

The pseudo- π method examined for the computation of multicenter aromaticity indices

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This paper examines the applicability of the so-called pseudo- π method for the calculation of multicenter indices. The pseudo- π method allows for substantial reductions in required computer time, without significant loss of chemical insight. It is found to be a good alternative for the Hückel MO approach and the full *ab initio* approach involving large basis sets.

KEY WORDS: aromaticity, pseudo-pi, delocalization index

1. Introduction

Aromaticity is probably one of the most used concepts in chemistry and has tremendous practical importance [1], although it remains without proper quantum mechanical definition. This has given rise to a multitude of sometimes divergent indices that aim at providing a quantitative measure of aromaticity [2, 3].

Among these we have been using the so-called multicenter indices, which were shown to yield a lot of insight in the aromaticity of polycyclic hydrocarbons [4–7] and also less obvious cases such as homoaromaticity in bicyclic compounds [8]. The calculation of these multicenter indices for a set of atoms $ABC \dots K$ occurs via:

$$I(ABC \dots K) = N \sum_{\nu \in A} \sum_{\mu \in B} \sum_{\sigma \in C} \dots \sum_{\gamma \in K} \sum_i \Gamma_i [(\mathbf{PS})_{\nu\mu} (\mathbf{PS})_{\mu\sigma} \dots (\mathbf{PS})_{\gamma\nu}]. \quad (1)$$

In equation (1), the Mulliken approach is used where \mathbf{P} is the charge and bond order matrix and \mathbf{S} is the overlap matrix between the basis functions. The

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summations over the basis functions are restricted to the atoms involved in the delocalization, and Γ is a permutation operator which generates all the terms involved. N is a scaling constant. In a very similar fashion, an AIM based measure can be used via [7]:

$$\Delta_{ABC\dots K} = N' \sum_i \sum_j \sum_k \dots \sum_x \sum_\alpha \Gamma_\alpha \left[(\Sigma)_{ij}^A (\Sigma)_{jk}^B \dots (\Sigma)_{xi}^K \right], \quad (2)$$

where the $(\Sigma)_{ij}^A$ is now the overlap matrix over the MOs i and j integrated over the domain of atom A ; and the summations run over all occupied spin orbitals. Again a permutation operator is introduced which generates all necessary terms and a scaling factor N' is introduced.

The multicenter indices, in fact, follow a similar philosophy as the so-called Para Delocalization Indices (PDI), where aromaticity is gauged via computing the average of the delocalization indices between two atoms in para position, typically in a benzenoid ring [9]. This PDI index has been used quite frequently, giving quite a fair amount of insight in aromaticity [10]. It is, however, clear that this PDI index is somewhat limited to molecules where one can clearly establish para relationships between different atoms. Also it somewhat overemphasizes Dewar structures [6, 7].

The main disadvantage of the multicenter indices is that they are not always as easy to obtain. They require a lot of computational effort for the higher order indices. Indices involving up to six atoms are computed readily, but beyond that the computer time becomes a limiting factor and the computation of the multicenter index becomes the rate determining step. One possible alternative is to compute the measures at lower level of theory. The Hückel MO method has been shown to give results that are essentially identical to the *ab initio* ones [11], but Hückel theory of course has a limited application due to the lack of any geometry. An interesting alternative was proposed by Fowler and Steiner [12]. In fact, their approach is based on the remarkable analogy between the π system in benzene and a cycle of hydrogen atoms, as originally reported by London [13]. According to Paoloni et al., chemical ideas related to the electron distribution seem to show no preference for the use of $2p\pi$ functions, and nodeless functions work equally well for the description of benzene conjugated system, if not better [14].

Fowler et al. found that when in a (*ab initio* geometry optimized) molecule the carbon atoms were replaced by hydrogen atoms with STO-3G s-type gaussian basis functions and retaining the geometry; the same picture of ring currents remains [12, 15]. This is very interesting since it could open a way to computing approximate multicenter indices very efficiently by a two-step procedure. In the first step, the molecule is conventionally optimized with an *ab initio* method of choice. Subsequently, the carbon atoms are replaced by hydrogen atoms with STO-3G basis functions and the charge and bond order density matrix computed. Finally, the multicenter index can be computed.

