On the performance of 3D-space based atoms in molecules methods for electronic delocalization aromaticity indices.

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Abstract

Several definitions of an atom in a molecule (AIM) in three dimensional space, including both fuzzy and disjoint domains, are employed to calculate electron sharing indices (ESI) and related electronic aromaticity measures, namely I_{ring} and multicenter indices (MCI), for a wide set of cyclic planar aromatic and non-aromatic molecules of different ring size. The results obtained using the recent iterative Hirshfeld scheme are compared to those derived from the classical Hirshfeld method and from Bader's quantum theory of atoms in molecules. For bonded atoms all methods yield ESI values in very good agreement, especially for C-C interactions. In the case of non-bonded interactions there are relevant deviations, particularly between fuzzy and QTAIM schemes. These discrepancies directly translate into significant differences in the values and the trends of the aromaticity indices. In particular, the chemically expected trends are more consistently found when using disjoint domains. Careful examination of the underlying effects reveals the different reasons why the aromaticity indices investigated give the expected results for binary divisions of three dimensional space.

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1 Introduction

From a genuine chemical point of view, a molecule is conceived as a system built up from interacting atoms, the elementary units in chemistry. Chemical information such as partial atomic charge, bonding interactions, steric repulsion, functional group, etc. rely entirely on the concept of an atom in a molecule (AIM). According to quantum mechanics all physical information on a system is contained in the wavefunction, and well-defined observables can be obtained via the expectation values using the appropriate operator. Unfortunately, the AIM is not an observable. One may argue that since only observables have physical meaning one should restrict oneself to their study. However, one can not dismiss the vast chemical knowledge gathered over almost hundred years since the advent of Quantum Mechanics. [1]

There is a growing interest in devising analysis tools that permit connecting the results of an *ab initio* calculation with classical chemical concepts. Clearly, the definition of an AIM is at the heart of any of these analyses. One can distinguish two main types of atomic definitions that lead to the partitioning of global quantities into their corresponding atomic contributions. The atoms can be identified with the nucleus and the subspace of basis functions centered on (or assigned to) that nucleus. This is often called Hilbert-space analysis, and obviously can only be applied if one-electron atom-centered basis functions have been used in the *ab initio* calculation. Classical methods like Mulliken Population Analysis [2, 3, 4, 5] or Mayer-Wiberg bond orders [6, 7] are based on this atomic partitioning. An alternative that has recently gained more interest is to decompose the three-dimensional space into atomic regions, also called atomic domains. In the latter case, the atomic contribution to a global quantity like the expected value of an operator is obtained by integrating over the corresponding atomic domain.

Within this group one can further distinguish two main lines of thought. First there are several partitioning schemes presenting sharp boundaries between the atomic domains, such as Voronoi cells, [8] Daudel loges [9] or the electron localization function (ELF) basins, [10, 11, 12] but the most widely used in the literature is that derived from Bader's quantum theory of Atoms in Molecules (QTAIM), [13] where the atomic boundaries are determined from the zero-flux surface condition of the gradient of the one-electron density. Second, in a more general framework, the atomic domains can be represented by assigning non-negative atomic weight functions $w_A(\vec{r})$ to each atom A with the requirement

$$\sum_A w_A(\vec{r}) = 1 \tag{1}$$

for each point of the physical space. This representation permits to treat the most different atomic partition schemes with a common formalism. In this sense, the QTAIM is a special case where $w_A(\vec{r}) = 1$ within the atomic domain of atom A or zero otherwise.

In the case of so-called *fuzzy atoms*, the value of the atomic weight function $w_A(\vec{r})$ is close to unity in the vicinity of the atom A and gradually decreases to zero. Hence, the atoms in a molecule are allowed to share the 3D-space to some extent, which permits the definition of overlap populations in the spirit of the classical Mulliken analysis. The numerical integrations over QTAIM atomic basins are sometimes cumbersome due to the rather complicated shapes they may exhibit. In the case of *fuzzy atoms* they are much more straightforward and accurate, which makes these methods more appealing for wider applications.

The *fuzzy atoms* were first introduced by Hirshfeld [14] in his landmark stockholder's scheme. In the Hirshfeld method, the weight or share of an atom is identified with the ratio of its isolated atomic density $\rho_A^0(\vec{r})$ and the promolecular density $\sum_A \rho_A^0(\vec{r})$, obtained by simple superposition of isolated atomic densities

$$w_A(\vec{r}) = \frac{\rho_A^0(\vec{r})}{\sum_A \rho_A^0(\vec{r})} \tag{2}$$

The promolecular density is built for exactly the same geometry as the actual molecule and typically using spherically-averaged densities of the ground-state of the isolated atoms.

One of the main uses of the Hirshfeld method lies in the population analysis. Atomic populations can be obtained by integration of the atomic density of the AIM

$$N_A = \int \rho_A(\vec{r}) d\vec{r} = \int w_A(\vec{r}) \rho(\vec{r}) d\vec{r} \tag{3}$$

The main criticism to the classical Hirshfeld method is that the choice of the electronic state of the isolated atoms can seriously influence the resulting atomic population. This is particularly evident when using ionic atomic densities. [15, 16, 17, 18]

This drawback has been recently overcome by Bultinck *et al.* with the so-called Iterative Hirshfeld approach or Hirshfeld-I. [18, 19] The essence of the method is that the density of the isolated atoms must integrate to the same population of the atom in the actual molecule, that is

$$N_A = \int \rho_A^0(\vec{r}) d\vec{r} = \int \rho_A(\vec{r}) d\vec{r}. \tag{4}$$

