

Comparison of the AIM Delocalization Index and the Mayer and Fuzzy Atom Bond Orders

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In this paper the behavior of three well-known electron-sharing indexes, namely, the AIM delocalization index and the Mayer and fuzzy atom bond orders are studied at the Hartree–Fock level. A large number of five-membered ring molecules, containing several types of bonding, constitute the training set chosen for such purpose. A detailed analysis of the results obtained shows that the three indexes studied exhibit strong correlations, especially for homonuclear bonds. The correlation is somewhat poorer but still significant for polar bonds. In this case, the bond orders obtained with the Mayer and fuzzy atom approaches are normally closer to the formally predicted bond orders than those given by the AIM delocalization indexes, which are usually smaller than those expected from chemical intuition. In some particular cases, the use of diffuse functions in the calculation of Mayer bond orders leads to unrealistic results. In particular, noticeable trends are found for C–C bonds, encouraging the substitution of the delocalization index by the cheaper fuzzy atom or even the Mayer bond orders in the calculation of aromaticity indexes based on the delocalization index such as the para-delocalization index and the aromatic fluctuation index.

Introduction

Since the early work of Mulliken,¹ when one desires to characterize the chemical structure of a certain molecule, the first attempts usually point toward density-based descriptors. Most popular indicators of electron distribution in a molecule are the electron population and the bond order. The latter, together with the quantities more generally labeled as “electron-sharing indexes”—borrowing Fulton’s² terminology—have gained first place in order to characterize the nature of the chemical bond.

A number of bond orders are nowadays available for such purposes: delocalization index (DI),³ Mayer bond order (MBO),⁴ those derived from natural bond orbital (NBO) analysis,⁵ or fuzzy atom bond order (FBO)⁶ are just a few examples in a never-ending list of indexes. The question of whether these indexes can predict the same electron-sharing between the atoms of a molecular system is still open. In this paper we choose three of the most popular electron-sharing indexes (DI, MBO, and FBO) with the aim of assessing their similarities and analyzing possible divergences. As shown before,^{3,6,7} at the Hartree–Fock (HF) level of theory these three indexes have a similar expression since all of them share the same formula but define the atomic regions in a different way. Thus, at least a general agreement in their magnitudes is expected.

These bond orders have been sometimes referred to as covalent bond orders.^{8,9} In fact, it has been also shown that at the RHF level of theory the bond order between two atoms is proportional to the expected value of the spin coupling between their unpaired electrons.¹⁰

Theory. The three bond orders or electron-sharing indexes studied in this work arise from the analysis of the so-called

exchange-correlation density:¹¹

$$\gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \gamma^1(\mathbf{r}_1)\gamma^1(\mathbf{r}_2) - \gamma^2(\mathbf{r}_1, \mathbf{r}_2) \quad (1)$$

which is defined through the diagonal terms of the spinless first-order, $\gamma^1(\mathbf{r})$, and second-order,¹² $\gamma^2(\mathbf{r}_1, \mathbf{r}_2)$, density matrixes. The exchange-correlation density accounts for the difference between an independent electron model and a “true” electron pair one and integrates to the number of electrons in the system:

$$\int \int \gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 = N^2 - N(N - 1) = N \quad (2)$$

For a single determinant wave function, hence within the HF framework, the second-order spinless density matrix can be obtained through the nondiagonal terms of the first-order one:

$$\gamma^2(\mathbf{r}_1, \mathbf{r}_2) = \gamma^1(\mathbf{r}_1)\gamma^1(\mathbf{r}_2) - \frac{1}{2}\gamma^1(\mathbf{r}_1, \mathbf{r}_2)\gamma^1(\mathbf{r}_2, \mathbf{r}_1) \quad (3)$$

Thus, the HF exchange-correlation density takes the well-known simple form:

$$\gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\gamma^1(\mathbf{r}_1, \mathbf{r}_2)\gamma^1(\mathbf{r}_2, \mathbf{r}_1) = \frac{1}{2}|\gamma^1(\mathbf{r}_1, \mathbf{r}_2)|^2 \quad (4)$$

Note that we could have written γ_x instead of γ_{xc} in eq 4 as at the HF level the Coulomb correlation is not included. Substitution of eq 4 into eq 2 leads to

$$N = \int \int \gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 = \frac{1}{2} \int \int \gamma^1(\mathbf{r}_1, \mathbf{r}_2)\gamma^1(\mathbf{r}_2, \mathbf{r}_1) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (5)$$

The goal now is to exactly decompose the two-electron integral of eq 5 into one- and two-atom contributions. The corresponding diatomic contributions give rise to the bond order between the two atoms involved (the one-atom contributions are called

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localization indexes within the Atoms in Molecules (AIM)^{13,14} framework, whereas twice the diatomic contributions are often referred as delocalization indexes (DIs)^{3,15}. The strategy that allows us to obtain such one- and two-atom contributions is briefly discussed below.

