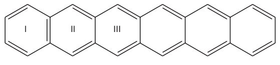
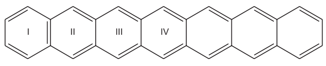
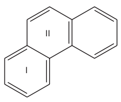
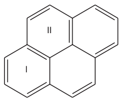
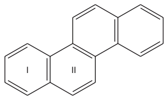
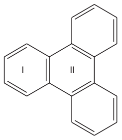
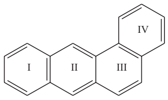
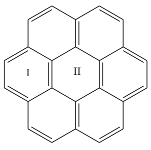
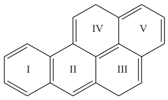
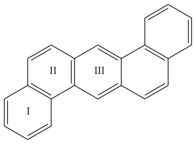
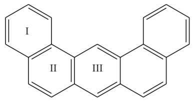
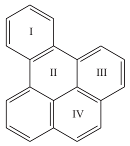
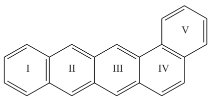
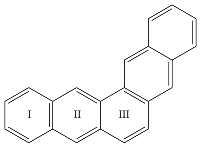
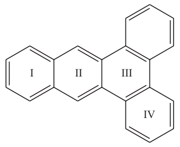
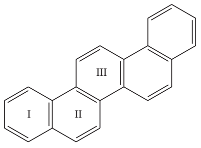
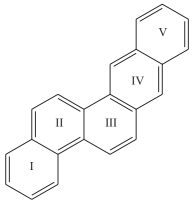
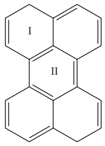
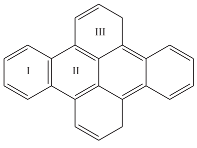
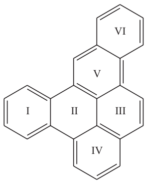
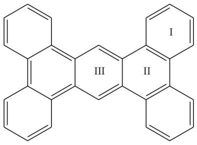
	**1** Benzene
	**2** Naphthalene
	**3** Anthracene
	**4** Tetracene
	**5** Pentacene
	**6** Hexacene
	**7** Heptacene
	**8** Phenantrene
	**9** Pyrene
	**10** Chrysene
	**11** Triphenylene
	**12** 1,2-Benzoanthracene
	**13** Coronene
	**14** 3,4-Benzopyrene
	**15** 1,2,5,6-Dibenzoanthracene
	**16** 1,2,7,8-Dibenzoanthracene
	**17** 1,2-Benzopyrene
	**18** 1,2-Benzotetracene
	**19** Pentaphene
	**20** 1,2,3,4-Dibenzoanthracene

TABLE I (cont.)

	**21** Picene
	**22** 2,3,7,8-Dibenzophenanthrene
	**23** Perylene
	**24** 1,2-6,7-Dibenzopyrene
	**25** 1,2-4,5-Dibenzopyrene
	**26** 1,2-3,4-5,6-7,8-Tetrabenzoanthracene

The symmetry unique rings in every molecule are labelled by Roman numbers for easy reference. For all molecules, the idealized carbon skeleton geometry was constructed first by combining the carbon rings of B3LYP/6–31G* optimized benzene. After having constructed the carbon skeleton of the PAH, the hydrogens were added as appropriate using idealized CH bond distances and assuming idealized CCH bond angles. In this approach, no geometry optimization was performed in order to retain as much correspondence to the classical Hückel approach as possible. The Hückel approach does not explicitly use a molecular geometry, but rather a topological matrix reflecting only the carbon-carbon primary bonding pattern. Yet, the assumption of equality of all α and β integrals in the Hückel method can be viewed as equivalent to using ideal benzene ring geometries. Once these geometries were constructed, Gaussian03[29] was used for calculation of charge and bond order matrices using the B3LYP[30–32] hybrid density functional and the 6–31G* basis set.[33–34] NOEL indices between a benzenoid ring in molecule M and the benzenoid ring of benzene were obtained using in-house written software, fully interfaced to Gaussian03. In addition to NOEL values and its components, Table II also presents the values of another recently proposed aromaticity measure, namely the six-center bond index (SCI).[14] This index is based on Generalized Population Analysis (GPA),[35] which allows quantification multicenter bonding, even in difficult cases such as multicenter bonding in homoaromatic systems.[36]