This is accomplished in an iterative manner by constructing the isolated atomic densities by interpolation between the densities of the isolated atoms computed with different number of electrons. In particular, Bultinck *et al.* used the expression

$$\rho_A^{0,N_A}(\vec{r}) = (uint(N_A) - N_A)\rho_A^{0,lint(N_A)}(\vec{r}) - (lint(N_A) - N_A)\rho_A^{0,uint(N_A)}(\vec{r}), \tag{5}$$

where $lint(N_A)$ and $uint(N_A)$ represent the lowest and upper integer values of the actual fractional population of the AIM. For an exact theory, this yields exact atomic electron densities for fractional numbers of electrons. The interpolated isolated atomic densities are superposed to build the new promolecular density and to compute the new atomic weight functions. The process is iterated until eq. 4 is fulfilled for each atom within a given numerical threshold. The Hirshfeld-I scheme has been shown to converge to a unique solution and exhibit only very small basis set dependence [20] while at the same time giving atomic charges that reproduce very well the molecular electrostatic potential.[21]

A fundamental difference between Hirshfeld and Hirshfeld-I partitionings is that in the former the same type of atoms are treated in the same fashion irrespective of the chemical environment. The *same* isolated atomic density of a hydrogen atom would be used to obtain the atomic weights of all H atoms of a given ring in a molecule, irrespective of more proton or hydride character.

That is, the partial ionic nature of the atoms may not be properly described. This is also the case of other *fuzzy atom* schemes such as Becke's fuzzy Voronoi polyhedra, where the shape of the atoms is controlled by a set of empiric atomic radii. [22] It is important to note that this is not the case of Hirshfeld-I or QTAIM schemes where the atoms corresponding to the same element are treated on different footing according to either their partial atomic charges (Hirshfeld-I) or roughly the position of their zero-flux boundaries (QTAIM).

Assignment of atomic contributions to physical magnitudes usually require an AIM partitioning; therefore AIMs are used in a plethora of situations in quantum chemistry. Since many AIMs have been put forward, an analysis of the performance of the AIMs is timely and could be of immense importance to reveal the limitations and characteristics of the AIMs. This is particularly important for recently designed AIMs, such as the Hirshfeld-I, which should be analyzed throughout. In this paper, the focus is on the performance of several AIM partitionings in three dimensional space for the calculation of electronic sharing indices (ESI) and related electronic aromaticity measures. Both AIM models presenting sharp boundaries such as Bader's QTAIM, [13] and several *fuzzy atom* definitions including Hirshfeld, [14] the recently introduced Hirshfeld-I, [18, 19] and Becke's fuzzy Voronoi cells are considered. [23] First we discuss the performance of the methods based on an extensive comparison of numerical values obtained for a large set of molecules. Afterwards, a deeper analysis of the discrepancies found is made and the reasons for these disagreements are shown. This will put forward an important limitation of AIMs for their application in aromaticity calculations.

2 Theory

Borrowing Fulton's terminology,[24] the ESI aim to quantify the extent electrons are shared by two (or more) atoms. The classical chemical analog is the concept of bond order. There is a myriad of ESI definitions in the literature derived from ab initio calculations, especially for correlated wave functions. [25] However, in the case of a closed-shell single-determinant wave function it is quite established that the ESI originate from the spinless exchange density

$$\rho_x(\vec{r},\vec{r}\,') = \frac{1}{2}\rho(\vec{r},\vec{r}\,')\rho(\vec{r}\,',\vec{r}), \tag{6}$$

where $\rho(\vec{r},\vec{r}\,')$ stands for the off-diagonal part of the spinless first-order density matrix. The exchange density originates from the antisymmetry requirement of the wave function and describes the Fermi hole. Its normalization

$$\iint \rho_x(\vec{r},\vec{r}\,')d\vec{r}d\vec{r}\,' = N \tag{7}$$

yields N, the total number of electrons of the system. By inserting the identity $\sum_A w_A(\vec{r}) = 1$ twice in the equation above one obtains

$$\begin{aligned} 2N &= \iint \left(\sum_A w_A(\vec{r})\right) \rho(\vec{r},\vec{r}\,') \left(\sum_B w_B(\vec{r}\,')\right) \rho(\vec{r}\,',\vec{r}))d\vec{r}d\vec{r}\,' = \\ &= \sum_A \sum_B \iint w_A(\vec{r})\rho(\vec{r},\vec{r}\,')w_B(\vec{r}\,')\rho(\vec{r}\,',\vec{r}))d\vec{r}d\vec{r}\,' = \\ &= \sum_A B_{AA} + \frac{1}{2}\sum_A \sum_{B\neq A} B_{AB} \end{aligned} \tag{8}$$

a decomposition of the number of electrons pairs in terms of monoatomic (B_{AA}) and diatomic (B_{AB}) contributions. The quantity B_{AB} is identified as the covalent bond order or delocalization index between atoms A and B, [26, 27] whereas the monoatomic counterpart accounts for electron localization. Substituting in the bond-order expression the expansion of the first-order density in terms of the set of doubly-occupied orbitals, we obtain after trivial rearrangements

$$B_{AB} = 4\sum_{i,j}^{occ} \left(\int w_A(\vec{r})\phi_i^*(\vec{r})\phi_j(\vec{r})d\vec{r}\right) \left(\int w_B(\vec{r}\,')\phi_j^*(\vec{r}\,')\phi_i(\vec{r}\,')d\vec{r}\,'\right) = 4\sum_{i,j}^{occ} S_{ij}^A S_{ji}^B, \tag{9}$$

where

$$S_{ij}^A = \int w_A(\vec{r})\phi_i^*(\vec{r})\phi_j(\vec{r})d\vec{r}, \tag{10}$$

are the elements of the so-called atomic overlap matrix over the molecular orbitals.