Delocalization Index (DI). The basic idea behind a 3D physical space partitioning analysis is to assign every point \mathbf{r} of the physical space to a given atom. That is, each atom has a region of the space assigned to it (usually called “atomic domain” or “atomic basin”). The integral of a mono-electronic function can be performed, often numerically, over each atomic domain giving the corresponding atomic contribution to it. It is evident that if the partitioning of the physical space is exhaustive, the total integral can be exactly recovered by summing all atomic contributions. Similarly, the integral of a two-electron function will be decomposed as the sum over all pairs of atomic contributions.

The decomposition of the space into atomic domains is usually carried out within the framework of the AIM theory.^{13,14} In this context, the so-called DI,^{3,15,16} $\delta^{\text{AIM}}(\text{A,B})$, between atoms A and B is obtained by integration of the exchange-correlation density over the atomic domains of atoms A and B (Ω_A and Ω_B):

$$\delta^{\text{AIM}}(\text{A,B}) = \int_{\Omega_A} \int_{\Omega_B} \gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \int_{\Omega_B} \int_{\Omega_A} \gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = 2 \int_{\Omega_A} \int_{\Omega_B} \gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (6)$$

By virtue of the relation (eq 1), the previous expression can be written as

$$\delta^{\text{AIM}}(\text{A,B}) = 2 \int_{\Omega_A} \int_{\Omega_B} \gamma^1(\mathbf{r}_1) \gamma^1(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - 2 \int_{\Omega_A} \int_{\Omega_B} \gamma^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = 2 \langle N_A \rangle \langle N_B \rangle - 2 \langle N_A N_B \rangle \quad (7)$$

where the quantities $\langle N_A \rangle$ and $\langle N_A N_B \rangle$ correspond to the expected number of electrons and electron pairs over the atomic domain Ω_A and the atomic pair domain $\{\Omega_A, \Omega_B\}$, respectively. Equation 7 is very important as it shows that the DI can be related to the *covariance* of the populations in the domains of atoms A and B:

$$\text{Cov}[N_A, N_B] = \langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle \quad (8)$$

which in turn is a measure of the correlation between both populations. When the wave function is expressed as a single determinant, like in the present work, the DI can be easily obtained from the numerical integration of eq 5 over the atomic domains:

$$\delta^{\text{AIM}}(\text{A,B}) = \frac{1}{2} \int_{\Omega_A} \int_{\Omega_B} \gamma^1(\mathbf{r}_1, \mathbf{r}_2) \gamma^1(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \int_{\Omega_B} \int_{\Omega_A} \gamma^1(\mathbf{r}_1, \mathbf{r}_2) \gamma^1(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 = \int_{\Omega_A} \int_{\Omega_B} |\gamma^1(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (9)$$

For a closed-shell system, the DI can be expressed as

$$\delta^{\text{AIM}}(\text{A,B}) = 4 \sum_{ij} S_{ij}^A S_{ij}^B \quad (10)$$

where S_{ij}^A is the overlap between doubly occupied molecular orbitals (MOs) i and j over the basin of atom A.

Using the expansion of the MOs as a linear combination of atomic orbitals (LCAO), the first-order density matrix for a single-determinant closed-shell wave function

$$\gamma^1(\mathbf{r}, \mathbf{r}') = \sum_{\mu\nu} D_{\mu\nu} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}') \quad (11)$$

can be expressed in terms of the set of basis functions $\{\chi_{\mu}\}$ where the wave function is expanded, and the elements of the so-called density matrix, D , are defined as:

$$D_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i}^* \quad (12)$$

with C being the matrix containing the MO coefficients. Substituting eq 11 into eq 9, we are left with an alternative expression for $\delta^{\text{AIM}}(\text{A,B})$:

$$\delta^{\text{AIM}}(\text{A,B}) = \sum_{\mu, \lambda} (DS^A)_{\mu\lambda} (DS^B)_{\lambda\mu} \quad (13)$$

where the atomic overlap matrix elements of atom A are given by

$$S_{\mu\nu}^A = \int_{\Omega_A} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (14)$$

An interesting property of the DI thus defined is that it is a nonnegative quantity. Indeed, according to eq 4 the exchange-correlation density for a single-determinant wave function is a nonnegative two-electron function. Even though this property of the exchange-correlation density does not hold at the correlated level, the DIs are necessarily nonnegative because, for a given pair of atoms, any increase of $\langle N_A \rangle$ necessarily implies a decrease of $\langle N_B \rangle$; hence the covariance¹⁷ of both quantities is negative (negative slope).