2. Computational methods

In order to test the pseudo- π approach, a total of 26 planar polyaromatic hydrocarbons were chosen as a first test set. The molecules chosen include all planar molecules used previously by us for the calculation of the multicenter aromaticity indices [4]. Geometries were optimized at B3LYP/6-31G* level, and verified to be minima. Multicenter indices were computed in the normal fashion using self-written software. In the next step, the hydrogen atoms in the molecule were removed and the carbon atom network was replaced by a hydrogen atom network, keeping the molecular geometry fixed. An *ab initio* calculation is performed using the STO-3G basis set, and the multicenter indices computed using the pseudo- π MOs.

After this application, to test the approach in a more difficult setting; we performed calculations on stepwise more clamped benzene molecules. We computed multicenter indices in the regular and pseudo- π ways for benzene with 1–3 fused rings. It has been shown by ring current calculations and Valence Bond Theory studies that the delocalization of benzene is nearly completely destroyed in the essentially cyclohexatriene ring in the clamped benzenes [16, 17]. First the trend will be established using the regular, full basis set 6-center index (SCI), and then it will be investigated if the same trend is found using the pseudo- π approach.

3. Results and discussion

Table 1 reports the values for the SCI and the PDI for some well-known molecules in the first test set. A Mulliken approach was used throughout, making the PDI reported here equivalent to the previously reported Average Two-center Index (ATI) [4]. For a scrutiny of these values the reader is referred to the works of Bultinck et al. [4–7] and the works of Sola and co-workers [9, 18–20]. Table 1 also reports the values obtained using the pseudo- π method.

As it is immediately seen, the agreement is very good for the SCI and PPSCI, establishing that the pseudo- π method can be a viable alternative to the more time consuming regular method. For the PDI index, the agreement is also very good (R^2 for the set of table 1 0.98). The use of the pseudo- π method allows for a very significant reduction in computer time. Also, the gain becomes more important as one goes to larger molecules. For the smaller molecules in table 1, the gain is of the order 80, but strongly increases for larger molecules. For picene, the time gain is already of the order 200 for the calculation of PPSCI versus SCI.

Figure 1 shows the global correlation for all 79 symmetry unique benzenoid rings in the 26 molecules of the test set. It is found that the correlation is excellent. Not only the trends are confirmed, but also the numerical values

Table 1
 SCI and PDI values computed at B3LYP/6-31G* level and values obtained with the pseudo- π method (PPSCI and PP-PDI) for the benzenoid rings in some well-known compounds.

| Molecule | Ring | SCI | PPSCI | PDI | PP-PDI |
|--------------|-------|--------|--------|--------|--------|
| Benzene | | 0.0484 | 0.0494 | 0.0974 | 0.1111 |
| Naphthalene | | 0.0263 | 0.0267 | 0.0670 | 0.0776 |
| Anthracene | Inner | 0.0189 | 0.0180 | 0.0606 | 0.0669 |
| | Outer | 0.0199 | 0.0203 | 0.0570 | 0.0669 |
| Phenanthrene | Inner | 0.0119 | 0.0123 | 0.0391 | 0.0435 |
| | Outer | 0.0314 | 0.0318 | 0.0729 | 0.0847 |
| Coronene | Inner | 0.0079 | 0.0090 | 0.0328 | 0.0257 |
| | Outer | 0.0164 | 0.0167 | 0.0444 | 0.0508 |

are found to nearly coincide, which is exemplified by a linear correlation with nearly $PPSCI = 1.000 \times SCI + 0.000$ as regression equation. This is in agreement with the findings of Fowler and Steiner [12] and recently by Monaco et al. [15]. Table 1 and figure 1, however, are an independent proof of the validity of the pseudo- π method; since it is now shown that indeed this rather simple approach does retain the delocalization characteristics of the π density in the σ system of the hydrogen network.

Looking at somewhat more difficult cases, the delocalization characteristics are also reconfirmed with the pseudo- π scheme. For example in coronene, the inner ring shows rather small delocalization compared to the outer rings according to the SCI. This is quite well reflected also in the pseudo- π values (see table 1).