It is worth noting that the expression 9 holds for any AIM based on the partitioning of the 3D-space; the differences in the ESI values among the several *fuzzy atom* definitions and QTAIM arise only from the shape of the respective atomic weight functions. [28]

Aromaticity is usually claimed to be a multifold property, [29, 30, 31, 32, 33] because of its different manifestations that range from purely energy-based to structural ones. Furthermore, even the use of different aromaticity measures based on the same manifestation is recommended because, as some of us have recently shown, [34, 35] no aromaticity index is infallible. Lately aromaticity measures based on the electronic structure of molecules are becoming popular, and several research groups have contributed to the issue by providing new aromaticity indices. Among others we can mention the I_{ring} [36] of Giambiagi *et al.*, the Six Center Index (SCI) [37] of Bultinck and coworkers, the θ of Matta, [38] the PDI of Poater *et al.* [39] or the FLU of Matito et al. [40, 41]; for recent reviews see Refs. [42] and [43].

We are concerned with the calculation of the local aromaticity of a given molecule with at least one ring structure. Let us suppose such ring structure consists of n atoms, represented by the following string $\mathcal{A}$=$\{A_1$,A_2,...,$A_n\}$, whose elements are ordered according to the connectivity of the atoms in the ring. For such system we can calculate the following electronic aromaticity indices:

A Multicenter based index: $\mathbf{I}_{ring}$

Based on the multicenter index, [44] which accounts for the simultaneous electron sharing of various centers, Giambiagi and coworkers proposed I_{ring} as a measure of aromaticity. [36] The formula reads as follows:

$$I_{ring}(\mathcal{A}) = \sum_{i_1,i_2,\ldots,i_n}^{occ} S_{i_1i_2}(A_1)S_{i_2i_3}(A_2)...S_{i_ni_1}(A_n) \tag{11}$$

where $S_{ij}(A)$ is the overlap of molecular orbitals i and j in the atom A. The larger I_{ring} (larger simultaneous electron sharing of all atoms in the ring), the more aromatic the ring.

The Multicenter Index: MCI

Bultinck and coworkers, [37] with the aim to improve I_{ring}, suggested to sum the contribution from all possible structures generated by permuting the position of all the atoms in the ring (not only the Kekulé structure as I_{ring} does). Such possibility was already discussed by Ponec and cowokers [45, 46] among others. [47] The formula thus reads:

$$\begin{aligned} MCI(\mathcal{A}) &= \sum_{\mathcal{P}(\mathcal{A})} I_{ring}(\mathcal{A}) = \\ &= \sum_{\mathcal{P}(\mathcal{A})} \sum_{i_1,i_2,\ldots,i_n}^{occ} S_{i_1i_2}(A_1)S_{i_2i_3}(A_2)...S_{i_ni_1}(A_n) \end{aligned} \tag{12}$$

where $\mathcal{P}(\mathcal{A})$ stands for $n!$ permutations of the elements in the string $\mathcal{A}$. The original proposal of MCI differs from this one by a numerical factor. In the present paper this factor is skipped for the reasons given in Ref. [48]. As I_{ring}, MCI produces large numbers for aromatic species, and the authors claim negative numbers are indicative of antiaromaticity. [49] The original definitions of MCI and I_{ring} are ring-size dependent, that is to say the number of overlaps multiplying in Eqns. 11,12 depends on the number of member rings. Thus, it is expected a reduction of the values of I_{ring} and MCI as the size of the ring increases. As a consequence, the values of the indices for rings of different sizes cannot be compared. [48] Recently some of us [48, 50] have proposed normalized versions of I_{ring} and MCI that avoid this ring-size dependence, yielding values close to the topological resonance energies per π-electron. [51] In this work, the focus is on the differences between atomic partitions, for which we have chosen the (unnormalized) original indices, so that the differences among the different partitions used are easier to notice.

The para-Delocalization Index: PDI

Fulton, [24] using Hückel theory, and Bader, [52] using QTAIM, showed - at those levels of theory and using those AIM definitions- that benzene has larger para-related atoms electron sharing than meta-related one. Based on this finding, Poater et al. [39] suggested the para-related atoms electron sharing (PDI) as a measure of aromaticity in six-membered rings:

$$PDI(\mathcal{A}) = \frac{\delta(A_1,A_4)+\delta(A_2,A_5)+\delta(A_3,A_6)}{3} \tag{13}$$

Let us briefly analyze here the differences between these three aromaticity measures. I_{ring} uses the overlap between orbitals integrated in atoms that are *formally* bonded, so we may say I_{ring} recovers the *connected-atoms interactions* in a given ring. This is tightly connected with the intuitive definition of aromaticity that defines it is a *measurable degree of cyclic delocalization of a π-electron system.*[53] On the other hand, MCI adds to I_{ring} the values of the products of overlaps between orbitals integrated in atoms non-connected in the ring. Thus, it is expected that the *non-connected-atoms interactions* may be recognized by comparing MCI to I_{ring} values for a given ring. Finally, PDI involves the overlaps of orbitals integrated in atoms in para-position. Some of us already recognized that atomic partitions behave differently for connected and non-connected interactions, and even between the non-connected atoms one may distinguish particular interactions as para-related positions in six-membered rings. [54, 55] It is thus particularly interesting to compare I_{ring}, MCI and PDI in order to analyze the performance of atomic partitions on different kinds of interactions, relevant to account for aromaticity.

