Aromaticity Measures from Fuzzy-Atom Bond Orders (FBO). The Aromatic Fluctuation (FLU) and the para-Delocalization (PDI) Indexes

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In the past few years, there has been a growing interest for aromaticity measures based on electron density descriptors, the para-delocalization (PDI) and the aromatic fluctuation (FLU) indexes being two recent examples. These aromaticity indexes have been applied successfully to describe the aromaticity of carbon skeleton molecules. Although the results obtained are encouraging, because they follow the trends of other existing aromaticity measures, their calculation is rather expensive because they are based on electron delocalization indexes (DI) that involve cumbersome atomic integrations. However, cheaper electron-sharing indexes (ESIs), which in principle could play the same role as the DI in such aromaticity calculations, can be found in the literature. In this letter we show that PDI and FLU can be calculated using fuzzy-atom bond order (FBO) measures instead of DIs with an important saving of computing time. In addition, a basis-set-dependence study is performed to assess the reliability of these measures. FLU and PDI based on FBO are shown to be both good aromaticity indexes and almost basis-set-independent measures. This result opens up a wide range of possibilities for PDI and FLU to also be calculated on large organic systems. As an example, the DI and FBO-based FLU and PDI indexes have also been calculated and compared for the C_{60} molecule.

Introduction

The quest for new aromaticity indexes[1] has recently put forward two new aromaticity indicators based on the electronic structure of molecules: the para-delocalization (PDI)[2] and the aromatic fluctuation (FLU)[3] indexes. These quantities have been calculated using the so-called delocalization index (DI),[4,5] an electron-sharing index (ESI) defined in the framework of the atoms-in-molecules (AIM) theory. In this approach, the zero-flux condition over the electron density provides a 3D exhaustive partitioning of the molecular space into atomic domains, most often containing an atomic center. The integration of the exchange-correlation density over two different atomic domains leads to the DI between the corresponding atoms. Despite their widespread use throughout the literature, these indexes have a serious drawback: the numerical integrations over the atomic domains are often cumbersome because of the complicated and sharp shape of these atomic domains. As a result, the numerical precision gathered can sometimes be rather poor,[6] especially for calculations including electron correlation, where the number of elements of the second-order reduced density matrix is larger (for monodeterminantal wave functions the density matrices are diagonal regardless of their order).

Recently, we have shown that, together with the DI, another two ESIs, namely, the Mayer−Wiberg index (MWI)[7] and the fuzzy-atom bond orders (FBO),[8] give similar quantitive trends in their values for a large set of molecules.[9] In particular, the correlation of these three ESIs for carbon−carbon bonds is excellent. The Hilbert-space-based MWI index is determined easily. However, it is strongly basis-set-dependent, and unphysical negative values can be obtained for nonbonded interactions, such as the ones used to construct the PDI index. On the contrary, the FBO values are less sensitive to basis-set variations and the computational cost of the required numerical integrations[8] is reduced enormously with respect to the DI.

With this in mind, the aim of this letter is twofold. On one side, we will explore the use of FBO for the determination of FLU and PDI indexes for a set of aromatic and nonaromatic molecules and compare the values with those of our previous work,[3] where DIs were used, instead. Second, we will assess the dependence of the aromaticity indexes upon the basis set used. The validity of very modest basis sets such as STO-3G and 3-21G is also addressed with the aim of being able to further extend the present study to much larger organic systems.

Fuzzy Bond Order and Delocalization Index. The ESIs we will use in this letter are based upon the exhaustive partitioning of the molecular space into atomic domains. This allows the integration of any function restricted to a particular atomic domain to provide the respective atomic contribution to its total value. Such partitioning of the space can generally be expressed in terms of some nonnegative weight factors, $w_A(\mathbf{r})$, defined at each point $\boldsymbol{r}$ of the space for every atom A, in such a way that the following condition is fulfilled:

$$\sum_A w_A(\mathbf{r}) = 1 \qquad (1)$$

where the summation runs for all atoms of the molecule.