RESULTS AND DISCUSSION

As said above, the main goal of this study is to demonstrate the applicability of the NOEL index (12) to quantitative characterization of the aromaticity of individual benzenoid rings in PAH's. The calculated values of the NOEL index as well as its σ and π components are summarized in Table II. The same table also contains the values of the original Polansky HMO similarity index and the values of six-center bond indices (SCI),[14] which were recently proposed as a new measure of aromaticity.[14]

TABLE II. Aromaticity indices computed for the entire PAH set shown in Table I

Comp. No.	Ring label	SCI	$P_{\mathrm{LL}_0}\cdot 10^3$	$Z_{\mathrm{LB}}^{\mathrm{total}}$	Z_{LB}^{σ}	Z_{LB}^{π}
1	I	0.048	1000	35.082	29.082	6.000
2	I	0.026	912	34.404	28.692	5.712
3	I	0.022	893	34.339	28.695	5.644
3	II	0.017	840	33.778	28.287	5.491
4	I	0.020	888	34.314	28.697	5.617
4	II	0.015	825	33.731	28.287	5.443
5	I	0.020	886	34.302	28.697	5.605
5	II	0.014	821	33.713	28.289	5.423
5	III	0.013	811	33.689	28.287	5.402
6	I	0.019	888	34.297	28.697	5.600
6	II	0.014	824	33.704	28.289	5.415
6	III	0.013	816	33.674	28.289	5.385
7	I	0.019	885	34.295	28.697	5.598
7	II	0.014	819	33.700	28.289	5.411
7	III	0.012	806	33.667	28.289	5.377
7	IV	0.012	804	33.660	28.291	5.368
8	I	0.030	928	34.497	28.725	5.772
8	II	0.013	813	33.713	28.310	5.403
9	I	0.022	882	34.174	28.547	5.628
9	II	0.013	818	33.771	28.351	5.420
10	I	0.029	923	34.485	28.728	5.757
10	II	0.014	832	33.806	28.338	5.468
11	I	0.033	940	34.589	28.773	5.815
11	II	0.006	714	33.002	27.899	5.104
12	I	0.023	899	34.357	28.693	5.664
12	II	0.018	850	33.846	28.315	5.531

(cont.)

TABLE II (cont.)

Comp. No.	Ring label	SCI	$P_{LL_0}\cdot 10^3$	Z_{LB}^{total}	Z_{LB}^{σ}	Z_{LB}^{π}
12	III	0.010	793	33.642	28.314	5.328
12	IV	0.031	930	34.516	28.730	5.785
13	I	0.016	837	33.884	28.403	5.481
13	II	0.007	753	33.232	27.987	5.245
14	I	0.026	913	34.447	28.726	5.721
14	II	0.011	795	33.501	28.139	5.361
14	III	0.011	802	33.714	28.355	5.359
14	IV	0.015	838	33.875	28.387	5.489
14	V	0.022	880	34.178	28.553	5.625
15	I	0.031	929	34.511	28.732	5.780
15	II	0.011	800	33.661	28.311	5.349
15	III	0.021	863	33.919	28.342	5.577
16	I	0.031	929	34.510	28.730	5.780
16	II	0.011	800	33.669	28.320	5.349
16	III	0.020	863	33.916	28.340	5.576
17	I	0.033	940	34.589	28.775	5.814
17	II	0.006	720	33.048	27.925	5.122
17	III	0.025	894	34.267	28.597	5.671
17	IV	0.013	818	33.769	28.359	5.410
18	I	0.021	890	34.325	28.697	5.628
18	II	0.016	829	33.740	28.285	5.455
18	III	0.016	834	33.790	28.314	5.475
18	IV	0.009	787	33.614	28.316	5.298
18	V	0.031	931	34.520	28.731	5.789
19	I	0.024	901	34.366	28.695	5.671
19	II	0.019	851	33.854	28.318	5.535
19	III	0.008	772	33.570	28.319	5.251
20	I	0.024	903	34.364	28.691	5.672
20	II	0.020	859	33.918	28.355	5.563
20	III	0.004	694	32.936	27.903	5.033
20	IV	0.034	942	34.603	28.780	5.823
21	I	0.029	924	34.490	28.730	5.760
21	II	0.014	827	33.793	28.341	5.452
21	III	0.017	850	33.897	28.365	5.532
22	I	0.028	922	34.478	28.728	5.750
22	II	0.015	836	33.828	28.343	5.486
22	III	0.011	812	33.736	28.342	5.394
22	IV	0.018	848	33.839	28.317	5.522
22	V	0.023	897	34.352	28.694	5.658
23	I	0.023	885	34.215	28.574	5.641
23	II	0.004	698	32.940	27.915	5.024
24	I	0.033	940	34.588	28.775	5.813
24	II	0.005	719	33.041	27.928	5.113
24	III	0.027	906	34.364	28.650	5.713
25	I	0.034	941	34.603	28.782	5.822
25	II	0.004	704	32.993	27.928	5.065
25	III	0.015	838	33.878	28.400	5.478
25	IV	0.024	891	34.268	28.605	5.663
25	V	0.012	804	33.574	28.180	5.394
25	VI	0.027	917	34.452	28.723	5.729
26	I	0.033	940	34.598	28.783	5.816
26	II	0.005	701	32.966	27.908	5.058
26	III	0.024	868	34.049	28.404	5.645