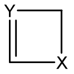
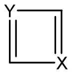
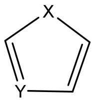
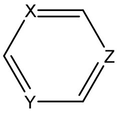
3 Computational Details

The training set of molecules is a collection of three-, four-, five- and six-membered rings (n-MR) molecules (see Fig. 1). All calculations have been performed with Gaussian 03, [56] at the HF level of theory with the 6-311++G(d,p) basis set, [57, 58] restricting the symmetry of the systems to C_s point group. Calculation of the atomic overlap matrices in the framework of Becke's fuzzy-atom has been carried out with a modified version of the AFUZZY program, [59] in order to deal with both Hirshfeld and Hirshfeld-Iterative methods. For numerical integrations we have used a combination of 70 radial and 434 angular points. Details of the implementation can be found elsewhere. [23] The set of covalent radii by Koga, [60] combined with a stiffness parameter [22] of $k = 3$, has been used in the case of the simplest Becke atoms. For both Hirshfeld and Hirshfeld-Iterative models, spherically-averaged atomic promolecular densities, computed for each atom at the same level of theory and basis set as the corresponding molecular calculation, have been used. Open-shell species have been computed at the ROHF level of theory. In the case of the QTAIM model, the atomic overlap matrices have been obtained with the AIMPAC set of programs. [61] Calculation of atomic charges and ESI have been carried out with both AFUZZY [59] and ESI-3D programs. [62] The latter has been also used to compute all electronic aromaticity indices included in this work.

4 Results

For the sake of clarity we will refer to the molecules as n-X;Y with $n = 3 - 5$ or as 6-X;Y;Z, where n is the number of members in the ring, and X, Y and Z are the substituents, according to Fig. 1. 4-MRs, which may have one or two double-bonds, will be explicitly distinguished in the text.

Figure 1: The set of molecules considered in this study.

	X=CH$_2$, CH$^+$, CH$^-$, O, NH, PH, S Y=CH, N, P	21
	X= CH$_2$, O, NH, S, PH Y=CH, N, P	15
	X=CH, N, P Y=CH, N, P	6
	X=, CH$^+$, CH$^-$, O, NH, PH, S, CH$_2$ Y=CH, N, P	21
	X= CH, N, P Y= CH, N, P Z= CH, N, P	10
		$\sum = 73$

4.1 Electron Sharing Indices

First, we will briefly examine the behavior of the atomic charges obtained with the different AIM definitions, specially in the case of Hirshfeld-I scheme. The set of molecules of Fig. 1 contains 559 atoms, including 210 C, 252 H, 42 N, 9 O, 42 P and 4 S atoms. The atomic populations are quite dependent on the AIM definition (see Tables S1-S3 from Supporting Information). In short, QTAIM charges show the widest range of values, even resulting in charges exceeding 2.0 for P atoms. Classical Hirshfeld and Becke atoms yield a lesser degree of polarization and atomic charges rarely exceed 0.5 in absolute value. Hirshfeld-I values lie somewhat in between QTAIM and Hirshfeld, with largest and smallest values of 1.27 and -1.13, respectively. The fact that Hirshfeld-I charges are significantly larger compared to the classical Hirshfeld ones is in line with previous findings by Bultinck et al.[18]

Fig. 2 shows the comparison of Hirshfeld-I charges with both QTAIM and Hirshfeld. The largest differences between Hirshfeld-I and QTAIM are found for P atoms (filled triangles in Fig. 2). Hirshfeld-I charges range from -0.30 to 1.10 whereas for QTAIM they are almost in all cases greater than 1.0 and positive. Quite large discrepancies are also found for negatively charged C atoms in the anionic species, where QTAIM charges are around -1.7 and Hirshfeld-I yields values around -0.7, in better agreement with chemical intuition. The slope of the correlation is 2.0 and the R^2 value is 0.67.

The data is much less scattered when comparing Hirshfeld-I and Hirshfeld values. The slope and R^2 values of the correlation are 0.32 and 0.75, respectively. The individual correlations for different atoms are poor. Bultinck *et al.*[18] reported a somewhat better correlation ($R^2 = 0.82$) and a larger slope for the correlation of Hirshfeld with Hirshfeld-I (3.09 vs 2.33 [1]) for a larger set of molecules containing C, H, N, O, F and Cl atoms. However, the conclusion remains that the Hirshfeld-I charges are significantly larger than Hirshfeld ones.

ESI are typically less dependent on the AIM definition than the electron populations, especially for bonded atoms. [54] However, for non-bonded pairs of atoms significant differences can be observed between non-overlapping AIM models, such as QTAIM, and fuzzy ones like Hirshfeld or Becke. In general, ESI values between non-bonded atoms tend to be larger when using fuzzy atoms.

For clarity, in order to compare the behavior of the Hirshfeld-I method with respect to the other fuzzy atom definitions and QTAIM we will consider three different sets of ESI data, namely between bonded atoms, non-bonded atoms of the ring and non-bonded atoms involving H atoms. The latter is not relevant for this study and will not be discussed. The first and second type of ESI are those that explicitly or implicitly occur in the expression of the electronic aromaticity indices and our findings are described next.

For bonded atoms the ESI values obtained with Hirshfeld-I are in excellent agreement with both the Hirshfeld and Becke methods, with R^2 values of 0.98 and slopes very close to unity (1.06 and 1.07, respectively). When comparing with QTAIM values the agreement is somewhat worse and the correlation coefficient drops to 0.83. In Fig. 3 we show the comparison of Hirshfeld-I and QTAIM

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[1] This is the value of the slope for the reverse correlation, Hirshfeld vs Hirshfeld-I.

Figure 2: Hirshfeld and QTAIM partial atomic charges versus Hirshfeld-I. Filled triangles correspond to QTAIM values for phosphorus atoms (see text). Units are electrons.