Alternatively, both the DI and FBO for monodeterminantal wave functions arise from the integration of the so-called exchange density.[4] For a closed-shell single determinant wave function, it can be obtained easily through the nondiagonal part of the spinless first-order reduced density matrix, $\gamma^1(\mathbf{r},\mathbf{r}')$, as

$$\gamma_x(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2}\gamma^1(\mathbf{r}_1,\mathbf{r}_2)\,\gamma^1(\mathbf{r}_2,\mathbf{r}_1) = \frac{1}{2}|\gamma^1(\mathbf{r}_1,\mathbf{r}_2)|^2 \qquad (2)$$

The double integration over the whole space of the exchange

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density provides the number of electrons of the system

$$\int\int \gamma_x(\mathbf{r}_1,\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = N \qquad (3)$$

Now, to obtain the atomic and atom pair contributions of this integral, one simply inserts the identity (eq 1) into the integration (eq 3) for each electron coordinate and interchanges the summation and integration symbols to get

$$\sum_{\mathrm{A}}\sum_{\mathrm{B}}\int\int w_{\mathrm{A}}(\mathbf{r}_1)\, w_{\mathrm{B}}(\mathbf{r}_2)\, \gamma_x(\mathbf{r}_1,\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = \frac{1}{2}\sum_{\mathrm{A}}\sum_{\mathrm{B}}\int\int w_{\mathrm{A}}(\mathbf{r}_1)\,\gamma^1(\mathbf{r}_1,\mathbf{r}_2)\, w_{\mathrm{B}}(\mathbf{r}_2)\,\gamma^1(\mathbf{r}_2,\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = \frac{1}{2}\sum_{\mathrm{A}}\sum_{\mathrm{B}}\int\int \gamma^1_{\mathrm{A}}(\mathbf{r}_1,\mathbf{r}_2)\,\gamma^1_{\mathrm{B}}(\mathbf{r}_2,\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = N \qquad (4)$$

where $\gamma^1_{\mathrm{A}}(\mathbf{r}_1,\mathbf{r}_2)$ can be seen as the atomic nondiagonal first-order density matrix of atom A.

The DI and FBO between two atoms A and B are defined simply as

$$\delta(\mathrm{A,B}) = \int\int w_{\mathrm{A}}(\mathbf{r}_1)\, w_{\mathrm{B}}(\mathbf{r}_2)\,\gamma_x(\mathbf{r}_1,\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 + \int\int w_{\mathrm{B}}(\mathbf{r}_1)\, w_{\mathrm{A}}(\mathbf{r}_2)\,\gamma_x(\mathbf{r}_1,\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = \int\int \gamma^1_{\mathrm{A}}(\mathbf{r}_1,\mathbf{r}_2)\,\gamma^1_{\mathrm{B}}(\mathbf{r}_2,\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \qquad (5)$$

whereas the localization index of atom A, $\lambda(\mathrm{A})$, stands for the integration of both electron coordinates over the same atomic basin

$$\lambda(\mathrm{A}) = \int\int w_{\mathrm{A}}(\mathbf{r}_1)\, w_{\mathrm{A}}(\mathbf{r}_2)\,\gamma_x(\mathbf{r}_1,\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 = \frac{1}{2}\int\int |\gamma^1_{\mathrm{A}}(\mathbf{r}_1,\mathbf{r}_2)|^2\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \qquad (6)$$