The DI was originally defined by Bader as a *measure of the extent of the correlative interactions between electrons into different regions*¹⁵ and was only later studied as a bond order.^{2,7,9} The fact that for unequally shared electron pairs the DI provides a bond order value lower than the formally expected¹⁸ supports the association of the DI with a *covalent* bond order.^{8,9,19} In 1999, Fradera et al.³ revised the index and defined it as an electron-sharing index, refusing the idea of using it as a bond order (covalent or not) for several reasons.^{3,20} It is worth mentioning that, in the single-determinant approach, the definitions of the bond order given by Fulton and co-workers^{2,21–24} and Ángyán et al.⁷ fully coincide with the DI defined in the framework of the AIM theory. Finally, this index has been studied at both correlated (CISD)^{3,25–27} and non-correlated levels (HF), and with the intention of computing the indexes for a DFT calculation, Kohn–Sham orbitals were also used as an approximation to recover the pair density.²⁶

Fuzzy Atom Bond Order (FBO). Another approach that has been recently explored in the context of population analysis^{28,29} and later on bond order⁶ and energy decomposition schemes³⁰ is the use of “fuzzy atoms”, where the atomic domains do not have boundaries. Instead, at every point \mathbf{r} of the space a weight factor $w_A(\mathbf{r})$ is defined for each atom (A) to measure to which extent the given point belongs to atom A. These atomic weight factors are chosen to be nonnegative and to satisfy the following condition when summing over all atoms of the system:

$$\sum_A w_A(\mathbf{r}) = 1 \quad (15)$$

To decompose the exchange-correlation density into atomic pair contributions, one simply substitutes eq 11 in the right-hand side of eq 5 and inserts the identity of eq 15 for the coordinates of the two electrons in each of the integrals to obtain

$$N = \sum_{\mu\nu\lambda\sigma} D_{\mu\nu} D_{\lambda\sigma} \int \chi_{\nu}^*(\mathbf{r}_1) \sum_A w_A(\mathbf{r}_1) \chi_{\lambda}(\mathbf{r}_1) d\mathbf{r}_1 \times \int \chi_{\sigma}^*(\mathbf{r}_2) \sum_B w_B(\mathbf{r}_2) \chi_{\mu}(\mathbf{r}_2) d\mathbf{r}_2 = \sum_A \sum_B \sum_{\mu\nu\lambda\sigma} D_{\mu\nu} D_{\lambda\sigma} \times \int \chi_{\nu}^*(\mathbf{r}_1) w_A(\mathbf{r}_1) \chi_{\lambda}(\mathbf{r}_1) d\mathbf{r}_1 \int \chi_{\sigma}^*(\mathbf{r}_2) w_B(\mathbf{r}_2) \chi_{\mu}(\mathbf{r}_2) d\mathbf{r}_2 = \sum_A \sum_B \sum_{\mu\lambda} (DS^A)_{\mu\lambda} (DS^B)_{\lambda\mu} \quad (16)$$

where “atomic” overlap matrix elements for an atom A are now

$$S_{\mu\nu}^A = \int \chi_{\mu}^*(\mathbf{r}) w_A(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (17)$$

The bond order between atoms A and B is defined analogously to eq 13 as

$$\delta^{\text{FBO}}(\text{A,B}) = \frac{1}{2} \sum_{\mu,\lambda} (DS^A)_{\mu\lambda} (DS^B)_{\lambda\mu} + \frac{1}{2} \sum_{\mu,\lambda} (DS^B)_{\mu\lambda} (DS^A)_{\lambda\mu} = \sum_{\mu,\lambda} (DS^A)_{\mu\lambda} (DS^B)_{\lambda\mu} \quad (18)$$

Note that eqs 13 and 18 only differ in the definition of the atomic overlap matrix elements. Also, since the weight factors are strictly nonnegative, the bond order within the framework of the fuzzy atoms is a positive quantity as well.

Finally, the DI can be understood as a special case of the FBO where the weight factors are simply defined as $w_A(\mathbf{r}) = 1 \wedge w_B(\mathbf{r}) = 0 \forall B \neq A$ if $\mathbf{r} \in \Omega_A$, that is, a Bader atom.