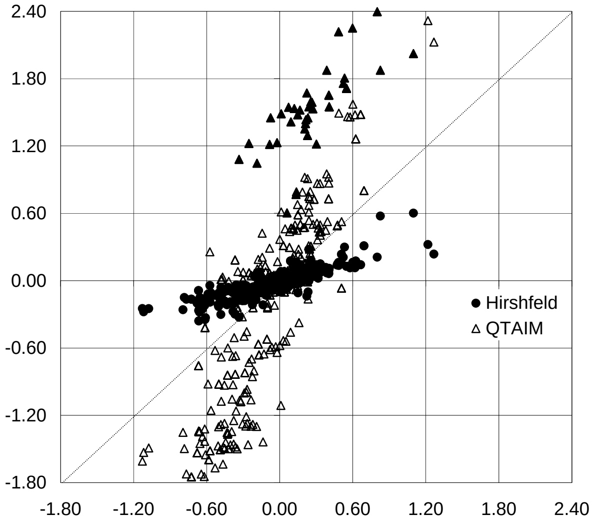
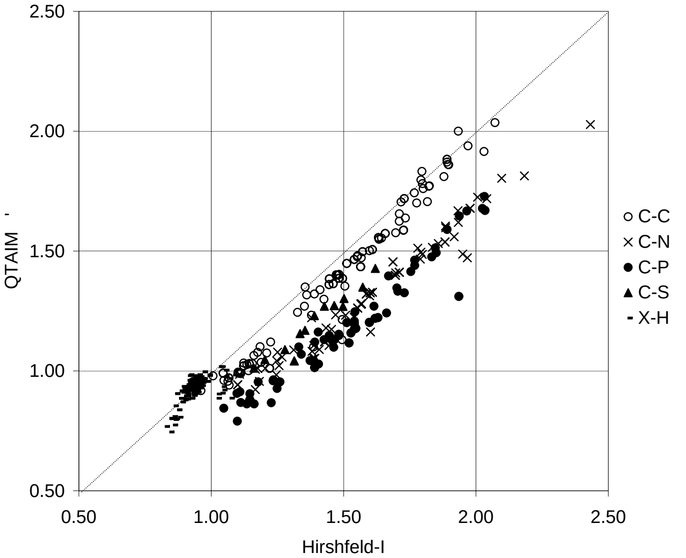


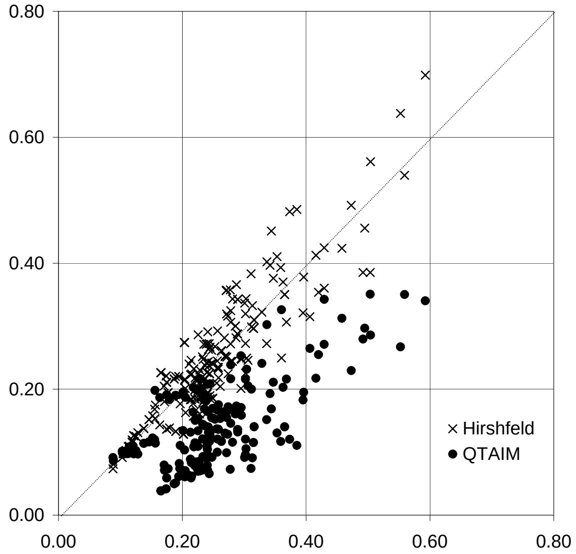
Figure 3: Comparison between Hirshfeld-I and QTAIM ESI values for the more relevant types of bonded interactions. Units are electrons.



ESI values including C-C, C-N, C-P, C-S and bonds involving H atoms. Almost in all cases the Hirshfeld-I values are larger than the QTAIM ones. The trends are similar for each type of bond between the two AIM methods and for the C-C interactions even the differences between the two AIM definitions are small. It is striking to see that the large differences observed between both methods for the partial charges of the P atoms (including sign change) are barely transferred to the corresponding ESI values. Since the H atoms are not part of the rings, their ESI values are not relevant as far as the aromaticity is concerned. Nevertheless it is worth mentioning that the ESI involving H atoms are precisely the ones that show larger discrepancies between Hirshfeld-I and QTAIM. The values are characteristic of a single-bond, ranging from 0.75 to 1.1, but the correlation between both AIM methods is very poor ($R^2 = 0.37$).

The comparison of Hirshfeld-I with Hirshfeld and QTAIM values for ESI between non-bonded atoms of the ring system is displayed in Fig. 4. The data set includes 237 values. The agreement between the different AIM definitions is clearly poorer for the non-bonded interactions. QTAIM values are almost in all cases smaller than those obtained with Hirshfeld-I and their correlation coefficient drops to 0.46. Both Hirshfeld methods are in much better agreement

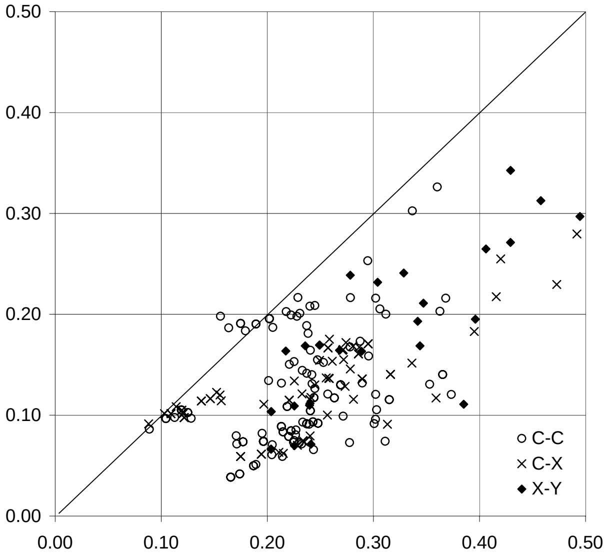
Figure 4: Hirshfeld and QTAIM ESI values for non-bonded interactions versus Hirshfeld-I. Units are electrons.