By substitution of the definitions 5 and 6 into 4

$$N = \sum_{\mathrm{A}}\lambda(\mathrm{A}) + \sum_{\mathrm{A}}\sum_{\mathrm{B}>\mathrm{A}}\delta(\mathrm{A,B}) = \sum_{\mathrm{A}}\lambda(\mathrm{A}) + \frac{1}{2}\sum_{\mathrm{A}}\sum_{\mathrm{B}\neq\mathrm{A}}\delta(\mathrm{A,B}) \qquad (7)$$

the relationship between the electron population of a given atom, $N(\mathrm{A})$, and its localization and delocalization indexes arise naturally

$$N(\mathrm{A}) = \lambda(\mathrm{A}) + \frac{1}{2}\sum_{\mathrm{B}\neq\mathrm{A}}\delta(\mathrm{A,B}) \qquad (8)$$

Also, some authors[7] define the valence of an atom A, $V(\mathrm{A})$, as the sum of its bond orders

$$V(\mathrm{A}) = \sum_{\mathrm{B}\neq\mathrm{A}}\delta(\mathrm{A,B}) = 2[N(\mathrm{A}) - \lambda(\mathrm{A})] \qquad (9)$$

Finally, the only difference between the DI and FBO is given by the definition of the weight functions (eq 1). Hence, for the DI we have

$$w_{\mathrm{A}}(\mathbf{r}) = \begin{cases} 1 & r \in \Omega_{\mathrm{A}} \\ 0 & \text{otherwise} \end{cases} \qquad (10)$$

where Ω_{A} represents the spatial atomic domain of atom A. That is, $w_{\mathrm{A}}(\mathbf{r}) = 1$ if the point $\boldsymbol{r}$ belongs to the atomic basin of the atom A and is zero otherwise.

On the contrary, the weight factors could be allowed to vary between 0 and 1 in a continuous way, thus reflecting to which extent every point of the physical space belongs to each atom. In this way the atoms are fuzzy entities that overlap and penetrate into each other. There are many ways to define fuzzy atoms, depending on the shape and nature of the atomic weight factors (e.g., Hirshfeld,[10] Davidson,[11] etc.). In this letter we have used the original definition of the FBO, in which the weight factors are simply taken as those derived by Becke[12] for his multicenter integration scheme, tuned with the set of covalent atomic radii of Koga.[13]

Aromaticity Indexes

PDI. Despite the fact that electron delocalization is the key point to the aromaticity, there have been just few attempts[2,3,14−20] to give quantitative aromaticity measures from ESIs. Because these indexes measure the electron sharing between pairs of atoms, one would expect to obtain from them a reliable measure of the degree of delocalization in a given ring. The PDI was one of the first local measures of aromaticity proposed based on ESIs.[2] The PDI is calculated as the average of the three DIs between pairs of atoms in para position in a six-membered ring (6-MR). Although quite simple and resolutive, the PDI has a serious disadvantage: it can be computed only for 6-MR molecules. An alternative definition of the PDI for 5-MR has been suggested $(\Delta\mathrm{DI})^2$, but unfortunately the results are less successful than those obtained from the original 6-MR PDI.

FLU. The electron fluctuation index (FLU) is an appealing proposal to calculate the aromaticity from electron-density-based descriptors.[3] Unlike PDI, FLU can cope with different ring sizes and has been proven to reproduce the trends of other aromaticity indexes in the literature. It is worth noticing that some of us have recently pointed out that the FLU and HOMA indexes should be applied with care to the study of chemical reactivity because they fail to recognize those cases where the aromaticity is enhanced upon deviation from the equilibrium geometry, as is the case of the Diels−Alder reaction.[21] Fortunately, the systems with such behavior are scarce.