Mayer Bond Order (MBO). Substitution of the exchange-correlation density corresponding to a closed shell monodeterminantal wave function (eq 11) into eq 5, followed by LCAO replacement of the MOs and substitution of the integrations over atomic basins by a Mulliken-like partitioning of the corresponding integrals leads to, after trivial manipulations, the well-known definition of the Mayer bond order (MBO):^{4,31–34}

$$\delta^{\text{MBO}}(\text{A,B}) = \frac{1}{2} \sum_{\mu \in A} \sum_{\lambda \in B} (DS)_{\mu\lambda} (DS)_{\lambda\mu} + \frac{1}{2} \sum_{\mu \in B} \sum_{\lambda \in A} (DS)_{\mu\lambda} (DS)_{\lambda\mu} = \sum_{\mu \in A} \sum_{\lambda \in B} (DS)_{\mu\lambda} (DS)_{\lambda\mu} \quad (19)$$

where the overlap matrix elements are defined as:

$$S_{\mu\nu} = \int \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d\mathbf{r} \quad (20)$$

It is worth noting that the expressions for the DI, FBO, and MBO given in eqs 13, 18, and 19, respectively, only differ in the definition of the atomic overlap matrix elements.

The same expression can be derived from the *one-atom spinless first-order density matrix*,³⁵ defined as follows:

$$\gamma_A^1(\mathbf{r}, \mathbf{r}') = \sum_{\mu \in A, \nu} D_{\mu\nu} \chi_{\nu}^*(\mathbf{r}) \chi_{\mu}(\mathbf{r}') \quad (21)$$

being the total first-order density the sum of the atomic contributions:

$$\gamma^1(\mathbf{r}, \mathbf{r}') = \sum_A \gamma_A^1(\mathbf{r}, \mathbf{r}') \quad (22)$$

An effective HF exchange-correlation density between atoms A and B can be built from the corresponding pairs of one-atom densities of atoms A and B according to

$$\gamma_{xc}^{\text{AB}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \gamma_A^1(\mathbf{r}_1, \mathbf{r}_2) \gamma_B^1(\mathbf{r}_2, \mathbf{r}_1) + \frac{1}{2} \gamma_B^1(\mathbf{r}_1, \mathbf{r}_2) \gamma_A^1(\mathbf{r}_2, \mathbf{r}_1) = \gamma_A^1(\mathbf{r}_1, \mathbf{r}_2) \gamma_B^1(\mathbf{r}_2, \mathbf{r}_1) \quad (23)$$

The integration of this function gives directly the same expression as eq 19 for the bond order between atoms A and B in a more intuitive way:

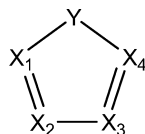
$$\delta^{\text{MBO}}(\text{A,B}) = \int \gamma_A^1(\mathbf{r}_1, \mathbf{r}_2) \gamma_B^1(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 = \sum_{\mu \in A, \nu} \sum_{\lambda \in B, \sigma} D_{\mu\nu} D_{\lambda\sigma} S_{\nu\lambda} S_{\sigma\mu} = \sum_{\mu \in A} \sum_{\lambda \in B} (DS)_{\mu\lambda} (DS)_{\lambda\mu} \quad (24)$$

The MBO, as most of the Hilbert-space based methods, is especially sensitive to the basis set used in the calculation.^{7,36} Particularly, the inclusion of diffuse functions that lack of a marked atomic character can destroy the chemical picture of the molecular system. The index is also ill-defined when bond functions are included or for a non-LCAO-type calculation. It is, however, very easy to calculate and computationally inexpensive. In particular, the DI involves numerical integration over the atomic domains, which is sometimes a CPU demanding procedure due to the complex topology the domains can exhibit (sometimes the integration can fail). Also, if nonnuclear attractors are found in the electron density the chemical picture of the molecule is lost, since there are regions of the physical space that are not assigned to any atom of the molecule. On the other hand, both the DI and FBO are more stable with respect to the change in the basis set,^{3,6,16} at the expense of a bigger computational effort.

The numerical integrations to be carried out within the fuzzy atom framework are sensibly less expensive and straightforward than those involving the DI. Since the expression for the DI is analogous to that of the FBO, one is tempted to use the atomic overlap matrix elements obtained using fuzzy atoms and hence use the FBO for the calculation of other existing DI-based indices such as the para-delocalization index (PDI)^{37,38} and aromatic fluctuation index (FLU)³⁹ aromaticity descriptors. However, there is a certain degree of arbitrariness concerning the definition of the weight factors that characterize the fuzzy atoms. In the actual implementation of the method, the authors used Becke’s method⁴⁰ for multicentric integration, where the weight factors are obtained through an algebraic function for each atom that is equal to one in the vicinity of the respective nucleus and progressively decreases to zero with the distance. This function depends on some set of atomic radii and a so-called stiffness parameter that controls the “shape” of the atom. Other weight functions have been used, including Hirshfeld’s⁴¹ original idea of promolecular densities. Nevertheless, even though numerical experience seems to indicate that reasonable results can be obtained using Becke’s function, it is mandatory to explore the effect of, for example, using a different set of atomic radii.