($R^2 = 0.81$). One can also separate the non-bonded ESI values by type of atoms involved, as shown in Fig. 5. Among all atom pairs, the non-bonded C-C interactions are the ones that show the worst agreement between the corresponding ESI values, showing virtually no correlation. The data corresponding to the interactions involving a C atom and a heteroatom is somewhat less disperse but the agreement is still rather poor. Finally, the *best* agreement is found for ESI associated to interactions between heteroatoms, mainly N and P.

Concerning the rest of AIM schemes, Hirshfeld and Becke values exhibit again very good agreement, the former being systematically larger. This suggests that there are two main factors that influence the values of the ESI for non-bonded interactions. First, the use of disjoint domains, such as in the case of QTAIM, versus fuzzy atom approaches. The ESI values are systematically smaller for the former, in many cases for roughly a factor of two. And second, whether the AIM scheme accounts for the partial ionic character of the atoms, such as for Hirshfeld-I. When the size of the atoms is fixed, either by a single promolecular density (Hirshfeld) or by the atomic radius (Becke) the ESI values are very similar.

Figure 5: Comparison between Hirshfeld-I and QTAIM ESI values for selected types of non-bonded interactions. Units are electrons.



4.2 Electronic Aromaticity Indices

This subsection is devoted to the performance of the Hirshfeld-I method to be used as atomic partition to calculate several aromaticity indices. To this aim, we have computed the I_{ring}, MCI and PDI indices with different atomic partitions of the molecular space: QTAIM, Becke, Hirshfeld and Hirshfeld-I. The values have been scaled with respect to their minimum and maximum value. Notice that values are relative to the maximum/minimum value within a given group, and thus the most aromatic molecule in a given group is not necessarily an aromatic molecule. Namely, as we shall see, cyclobutene and cyclobutadiene are among the most aromatic molecules in the 4-MRs taken into study, while it is accepted that they belong to non-aromatic and anti-aromatic species, respectively. Therefore, one should bear mind that in these species the indices are measuring the degree of electron delocalization as it concerns to its aromatic character.

The values in Table 1 to Table 6 have also been classified in three groups according to the percentile they belong: 33th percentile in black, molecules with values higher than 33th percentile but lower than 67th percentile in blue, and those with higher values are colored in red.

Table 1 contains I_{ring} values for 3-MRs. Interestingly, the three most aromatic and the four least aromatic molecules are recognized by all partitions; values lying in between change from partition to partition. In general, the agreement is fair among Becke, Hirshfeld-I and Hirshfeld partitions, with the only exceptions anions that have lower values for Becke and 3-PH;X (X=P,N) molecules, which have greater values for Becke than the other partitions. QTAIM, on the other hand, gives systematically smaller values of aromaticity in all cases.

Table 2 displays I_{ring} values for 4-MRs with one double bond. The first three entries in the table give similar values of I_{ring} regardless the partition used. All partitions but QTAIM coincide also on the three least aromatic species in the group. However, QTAIM assigns a prominent aromatic character to two of these species, 4-O;P and 4-NH;P. There is also a fair agreement between the range of I_{ring} values given for the rest of molecules in the table according to all partitions but QTAIM, which gives sensibly larger values. We may also analyze the effect of *non-bonding* interactions by comparing I_{ring} values to MCI ones. Most molecules show no important changes upon summation of these extra terms (cf. Eq. 12). This is reminiscent of the case of polyaromatic hydrocarbons. [37] Notwithstanding, the least aromatic molecules (4-PH;P and 4-NH;P) and 4-PH;N (for all partitions but QTAIM) are more aromatic according to MCI, at the expense of O;N that substantially reduces its aromaticity. In the group of two-double bond 4MRs molecules (Table 3) there is a very good agreement among the different atomic partitions. The only exception being 4-N;P, which gives a quite large value in spite of being among the two least aromatic molecules. The inclusion of *non-bonding* terms in this group produces two drastic changes. 4-N;N, the most aromatic molecule according to I_{ring} values irrespectively of the partition, is now among the least aromatic molecules for all methods. All the partitions also agree on 4-CH;CH being the most aromatic molecule. On the other hand, 4-CH;P increases its aromaticity when adding non-bonding interactions.

Table 1: I_{ring} values$^{a)}$ for three-membered rings.

	AIM	BECKE	HIRSH	HIRSH-I
$CH^+;N$	88	100	100	100
$CH^+;CH$	100	97	97	99
$CH^+;P$	81	99	96	98
$CH^-;P$	44	62	68	74
$PH;CH$	48	72	71	74
$CH^-;N$	37	58	68	72
$CH^-;CH$	40	57	67	71
$NH;CH$	53	58	62	67
$CH_2;CH$	51	63	65	66
$CH_2;N$	47	65	66	65
$S;CH$	52	69	65	65
$CH_2;P$	53	62	62	64
$S;P$	49	64	60	59
$S;N$	42	67	61	59
$O;CH$	53	60	59	58
$PH;P$	42	71	55	47
$PH;N$	58	67	53	46
$NH;P$	9	25	16	10
$NH;N$	0	0	2	7
$O;P$	9	18	9	2
$O;N$	3	0	0	0

a) Values scaled according to the formula $x_{\text{norm}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \cdot 100$

Table 2: Scaled I_{ring} and MCI values$^{a)}$ for four-membered rings with one double-bond.