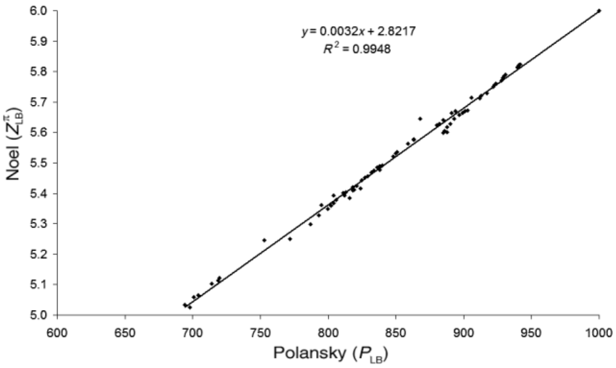


Figure 1. Correlation between the HMO Polansky index P_{LB} and the π component of NOEL Z_{LB}^{π} for the set of studied molecules.

To demonstrate the applicability of the NOEL index as an aromaticity index, it is first shown that there is indeed a close parallel between the NOEL index and the similarity index previously introduced by Polansky and Derflinger.[16] As the aromaticity of PAH is evidently due to the presence of extended delocalized π system, it seems reasonable to assume that such a parallel can be best expected between the original HMO index (3), which is inherently based only on π electron approximation, and the π component of the NOEL index Z_{LB}^{π}. The correlation between the corresponding quantities is displayed in Figure 1.

As Figure 1 shows, the correlation is indeed very good. This result is very important since the existence of the correlation clearly implies that the parallel between both types of indices is indeed very deep. This is especially noteworthy since two quite different quantum chemical theories are used to calculate them, namely the HMO and DFT methods. This proves that the agreement between Eqs. (3) and (12) bears more than a conceptual similarity. In fact, the application of Zero Differential Overlap approximation to equation (12) immediately leads to virtually the same expression as in Eq. (3).

The existence of the nearly perfect correlation between both types of indices also implies that the present quantum similarity approach can indeed be considered as a generalization of the original Polansky approach beyond the scope of HMO approximation. The only difference between the two types of indices is in the scaling. While the similarity of benzene to itself is characterized by the maximum value of the Polansky index 1, the NOEL index Z_{LB}^{π} is in this case equal to 6 (the number of overlapping π electrons between two benzene molecules). In all other cases, the values of both indices are smaller than the above limits and, in fact, the deviations of the actual values from these limits are just a measure of the extent of aromaticity of a given benzenoid ring in any particular case.