The FLU index was constructed following the HOMA philosophy, that is, measuring divergences (electron-sharing differences in the FLU framework) from typical aromatic molecules. To this end, the following formula is given for FLU

$$\mathrm{FLU} = \frac{1}{n}\sum_{\mathrm{A-B}}^{\mathrm{RING}}\left[\left(\frac{V(\mathrm{B})}{V(\mathrm{A})}\right)^{\alpha}\left(\frac{\delta(\mathrm{A,B}) - \delta_{\mathrm{ref}}(\mathrm{A,B})}{\delta_{\mathrm{ref}}(\mathrm{A,B})}\right)\right]^2 \qquad (11)$$

where the summation runs over all adjacent pairs of atoms around the ring, n is equal to the number of atoms of the ring, $V(\mathrm{A})$ is the valence (see eq 9) of atom A, $\delta(\mathrm{A,B})$ and $\delta_{\mathrm{ref}}(\mathrm{A,B})$ are the ESI values for the atomic pair A and B and its reference value, respectively, and

$$\alpha = \begin{cases} 1 & V(\mathrm{B}) > V(\mathrm{A}) \\ -1 & V(\mathrm{B}) \leq V(\mathrm{A}) \end{cases} \qquad (12)$$

Note that the ratio between the valences of the atoms has replaced the fluctuation measures in the original definition of FLU.[3] It can be shown easily that both definitions are equivalent. The second factor in eq 11 measures the relative divergences with respect to a typical aromatic system, and the first factor in eq 11 penalizes the highly localized electron systems.

The weakness of FLU, as is also the case of HOMA, is the need for typical aromatic systems as a reference. From the latter, the corresponding ESI for a given bond is used as a reference for the calculation of the aromaticity of other systems. Therefore, the main shortcoming for this kind of aromaticity measures is the somewhat arbitrary choice of the reference parameters. In a previous work,[3] the reference DI values for C−C and C−N bonds were obtained from benzene and pyridine, respectively. In a forthcoming work we will also give the reference parameter for B−N bonds.[22]

FLU$_\pi$. Because the lack of parameters is the main drawback of FLU, we explored the possibility of a π counterpart of it, FLU$_\pi$, which would measure the degree of global delocalization of the π system. In this way no reference parameters would be needed. The FLU$_\pi$ measure can only be exactly determined for planar molecules, where the corresponding ESIs can be exactly decomposed into its σ and π contributions. However, appropriate orbital localization schemes could be applied to obtain approximate π contributions of the ESI measures for nonplanar molecules. Research in this direction is under way in our laboratory.

The FLU$_\pi$ formula is indeed very similar to eq 11

$$\mathrm{FLU}_\pi = \frac{1}{n}\sum_{\mathrm{A-B}}^{\mathrm{RING}}\left[\left(\frac{V_\pi(\mathrm{B})}{V_\pi(\mathrm{A})}\right)^{\alpha}\left(\frac{\delta_\pi(\mathrm{A,B}) - \delta_{\mathrm{av}}}{\delta_{\mathrm{av}}}\right)\right]^2 \qquad (13)$$

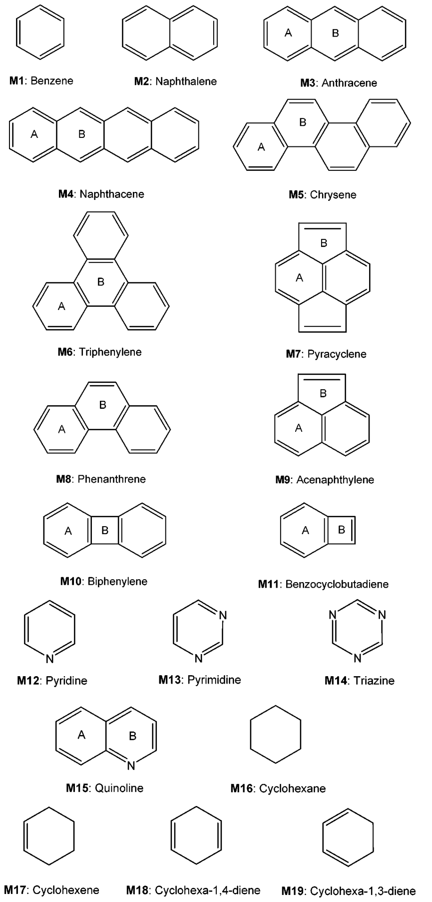
where now δ_{av} is the average value of the π component of the corresponding ESI, and only the π component of the ESI and valence is needed. The correlation between FLU$_\pi$ and FLU has been shown to be excellent for a series of organic compounds.[3] However, one should not expect it to always be like this. Indeed, FLU$_\pi$ is measuring the degree of homogeneous delocalization in a π system, whereas FLU is measuring the degree of similarity with respect to reference aromatic molecules. In this sense, when the aromaticity of the system comes from the delocalization of the π system, as is the case in organic species, both indexes should speak in the same voice. However, some differences can arise when the aromaticity of the system is given, for instance, by the delocalization of the σ electrons, as it could be the case of inorganic species.