	I_{ring}				MCI			
	AIM	BECKE	HIRSH	HIRSH-I	AIM	BECKE	HIRSH	HIRSH-I
$CH_2;CH$	97	100	100	100	94	98	100	100
$CH_2;N$	91	95	95	94	82	84	89	90
$CH_2;P$	88	78	70	73	85	81	64	70
$PH;CH$	59	62	69	69	42	78	74	77
$S;CH$	76	79	71	67	65	89	73	72
$NH;N$	80	35	50	58	69	31	43	55
$NH;CH$	88	34	51	57	86	53	57	66
$S;N$	80	86	61	52	54	84	53	48
$O;N$	83	37	48	49	66	0	19	26
$O;CH$	90	43	50	48	81	42	43	45
$PH;N$	68	59	52	38	46	100	72	60
$S;P$	66	53	39	35	54	63	33	36
$PH;P$	0	22	19	9	0	47	27	33
$O;P$	100	25	11	5	100	36	0	0
$NH;P$	85	0	0	0	95	41	12	18

a) Values scaled according to the formula $x_{\text{norm}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \cdot 100$

Table 3: Scaled I_{ring} and MCI values$^{a)}$ for four-membered rings with two double-bonds.

	I_{ring}				MCI			
	AIM	BECKE	HIRSH	HIRSH-I	AIM	BECKE	HIRSH	HIRSH-I
$N;N$	100	100	100	100	49	0	3	32
$CH;CH$	69	91	98	93	100	100	100	100
$CH;N$	75	94	96	91	71	72	72	78
$P;P$	61	84	62	70	75	84	47	62
$CH;P$	0	0	2	10	26	74	44	48
$N;P$	34	11	0	0	0	49	0	0

a) Values scaled according to the formula $x_{\text{norm}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \cdot 100$

Table 4 shows the I_{ring} and MCI values for 5-MRs. The values do not predict the same order of aromaticity, although it is worth noting that all partitions agree fairly well on which molecules should be in each group. There are some exceptions in the case of QTAIM, the most noticeable being 5-NH;P and O;P that give lower values for QTAIM than for the other partitions. We appreciate no change in the percentile classification of 5-MRs (no change of color) when we examine the MCI values against the I_{ring} ones.

6-MRs I_{ring} and MCI values are collected in Table 5. It is surprising that according to both Hirshfeld-I and Hirshfeld, benzene is the least of the second least (MCI and Hirshfeld-I) aromatic molecule among those in this group. Following chemical intuition, benzene should be the most aromatic species. This is indeed obtained with the QTAIM and Becke viewpoints. This naturally raises concerns to the extent that the Hirshfeld and Hirshfeld-I partitions are appropriate for the study of aromaticity using the presently described indices or alternatively, to what extent aromaticity indices like the MCI or I_{ring} can be applied universally (see discussion in the next section). The addition of *non-bonding* interactions does not change this situation, it only helps in finding agreement on which should be the least aromatic species, triazine.

Finally, PDI is evaluated with the different partitions in Table 6. All partitions agree on the surprising fact that 6-P;P;N is the most aromatic molecule in this group, more than benzene. Indeed, except for QTAIM, benzene is considered far less aromatic than several other molecules. This is partially due to the fact that the PDI measures the para-related ESI, which is substantial for molecules with larger atoms, such as N or P (see also discussion below). It has been previously observed that PDI is atom-size dependent and, *e.g.*, attributes larger aromaticity to N_6 chair structure than to benzene itself. [35]

All the aromaticity indices are shown to be dependent on the atomic partition used, especially I_{ring} and MCI for 6MRs. In particular, the performance of Hirshfeld-I and Hirshfeld in the latter case is most surprising and therefore merits closer examination.

Table 4: Scaled I_{ring} and MCI values$^{a)}$ for five-membered rings.

	I_{ring}				MCI			
	AIM	BECKE	HIRSH	HIRSH-I	AIM	BECKE	HIRSH	HIRSH-I
$NH;N$	63	86	100	100	75	86	89	90
$CH^-;CH$	100	100	97	91	100	100	100	100
$PH;P$	54	58	81	90	68	77	89	94
$CH^-;N$	72	86	89	84	80	89	91	90
$NH;P$	27	64	77	77	43	77	81	81
$CH^-;P$	71	68	82	75	78	79	88	83
$PH;N$	59	52	64	75	72	65	75	78
$O;P$	9	44	57	62	24	58	59	56
$PH;CH$	61	43	47	56	68	58	65	68
$S;P$	32	31	48	55	40	51	58	54
$O;N$	17	43	51	55	38	53	53	51
$NH;CH$	31	59	55	52	43	69	67	65
$CH^+;N$	11	10	36	49	12	3	0	4
$S;N$	40	27	39	46	54	44	51	47
$O;CH$	14	40	41	44	26	52	51	48
$CH^+;P$	4	5	29	43	9	0	0	0
$CH^+;CH$	3	6	29	39	0	9	15	13
$S;CH$	37	19	24	29	43	36	43	38
$CH_2;P$	0	2	7	8	15	25	20	9
$CH_2;N$	2	1	2	1	17	22	19	7
$CH_2;CH$	2	0	0	0	15	21	18	6

a) Values scaled according to the formula $x_{\text{norm}} = \frac{x-x_{\text{min}}}{x_{\text{max}}-x_{\text{min}}} \cdot 100$

Table 5: Scaled$^{a)}$ I_{ring} and MCI values for six-membered rings.

	I_{ring}				MCI			
	AIM	BECKE	HIRSH	HIRSH-I	AIM	BECKE	HIRSH	HIRSH-I
$P;P;N$	27	85	100	100	36	92	100	100
$P;P;P$	14	0	62	89	23	0	62	94
$P;P;CH$	47	39	53	62	55	43	56	74
$N;N;P$	19	73	71	57	22	61	58	51
$CH;P;N$	48	79	58	53	50	77	57	60
$CH;CH;P$	76	56	28	30	79	55	30	46
$N;N;CH$	33	62	27	14	32	45	16	19
$CH;CH;N$	66	79	20	12	64	73	19	28
$N;N;N$	0	30	25	7	0	0	0	0
$CH;CH;CH$	100	100	0	0	100	100	0	19

a) Values scaled according to the formula $x_{\text{norm}} = \frac{x-x_{\text{min}}}{x_{\text{max}}-x_{\text{min}}} \cdot 100$

Table 6: PDI values$^{a)}$ for six-membered rings.