Therefore, the aim of the present work is to shed light on the following questions: (a) to what extent three of the most popular electron sharing indexes can predict the same electron pair distribution in a molecule?; (b) can the fuzzy atom-based bond order be used instead of the more expensive AIM-based counterpart?; and (c) are the fuzzy atoms bond orders stable enough with respect to the change of the atomic radii used to define the weight factors? To this end, we have computed the

SCHEME 1: Structures of the Molecules Studied with $X_1, X_2, X_3, X_4 = \text{C, N or P, Y} = \text{BeH}^-, \text{B}^-, \text{BH}, \text{BH}_2^-, \text{O}, \text{S, NH, PH, CH}^-, \text{CH}_2, \text{CF}_2, \text{N}^-, \text{NH}_2^+, \text{Al}^-, \text{AlH}, \text{AlH}_2^-, \text{SiH}^+, \text{SiH}_2, \text{P}^-, \text{PH}_2^+, \text{GaH}, \text{GaH}_2^-, \text{GeH}^-, \text{GeH}^+, \text{GeH}_2, \text{As}^-, \text{AsH}, \text{AsH}_2^+, \text{Se, C}=\text{CH}_2, \text{C}=\text{O, C}=\text{S}$ or $\text{C}=\text{Se}$



DI, FBO, and MBO values for a subset of 117 five-membered ring molecules (see Scheme 1) of those 219 chosen by Cyrański et al.⁴² to test different aromaticity indexes. This set of molecules yielded 3619 different measures of the indexes, with a rich variety of bonds (see caption of Scheme 1), including a considerable number of C–C bonds in different bonding situations. With this large and diverse set of bonds we can better grasp reliable conclusions about Mayer, fuzzy atom, and AIM bonding description abilities.

It is worth noting that a comparison between the DI and MBO results was already carried out by Ángyán et al.⁷ and Bocchicchio et al.⁴³ for a reduced set of simple molecules. These authors concluded that the picture of bonding for nonpolar chemical bonds given by DI and MBO is practically equivalent. However, for polar bonds, the difference between these two indexes becomes significant. In particular, the DI yields bond ionicities much greater than the MBO approach. In the present work, we extend these previous investigations by performing a systematic and exhaustive study on 3619 different types of chemical interactions. In addition, for the first time, the analysis includes the recently defined FBOs. An especial attention will be paid to the C–C bond orders.

Computational and Technical Details

We have performed single-point calculations of all analyzed molecules at the HF level with the 6-311+G** basis set on the geometries reported by Cyrański et al.,⁴² which were optimized at the MP2 level with the same basis set. In some particular cases the 6-311G** basis has also been used (see below). All electronic structure calculations were performed with Gaussian 98.⁴⁴ The DIs were obtained using a slightly modified version of the AIMPACK⁴⁵ package. Fuzzy atom bond orders were calculated with the FUZZY code,^{6,46} which implements a Becke's multicenter integration algorithm with the Chebyshev and Lebedev radial and angular quadratures, respectively. A grid of 30 radial by 100 angular points per atom has been used in all cases. We have employed the Becke's algebraic function with the recommended stiffness parameter $k = 3$. We have used the set of atomic radii determined by Suresh and Koga,⁴⁷ except as otherwise indicated.

From the set of 219 molecules of Cyrański et al.,⁴² we have chosen those containing two conjugated double bonds, as detailed in Scheme 1. Additionally, the molecules were chosen on the basis of their accurate and easy numerical integration with program AIMPACK, so that we could get correct measures of DI. The total number of studied molecules was finally 117. As a whole, from 122 molecules with conjugated double bonds present in ref 42, we have ruled five out because of integration problems.⁴⁸

Results and Discussion

Figures 1–3 show the correlation between the MBO, the bond order derived from the partitioning of the molecular space in