Recently, Bultinck et al. have computed PDI values by using the Mulliken-like partition in the Hilbert space spanned by the basis functions instead of the AIM atomic basins for the integration of the exchange-correlation density. Somehow, they have decided to rename the index as an average two-center index (ATI).[14] The authors show that there is a good agreement between ATI and PDI for a large family of benzenoid rings of polycyclic aromatic hydrocarbons. In the same spirit the bond order index of aromaticity (BOIA) measure was also introduced, which, in our opinion, represents a simplified version of our already defined FLU index. Finally, it is worth mentioning in this context that a $\sigma-\pi$ separation for the ELF function has been proposed recently to analyze aromaticity.[19−20]

Computational Details

All calculations were performed with Gaussian 98,[23] AIMPAC[24] packages, and the FUZZY[25] and other software of our own for the FLU and PDI calculations. AIMPAC and FUZZY are freeware, and the FLU program is available upon request to the authors. The integration into the fuzzy atom domains have been carried out using our implementation of Becke's multicenter numerical integration. Particularly, a Gauss−Legendre grid of 30 radial points combined with a Lebedev quadrature of 110 angular points has been used throughout. The accuracy obtained with such a modest grid is comparable to that achieved by AIM integrations, though a much more extensive grid is necessary for the latter.

SCHEME 1: Set of Molecules and Aromatic Rings Studied



We have studied the same set of molecules as in ref 3 (see Scheme 1), calculated at the Hartree−Fock level of theory with the STO-3G, 3-21G, 6-31G*, 6-311G**, and 6-311++G-(3df,2pd) basis sets.

The reference FBO parameters for FLU calculations are 1.40 e for C−C and 1.58 e for C−N. They correspond to the FBO values of the C−C and C−N bonds obtained for the reference benzene and pyridine molecules at the HF/6-31G* level of theory. Note that the latter is slightly different than the suggested value of ref 3. Although the same general trends have been observed for both DI and FBO, the actual values for a given bond do differ and, in some exceptional cases,[6] the description of the bonding can, indeed, be very different.

To illustrate the computational saving in the numerical integration consider the following results: the calculation of benzene at the HF/STO-3G level of theory took about 3 s for FBO, 1 h for DI with the default PROAIM integration algorithm, and 6 h with the PROMEGA[26] one in a simple 1.6 GHz Linux PC. Although most of calculations can be performed with the simplest PROAIM algorithm, unpredictable numerical instabilities may appear eventually, forcing the use of the more robust PROMEGA algorithm to obtain reliable measures. This is especially true for inorganic compounds. For instance, for the Mg_3Na_2 system at the B3LYP/6-311+G* level of theory, about 10 h were needed for a PROMEGA integration, whereas FUZZY ran for just 20 s in the same PC.