Although the existence of the nearly perfect correlation between the original Polansky index and the π com-

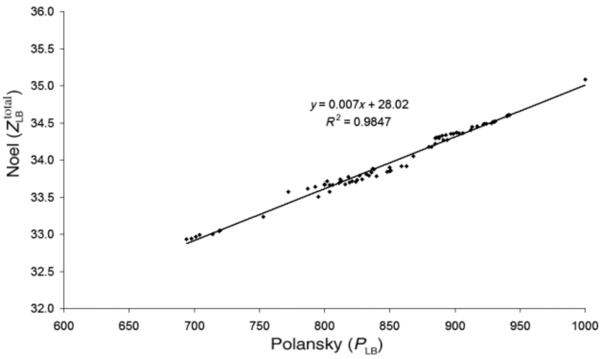


Figure 2. Correlation between Polansky indices P_{LB} and the NOEL index Z_{LB}^{total} for the set of studied molecules.

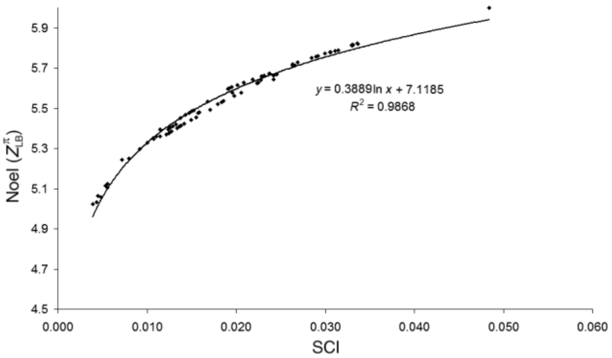


Figure 4. Correlation between the NOEL index Z_{LB}^{π} and the SCI index.

ponent of NOEL is indeed encouraging, it was also interesting to see to what extent the parallel between both indices can be affected by taking into account also the σ component of NOEL. Intuitively, one can expect that because the aromaticity is primarily connected with π electrons, inclusion of electron densities of the σ carbon backbone will probably result in deterioration of the correlation. An example of the correlation of original Polansky indices with the NOEL index Z_{LB}^{total} is shown in Figure 2.

Although the existence of the parallel between Polansky and NOEL indices is still clearly evident, the quality of the correlation is indeed slightly lower than in the previous case. This result is, in fact, not too surprising since the σ component of fragment electron density considered in NOEL can undoubtedly be affected by the steric strain, which in some molecules can result from the close approach of hydrogen atoms. An example of such a strained system can be, *e.g.,* the 3,4-benzophenanthrene (Figure 3) and indeed the point corresponding to ring I of this molecule represents an outlier in the correlation.

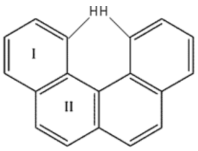


Figure 3. 3,4-benzophenanthrene with the two hydrogen atoms causing high steric strain.

The extent of this strain is, of course, slightly overestimated in our case where the geometry of the carbon skeleton was forced to be planar; in a real molecule, the geometry optimization would release part of this strain by allowing the system to deviate from the planarity.

Besides the above discussed results, another interesting trend lies in the correlation between Z_{LB}^{π} and the Six Center Index (SCI). It was found previously[14] that there is a very good agreement between the SCI and the Polansky index. The same good agreement exists between the SCI and Z_{LB}^{π}. The latter correlation is depicted in Figure 4 with a logarithmic relationship. Such a logarithmic relationship is reminiscent of the Polansky-SCI correlation reported previously.[14]

After having demonstrated the close parallel between Polansky and NOEL indices, let us discuss the relation of the new index to the existing aromaticity measures and indices. For this purpose, we report the results of the statistical analysis aimed at revealing the eventual existence of the mutual correlation between various aromaticity measures and indices. In this study, such a comparison is performed between NOEL and/or SCI and other aromaticity indices such as NICS, Average Two-center Indices (ATI) and the Bond Order Index of Aromaticity (BOIA), whose values were calculated in the same way as described previously.[14] The Harmonic Oscillator Model of Aromaticity (HOMA), a structural criterion,[5,37–38] was not considered in the present study since the use of fixed geometries would yield no differences between the different benzenoid rings.

Results of the mutual correlations of various aromaticity indices are summarized in Table III, which shows the values of the corresponding correlation coefficients R^2.