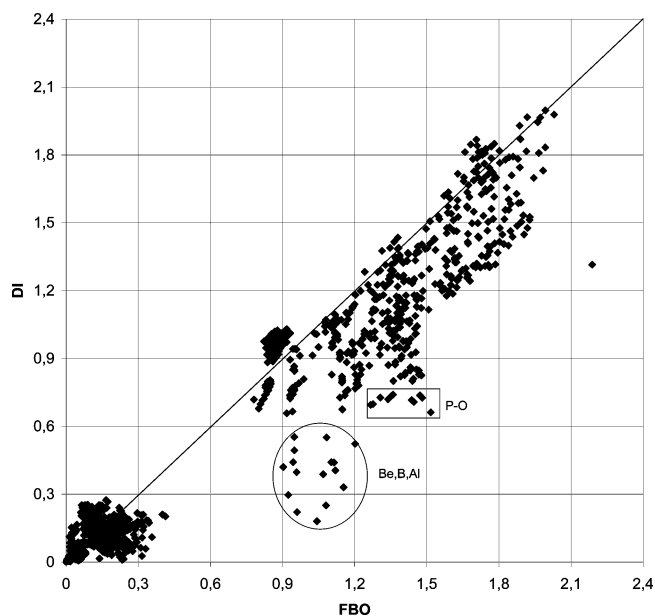


Figure 1. Plot of delocalization index (DI) against bond order from fuzzy partitioning (FBO).

fuzzy atoms (FBO) and the Bader's AIM DI. In all of the figures we can clearly distinguish two regions: one corresponding to the bonded pairs of atoms, with appreciable values for the bond order, and another containing nonbonded pairs, with values below 0.5. In the three plots, the points of nonbonded pairs of atoms organize on a round shape fashion, showing no clear tendency; fluctuating from index to index. This lack of trend leads us to assert that, apparently, no reliable comparison of the indexes can be done within nonbonded pairs of atoms. Nevertheless, we are currently exploring this issue in deeper detail.

The first plot (Figure 1) shows the correlation between the DI and the FBO indexes. The points corresponding to bonded pairs organize in a thick band centered slightly below the $y = x$ line; thus, almost all bonded pairs of atoms exhibit a higher value of the FBO than the DI. However, the correlation is quite good, especially for homonuclear apolar bonds. The two groups of points enclosed with a square and a circle in Figure 1 are the two major sets of uncorrelated bond orders. The first group consists of bond orders involving B, Be, or Al atoms. The number of electrons shared by these atoms is drastically decreased within the AIM framework. This is not surprising since DIs of 0.272, 0.503, and 0.393 were already reported³ for the corresponding hydrides (BeH_2 , BH_3 , AlH_3) at the HF/6-311++G** level of theory (electron correlation has a minor effect on these values^{3,26}). At the same level of theory, the FBOs are 0.986, 0.977, and 0.949, respectively. This difference in bond orders is the result of the different space partitioning, and it is in line with the big difference in the net atomic charges given by the two schemes. The calculated Bader atomic partial charges of Be, B, and Al atoms in the hydrides were +1.7, +2.1, and +2.36 au while the fuzzy atom approach leads to significantly smaller atomic charges of 0.06, -0.18, and 0.39, respectively. Indeed, in the case of BH_3 , when the atomic radius of B in the FBO calculation is adjusted in order to reproduce the AIM charges, the FBO value drops down to 0.519, quite close to the DI value. This seems to indicate that, similar to DI, the FBO values can be very small for bonded interactions provided that strong ionicity is also predicted. Nevertheless, since the adjusted value of the B radius is as low as 0.22 au, generally one should not expect FBO to provide such small values when using

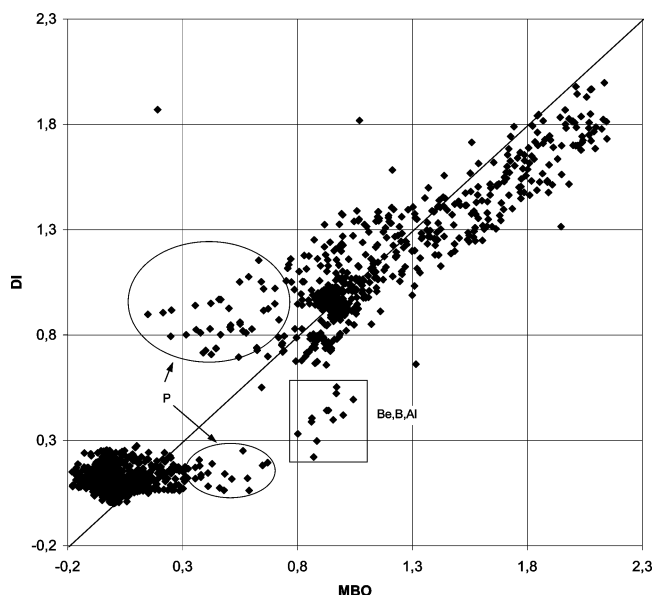


Figure 2. Plot of delocalization index (DI) against Mayer bond order (MBO).