Results

The values of the PDI, FLU, and FLU$_\pi$ indexes calculated at the HF/6-31G* level of theory using the FBOs for the set of

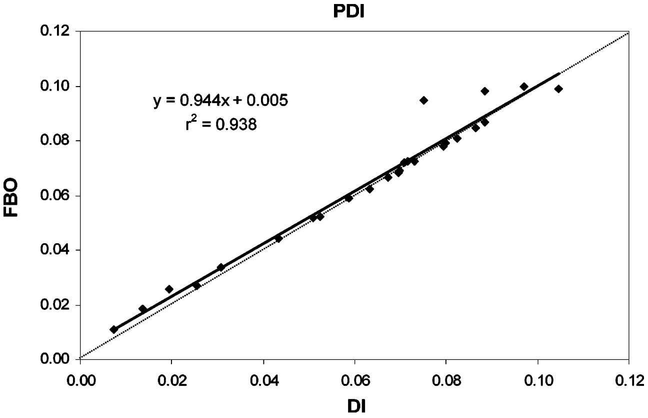


Figure 1. DI- vs FBO-based PDI measures for the set of molecules at the HF/6-31G* level of theory.

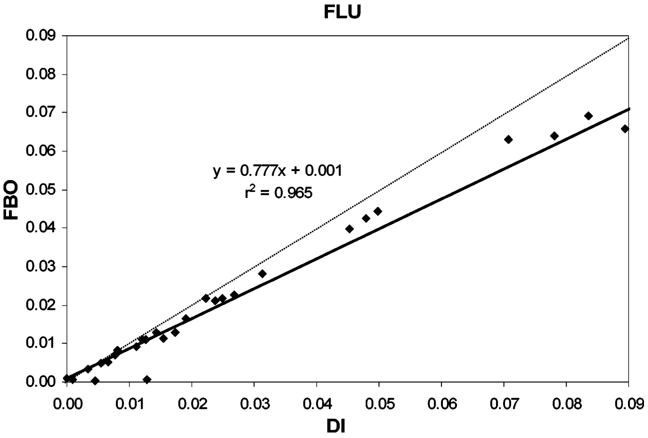


Figure 2. DI- vs FBO-based FLU measures for the set of molecules at the HF/6-31G* level of theory.

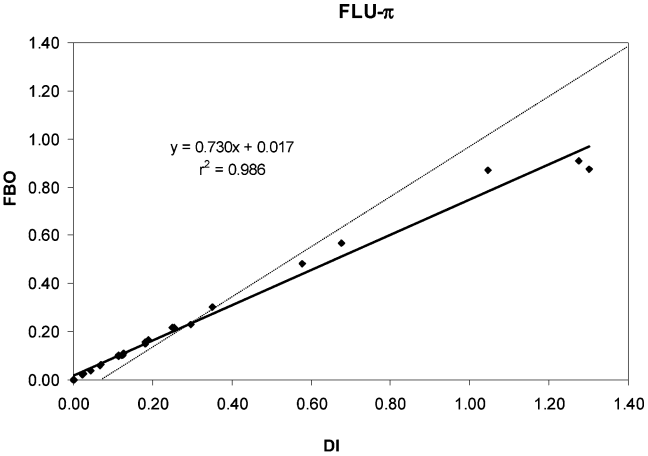


Figure 3. DI- vs FBO-based FLU$_\pi$ measures for the planar molecules of the set at the HF/6-31G* level of theory.

molecules in ref 3 are gathered in Table S1 of the Supporting Information. The corresponding results using DI from ref 3 are also included for comparison in this Table. Figures 1−3 show the correlation between values obtained using DIs and those employing FBOs. PDI was computed only for 6-MRs; likewise, FLU$_\pi$ was calculated only for planar molecules.

The PDI results obtained from DIs and FBOs are strikingly similar, especially for molecules containing only C−C bonds. The correlation depicted in Figure 1 is almost perfect, also with all points close to the $y = x$ line. The only exceptions are those corresponding to triazine and pyrimidine molecules, for which the FBO between the C and N atoms in the para position is larger than the corresponding DI. This can be explained on the basis of a larger polarization of the C−N bonds induced by the AIM partitioning (the AIM and fuzzy atom partial charges on the C atom of the reference pyridine are +0, 750, and −0.052 electrons) that is translated into a lesser availability of the electrons of the C atoms for ring delocalization.