As can be seen, very satisfactory correlations are observed not only between the NOEL index Z_{LB}^{π}, Polansky index P_{LB} and/or SCI, but correlation of similar quality exists also with another structural aromaticity index – BOIA ($R^2 = 0.94$). Slightly poorer is the correlation with ATI, which is an index related to another aromaticity index, namely the Para Delocalization Index (PDI).[39] On the other hand, there is practically no correlation between Z_{LB}^{π} and NICS. This result is not too surprising. These indices represent, namely, two different types of aromaticity measures (structural *vs.* magnetic), which are usually assumed to be orthogonal and the observed lack of correlation can thus be regarded as an indication of this orthogonality.[8–10]

Summarizing the above results, it is possible to conclude that the correlation between Z_{LB}^{π} and the Polansky index clearly demonstrates that the quantum similarity based index serves as an *ab initio* generalization of the

TABLE III. Correlation coefficients R^2 between different aromaticity indices for the PAH set

	SCI	P_{LB}	$Z_{\mathrm{LB}}^{\mathrm{total}}$	Z_{LB}^{σ}	Z_{LB}^{π}	NICS	ATI	BOIA
SCI	1.00	0.92	0.90	0.84	0.94	0.22	0.77	0.86
P_{LB}		1.00	0.98	0.93	0.99	0.33	0.77	0.92
$Z_{\mathrm{LB}}^{\mathrm{total}}$			1.00	0.98	0.97	0.27	0.70	0.85
Z_{LB}^{σ}				1.00	0.91	0.22	0.62	0.75
Z_{LB}^{π}					1.00	0.33	0.77	0.94
NICS						1.00	0.33	0.46
ATI						0.51	1.00	0.81
BOIA						0.46	0.81	1.00

HMO based Polansky index. It also shows that the quantum similarity theory can be used as the method to quantify concepts such as aromaticity, as it was suggested by Giambiagi *et al.* in their earlier work.[15]

CONCLUSIONS

The Polansky index, introduced in 1967, is based on assessing the similarity between benzenoid rings in polyaromatic hydrocarbons with benzene itself as a reference system. This approach applied the nowadays considered less accurate Hückel MO theory.

By using the quantum similarity theory, a new derivation has been proposed, allowing a generalization of the Polansky index to *ab initio* levels of theory. The similarity is now based on NOEL indices, which are shown to bear a high degree of similarity to the original index. The approach was applied to a set of polyaromatic hydrocarbons, for which the new NOEL indices were used to assess aromaticity. Excellent correlation is found with the Polansky index, especially when only the p electron density matrix is considered in the NOEL index.

The NOEL index of aromaticity can be regarded as a novel quantum similarity based approach to aromaticity. NOEL indices can be computed very efficiently, since they only require the density matrices of two molecules and the overlap matrix between the basis functions of both molecules.

Acknowledgements. – PB acknowledges the support to the Fund for Scientific Research – Flanders (FWO) for its continuous support to the quantum chemistry research group. PB also acknowledges the bilateral agreement between the FWO and the Czech Academy of Sciences allowing a research visit. RCD is grateful to the Ministerio de Ciencia y Tecnología for the grant: BQU2003-07420-C05-01, which partially sponsored this work, and also for the Salvador de Madariaga fellowship reference: PR2004-0547, permitting his stay at Gent University. RP thanks the grant agency of the Czech Academy of Sciences (grant No. IAA4072403) for its support to this work.

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SAŽETAK

Poopćeni indeks Polanskog kao mjera aromatičnosti policikličkih aromatskih ugljikovodika

Patrick Bultinck, Robert Ponec, Ana Gallegos, Stijn Fias, Sofie Van Damme i Ramon Carbó-Dorca

Na osnovi ideja kvantnokemijske sličnosti poopćen je indeks sličnosti Polanskog. Time je ovaj indeks, izvorno definiran u okviru jednostavne Hückelove teorije, u stanju bolje procijeniti udio pojedinačnih benzenskih prstenova u aromatičnosti benzenoida. Indeks se predlaže za novu definiciju aromatičnosti koja je u stanju pratiti svaku inačicu suvremenih *ab initio* računa. Ovaj indeks dobro korelira ne samo s izvornim indeksom Polanskog već i s indeksom na više središta u okviru poopćene populacijske analize.