Naturally, an interesting application also lies in computing electron delocalization indices in larger circuits. For instance, the 10-center index (TCI) in [10] annulenic circuits in the molecules of the first set. TCI values can hardly be computed at the B3LYP/6-31G* level and are only routinely within reach with HMO calculations. The pseudo- π method could offer an interesting method of lower computational burden without the HMO limitations. Here, the use of the pseudo- π method really allows impressive speed-ups. The TCIs in coronene for example are computed in less than 0.3 seconds on a current desktop computer, whereas it is hardly feasible for the 6-31G* calculation. Table 2 reports some (unscaled) TCI values for different rings in the same molecules as in table 1 (except naturally benzene).

The results of table 2 show that the pseudo- π method allows the very efficient calculation of delocalization indices of extended delocalized systems. The HMO results were previously shown [11] to be in good agreement with the Circuit-Resonance-Energies (CREs) of Aihara [21], and logically the TCI with the pseudo- π method (PPTCI) are also in good agreement with the latter data. The correlation coefficient between the HMO-TCI and PPTCI values is 0.998.

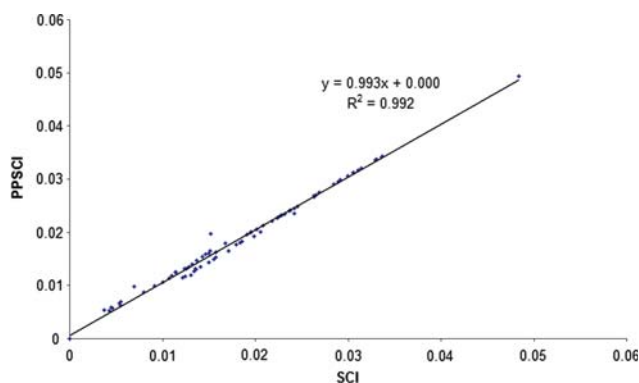


Figure 1. Correlation between SCI values computed at B3LYP/6-31G* level (SCI) and values obtained with the pseudo- π method (PPSCI) for 79 benzenoid rings in 26 polyaromatic hydrocarbons.

Table 2

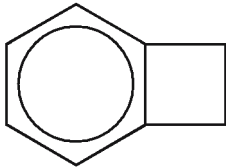
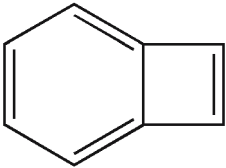
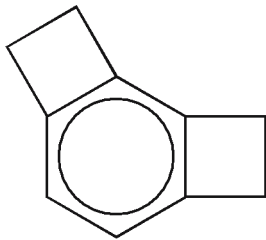
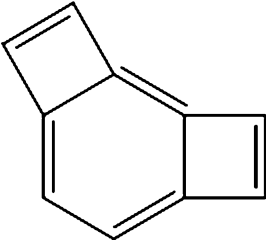
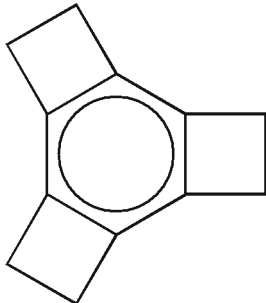
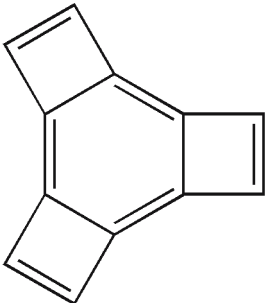
Ten Center Indices (TCI) for naphthalene fragments in some typical polyaromatic hydrocarbons, computed with the HMO (HMO-TCI) and pseudo- π methods (PPTCI). Also indicated are the benzenoid rings that build up the 10 atom fragment (o = outer, i = inner benzenoid ring).

| Molecule | Ring | HMO-TCI | PPTCI |
|--------------|-------|---------|--------|
| Naphthalene | | 0.0615 | 0.0577 |
| Anthracene | | 0.0373 | 0.0363 |
| Phenanthrene | | 0.0291 | 0.0265 |
| Coronene | o + o | 0.0170 | 0.0167 |
| | o + i | 0.0068 | 0.0067 |