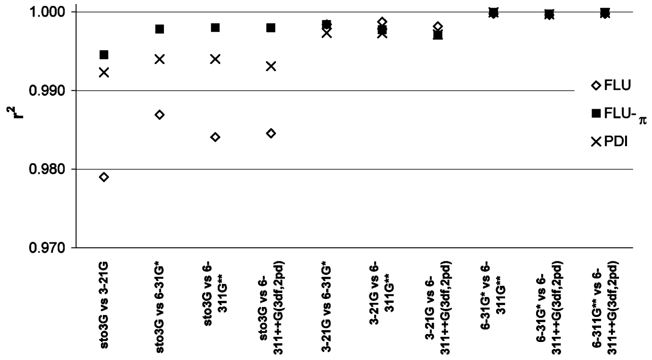


Figure 4. Correlation coefficients r^2 for the pairwise basis-set comparison of FBO-based PDI, FLU and FLU$_\pi$ indexes for the whole set of molecules studied.

The correlation corresponding to the FLU and FLU$_\pi$ results are displayed in Figures 2 and 3. In both cases all points are located below the $y = x$ line, which clearly indicates that the FBO-based values are systematically smaller than those obtained by using DI. The points corresponding to the genuinely nonaromatic molecules slightly leave out of the general trend, but it is well known that nonaromatic species are difficult to correlate, much more if they are included in the set of aromatic ones. Nevertheless, the correlation is again excellent.

The main discrepancy in the FLU correlation comes from the triazine species. In this case, the value of FLU is lower with FBO (nearly zero) than using DI. The reason is simple: the electron sharing of C−N when going from pyridine (taken as a value of reference) to triazine decreases from the DI point of view (leading to higher FLU and lower aromaticity), but stands with a similar magnitude from the FBO perspective (thus, leading to a quite aromatic molecule). Because the FLU$_\pi$ is based on averages rather than differences, this discrepancy is not observed. However, for the same reason, both pyridine and triazine are predicted to have the same degree of aromaticity.

In general, it seems that for aromatic rings the FBO between the same pair of bonded atoms are not too dependent on the actual molecule, so the reference and average values are expected not to be too different. Therefore, FLU and FLU$_\pi$ describe aromaticity in a very similar fashion.

Alternatively, the dispersion on the corresponding DI values is larger, which makes the FLU values larger, and thus they cover a wider range than the FBO-based ones. However, this effect is not translated into the FLU$_\pi$ results because no noticeable discrepancies are observed for the genuinely aromatic molecules of the set. Hence, this seems to indicate that the nature of the dispersion on the DI between bonded atoms is of σ origin. In short, FLU and FLU$_\pi$ are more prone to differ in the quantitative prediction of the aromaticity if using DI as descriptors.

To assess the consistency of the method, we have also carried out a systematic analysis of the basis-set effects on the values of the aromaticity indexes. In particular, we have used, in addition to the 6-31G* basis set, the STO-3G, 3-21G, 6-311G**, and 6-311++G(3df,2pd) basis sets. Each molecule has been fully optimized at the given level of theory, and the aromaticity indexes have been computed with the corresponding electron density using FBOs. In Figure 4 we have represented the r^2

TABLE 1: Buckminsterfullerene DI and FBO (in Electrons) and C−C Distances (in Å) for Symmetrically Different C−C Pairs[a]