balanced sets of atomic radii. The fact that atomic charges and bond orders are not observables prevents distinguishing between any of the two possible interpretations of these results, that is, either the DI overemphasizes the ionic with respect to the covalent character or the FBO underestimates the ionic character of the chemical bonds. However, in this case, the FBO results are more consistent with the expected formal bond orders. The data within the square in Figure 1 correspond to P–O-type bonds. These are considered as single bonds within AIM ($\delta^{\text{AIM}}(\text{P},\text{O}) \approx 0.8$), while FBO reports a bond multiplicity between single and double ($\delta^{\text{FBO}}(\text{P},\text{O}) \approx 1.4$). Previous calculations by Chesnut^{49,50} on P–O bonds also yield DI values lower than expected from the formal multiplicity of the bonds. Thus, Chesnut reports for formally single P–O bonds DI values of 0.60–0.90 au and of 1.40 and 1.54 au for formal P=O double bonds. It seems clear from the data presented that DI values are sometimes too small to be considered as bond order indexes from the classical point of view. However, even though Bader and co-workers³ refuse the idea of using the DI as a bond order, its expression at the HF level is deeply connected with other bond order indexes. Thus, a priori one would have expected a more similar behavior between the DI and the analogous FBO indexes.

In Figure 2 the correlation of DI and MBO indexes is depicted. The data on this plot are somewhat more spread, especially in those regions marked with circles and a square, which will be discussed in greater detail later. Again, no correlation is observed for the nonbonding interactions (bottom left data) with DI values below 0.3 au. As a general trend, formal bond orders for homonuclear chemical bonds are well-reproduced by both DI and MBOs, whereas DI yields rather systematically lower bond orders than MBOs for polar bonds.^{7,43} In this sense, most values of the bond order tend to appear below the $y = x$ line. In fact, the largest calculated DI is 2.00, whereas for MBO values up to 2.15 have been frequently observed.

Although the correlation between both indexes is rather good, there are again some particular bond types that are poorly correlated. The encircled points mostly contain data obtained for bonds involving phosphorus atom, such as P–O, P–C, or P–N. The MBO values for these bonds are, in general, below 0.5, yielding negative values in some particular cases. The explanation for this odd behavior of the MBO in these cases is

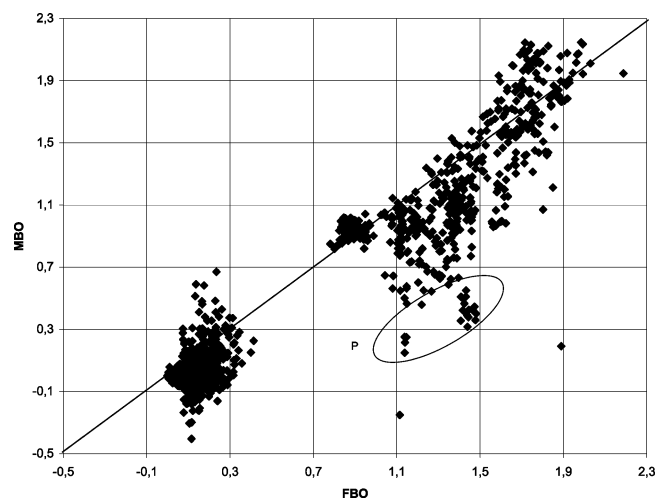


Figure 3. Plot of Mayer bond order (MBO) against bond order from fuzzy partitioning (FBO).

given below. The bonding interactions involving B, Be, and Al atoms (data inside the square) are in line with the aforementioned underestimation of the bond order by the DI in polar bonds. Now this hypothesis is put forward in the light of the values assigned by MBO, which yields values of ca. 0.9 for single (B, Be, Al)–X bonds, much closer to the FBO than to the DI. Finally, some points are clearly off the correlation. For instance, in the top left and center of the plot, two points with a DI of ca. 1.8 present a corresponding MBO of 0.25 and 1.1. These values correspond to C=S and C=Se bond types, respectively. The MBO values are clearly too small. We have repeated the calculation for these two molecules with different basis sets in order to determine whether it can be assigned to a basis set deficiency. It has been found that increasing the basis set quality up to 6-311++G(2df,2pd) barely changes the value of the bond order. However, with the 6-311G** basis set, the MBO values increase up to 1.89 and 1.76, respectively. Thus, as already reported,⁷ including diffuse functions in the calculation can dramatically affect the MBO values. This deficiency is also well-known for other Hilbert-space descriptors such as Mulliken charges.⁵¹ The observed discrepancies in the P–(C, N, O) bonds pointed out above can also be attributed to the effect of the diffuse functions on the calculation of MBOs.