It is well-known that aromaticity is quite well retained in benzenoid rings, even under important geometric distortions or the attachment of several functional groups. If the pseudo- π method is to be used for the investigation of “tailor-made” aromaticity, then it should first be established that it is able to reproduce trends obtained at DFT level. Again based on ring currents, Fowler et al. have shown that attaching three cyclobuteno groups to benzene gives only a small reduction of the diamagnetic ring current [16]. On the other hand, introduction of three cyclobutadieno groups causes a severe disruption of the ring current and the loss of the typical aromatic pattern. All this was recently confirmed by Hill et al. using Valence Bond Theory [17]. In order to check whether the multicenter indices can reproduce this, SCI values are shown for all six structures shown in table 3, together with pseudo- π values.

It is immediately seen that first the SCI indeed confirms what was found for structures with three attached rings by Fowler et al. and Hill et al., namely the conservation of aromaticity in molecule 3 and disruption of aromaticity in the tris(cyclobutadieno)benzene 3'; respectively. Furthermore, it is seen that within

Table 3
 SCI (plain numbers) and PPSCI (italic numbers) values for the benzenoid ring 3 cyclobuteno benzenes and three "clamped" cyclobutadieno benzenes.

| Number | Structure | SCI and <i>PPSCI</i> | Number | Structure | SCI and <i>PPSCI</i> |
|--------|--|-------------------------|--------|---|-------------------------|
| 1 |  | 0.0438 <i>0.0371</i> | 1' |  | 0.0341 <i>0.0345</i> |
| 2 |  | 0.0395 <i>0.0493</i> | 2' |  | 0.0100 <i>0.0096</i> |
| 3 |  | 0.0356 <i>0.0491</i> | 3' |  | 0.0030 <i>0.0030</i> |

the group of cyclobutadieno clamped benzenes the SCI varies in a continuous way, and this behavior is also reproduced within the pseudo- π scheme. However, in the case of the aromaticity retaining cyclobuteno benzenes a small problem appears. Obviously, only the carbon atoms involved in π bonding should be replaced by hydrogen atoms. This means that a very similar structure exists for all cyclobuteno benzenes and in the pseudo- π approach the hydrogen network differs only very slightly between all three molecules 1–3. As a consequence, the pseudo- π method agrees with the SCI in that the delocalization is not severely disrupted, but there is no similar decreasing trend observed in the PPSCI values compared to the SCI values. This is simply a consequence of the fact that geometry only cannot account for all changes in aromaticity, especially for relatively

small effects. As a result, the PPSCI values for the benzenes with two or three cyclobutenes attached, are nearly indistinguishable from benzene itself. Still, all the above shows that for the majority of possible applications, the pseudo- π method holds great promise.

It is worth considering why the method works so well. This appears to be consequence of a simple relationship between the π orbitals in the true molecule on the one hand, and the σ orbitals in the hydrogen networked molecule on the other hand. It is straightforward to see that from symmetry group theory there is a simple relationship through $\Gamma_{\sigma} = \Gamma_{\pi} \times \Gamma_z$. Naturally, this simple relationship will hold universally for planar molecules. In some cases, the relationship can even become $\Gamma_{\sigma} = \Gamma_{\pi}$ as for the radial π MOs on a curved surface [12]. As a consequence, Huckel theory can equally well be used within the pseudo- π approach, and even the same molecular orbitals will be found with the same expressions for the energies, of course all properly scaled [12]. It remains naturally quite impressive that there is such a good numerical agreement.

4. Conclusions

In this paper, the pseudo- π approach has been tested for the calculation of multicenter indices. It is found that the values obtained with the real molecular calculation are both qualitatively and quantitatively reproduced within the pseudo- π scheme. This allows to extend the range of multicenter index calculations that can be performed. Moreover, it also supplies completely independent proof for the use of it in ring current calculations, since the extent of delocalization is retained.

The approach was critically tested for a number of ring current containing and destroying substituted benzenes. The SCI values were found to be in agreement with the ring current studies of Fowler et al. and were found to agree very well with those computed via the pseudo- π approach.

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