atom B	$\delta^{FBO}(1,B)$	$\delta^{AIM}(1,B)^{b}$	$\mathbf{r}_{1,B}$	layer
4	0.069	0.053	2.369	1
5	1.135	1.118	1.464	1 (ortho)
11	0.003	0.002	4.525	2
12	0.013	0.012	3.583	2
13	0.073	0.056	2.467	1 (meta)
14	0.004	0.003	4.124	2
15	0.008	0.007	3.705	2
16	1.423	1.415	1.385	1 (ortho)
17	0.046	0.046	2.849	1 (para)
18	0.074	0.056	2.467	1 (meta)
23	0.013	0.012	3.583	1
24	0.004	0.003	4.124	2
25	0.003	0.002	4.525	2
26	0.000	0.000	5.217	3
27	0.001	0.000	5.419	3
34	0.000	0.000	6.146	4
35	0.001	0.000	5.797	3
36	0.001	0.000	5.489	3
37	0.007	0.008	4.836	2
38	0.003	0.003	4.609	2
42	0.000	0.000	7.114	4
44	0.000	0.000	6.708	4
45	0.000	0.000	6.961	4
51	0.001	0.000	5.489	2
52	0.000	0.000	6.146	3
53	0.000	0.000	6.672	4
54	0.001	0.000	5.797	3
55	0.002	0.002	6.073	3
56	0.000	0.000	6.978	4
57	0.000	0.000	6.518	4
58	0.000	0.000	6.672	4
PDI	0.046	0.046		
FLU (5-MR)	0.036	0.041		
FLU (6-MR)	0.018	0.020		

[a] Atom 1 has been chosen as a reference. [b] From ref 27.

coefficients for the linear correlation between each pair of basis sets and for each aromaticity index. The correlations are, once again, excellent. It is striking to see that, even for the PDI values, which are based on nonbonded interactions, the r^2 coefficient between the minimal STO-3G and the extended 6-311++G-(3df,2pd) basis sets exceeds 0.99. The least correlated values are obviously those from smaller basis sets, and concerning mainly the FLU index, whose values for the STO-3G basis set lay between 0.98 and 0.99. However, one must bear in mind that the $\delta_{ref}(A,B)$ value has not been changed from basis to basis, in order to use a *universal* DI of reference regardless of the basis set employed. It is worth noticing that despite the use of this universal reference the correlations coefficients are always above 0.98.

The validity of the results obtained with such minimal basis sets opens up a wide range of possibilities for PDI and FLU to be calculated on much larger organic systems, for which the calculation of other aromaticity indexes such as NICS could be prohibitive.

Finally, to show the applicability of the method to large systems, we have also determined the FBO-based FLU and PDI values for fullerene C_{60} and compared them with previous DI-based results from ref 27 (see Table 1). The calculations have been performed at the HF/6-31G*//AM1 level of theory and the atomic numeration together with the layer's nomenclature are also taken from ref 27. One can see clearly that results from FBO mimic those already reported with DI. Consequently, the same chemical picture of the aromaticity features of the system is obtained with a substantial reduction of the computational cost.

Conclusions

PDI, FLU, and its π counterpart, FLU_{π}, measures have been calculated for a series of aromatic and nonaromatic molecules replacing the DI from the AIM theory by FBO. The results obtained have been compared with the those from ref 3 obtained using DIs. The corresponding values for each aromaticity index are in excellent agreement, particularly for the molecules containing only C−C bonds. The correlation for the PDI index is surprisingly good, taking into account that it is based on the electron sharing between nonbonded atoms.

The slight deviations between the FBO and DI between C−C and C−N bonded atoms are translated into some differences between the FLU and FLU_{π} indexes, as the corresponding electron-sharing reference and average values change, respectively. Nevertheless, the correlation between the FBO- and DI-based FLU and FLU_{π} is still excellent.

In addition, a basis-set-dependence study has been performed to assess the reliability of the FBO-based indexes. The indexes are strongly insensitive to the basis set, even for the modest STO-3G basis set. This result opens up a wide range of possibilities for PDI and FLU to also be calculated on large organic systems.

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Supporting Information Available: The values of the PDI, FLU, and FLU_{π} indexes calculated at the HF/6-31G* level of theory using the FBOs for the set of molecules in ref 3 are gathered in Table S1. The corresponding results using DI from ref 3 are also included for comparison. This material is available free of charge via the Internet at http://pubs.acs.org.

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