	AIM	BECKE	HIRSH	HIRSH-I
$P;P;N$	100	100	100	100
$CH;P;N$	93	80	79	79
$CH;CH;N$	85	49	58	69
$CH;CH;P$	95	57	44	68
$P;P;CH$	83	47	39	68
$CH;CH;CH$	97	61	28	57
$N;N;P$	69	67	84	52
$N;N;CH$	53	35	68	46
$P;P;P$	48	0	0	35
$N;N;N$	0	6	68	0

a) Values scaled according to the formula $x_{\text{norm}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} \cdot 100$

5 Discussion and conclusions

In order to shed more light on the reasons why the Hirshfeld and Hirshfeld-I methods do not perform as expected, different further calculations were performed on benzene. For the sake of simplicity, we focus on the relative values of the non-bonded ESI between two carbon atoms in meta and in para position.

According to the work of Fulton,[24] using Hückel theory, the two atoms in para position have a larger ESI than those in meta position. In fact, the meta ESI is exactly zero at the Hückel level of theory, and almost zero for the CNDO case. Later work by Bader *et al.* has shown that using QTAIM the same is true at *ab initio* level. This is no longer the case using the Hirshfeld and Hirshfeld-I methods. Given that the QTAIM method does give the expected result, it could be suggested that the mere use of a set of isolated atomic densities lies at the basis of the disputable results. Recently, a new kind of iterative stockholder approach, known under the acronym ISA,[63, 64] has appeared in which a Hirshfeld-like idea is applied but where no reference is made to an isolated atomic density. [19] However, calculation of the ESI between the carbon atoms using the ISA method revealed that still the atoms in meta position (0.191) have a larger ESI than those in para position (0.122).

It is worth noting that the same effect was already found when using the simpler Becke atoms at both Hartree-Fock [55] and post-Hartree-Fock [25] levels of theory. One can easily tune the shape of the Becke atoms with two parameters, namely the set of atomic radii and the stiffness of the atomic weight function (k, in the original Becke paper [22]). Increasing the value of k decreases the overlap of the atomic Voronoi cells. Furthermore, the partial ionic nature of atoms can be recovered with Becke atoms simply by adjusting the relative size of each pair of atoms according to the position of the minimum of the electron density along the internuclear axis. [23] Such scheme was referred as Becke-rho in Ref. [25] and has also been used by Francisco *et al.* [65]

In Table 7 we provide meta and para ESI values for benzene using regular Becke and Becke-rho schemes and several stiffness values. The Becke-rho scheme tends to QTAIM for increasing values of the stiffness parameter k. In fact, one can almost reproduce QTAIM values with the combination Becke-rho and $k = 5$,

Table 7: HF/6-311++G** ESI values (meta-ESI and PDI) for benzene calculated using different atomic partitions (see text).

	meta-ESI	PDI
QTAIM	0.074	0.098
Becke $k = 3$	0.108	0.101
Becke $k = 4$	0.093	0.101
Becke $k = 5$	0.084	0.102
Becke-rho $k = 3$	0.093	0.092
Becke-rho $k = 4$	0.085	0.094
Becke-rho $k = 5$	0.079	0.095
ISA	0.191	0.122
Hirshfeld	0.192	0.114
Hirshfeld-I	0.203	0.120
Hirshfeld-ID	0.076	0.103

even though the Voronoi cells still exhibit significant overlap. Starting from the results using Becke with the conventional stiffness value $k = 3$, both changing only the atomic size (Becke-rho, $k = 3$) and only the stiffness (Becke, $k = 4$) induce a reduction of the value of the meta ESI. On the contrary, changing only the stiffness to $k = 4$ does not substantially affect the para ESI value (PDI). This is a clear indicator that the PDI is not governed by overlap (it is just necessary to recall that a CNDO calculation also yields a significant Mayer bond order for C atoms in para position).

The PDI does change with the change of atomic size, which for symmetry reasons in the case of benzene is entirely due to the effect of the H atoms. This effect can be quantified to be roughly of 0.007. On the contrary, the meta ESI is more affected by overlap, as the C atoms are close enough. Decreasing the extent of overlap does the same job as adjusting the atomic size. The global effect is to go from 0.108 for Becke $k = 3$ to 0.079 for Becke-rho $k = 5$. Being roughly 0.007 the effect of the C-H interaction, the overlap effects account for the remaining 0.022.

A similar analysis can be extended to the case of Hirshfeld-I in the following manner. After the standard Hirshfeld-I run, at every point in space the weight functions of all atoms are compared. The weight function of the atom with the largest weight function is then set to 1 and that for all other atoms reset to zero. This method, based on letting the atom with the highest Hirshfeld-I weight dominate, will be abbreviated Hirshfeld-ID. Using Hirshfeld-ID (see Table 7) to compute the atomic overlap matrices and ESI it is found that the PDI is now larger than the meta-ESI.

The unexpected trends of the I_{ring} and MCI indices are more difficult to analyze because of the many small contributions. From the analysis above, one can safely expect that the overlap effects must play a much more important role for these indices than for the PDI, which remains almost invariant in spite of the changes made to the atomic partition. Indices such as I_{ring} and MCI used with overlapping atomic domains give completely unexpected results. This therefore leads to the conclusion that these indices should only be used with AIM methods with minimal or zero overlap of atomic domains.

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7 Supporting Information

Individual correlations of the partial atomic charges and values of the aromaticity indices for different AIM definitions.

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