Finally, the correlation between MBO and FBO is shown in Figure 3. Most of the data appear below the $y = x$ line, so that the FBO values are in general larger than the MBO ones. Again, the bond type that exhibits more dispersion in the calculated values involves the phosphorus atoms due to poor MBO values induced by the use of diffuse functions. The most dramatic case, however, corresponds to an Al–C bond with a FBO value close to 1 that presents an unphysical negative MBO value. The corresponding MBO value calculated from a HF/6-311G** wave function yields 0.60.

In conclusion, we can say that there is a general good agreement in the trends showed by the three indexes. This is especially true for homonuclear interactions. In this case, unsurprisingly, the different methods of partitioning the molecular space produce comparable partitioning schemes and, consequently, lead to similar bond orders. The correlation becomes poorer for polar bonds. In particular, the DI values for polar bonds were normally slightly below the expected values. In addition, large deviations are found for bonds involving phosphorus atoms. In this latter group of molecules, the MBO method often fails to properly describe the bonding, due to the effect of diffuse functions lacking of marked atomic

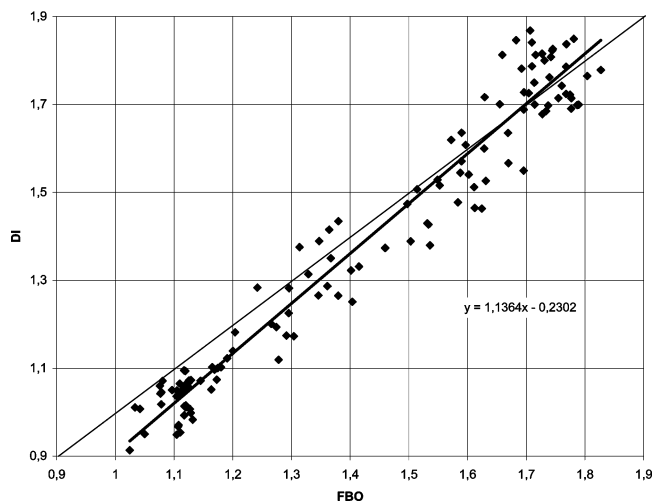


Figure 4. Correlation of delocalization index (DI) with bond order from fuzzy partitioning (FBO) for the 179 different C–C bonds contained in our training set of molecules; correlation coefficient $r = 0.9765$.

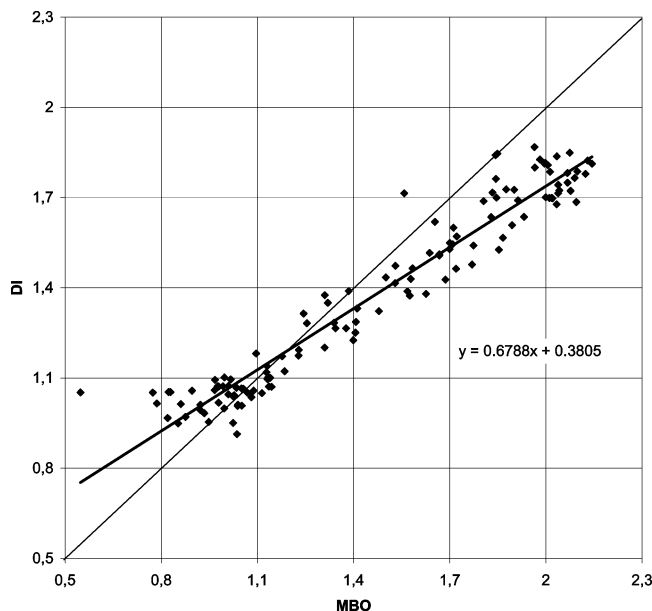


Figure 5. Correlation of delocalization index (DI) with Mayer bond order (MBO) for the 179 different C–C bonds contained in our training set of molecules; correlation coefficient $r = 0.9687$.

character. For bonds involving B, Be, and Al atoms, the DI values differ considerably from both FBO and MBO ones, leading to unrealistically low bond orders.

From the groups of indexes studied we have extracted those concerning C–C bonding interactions. Analogous correlations to those depicted in Figures 1–3 have been constructed for this subset, consisting of 179 values, and plotted in Figures 4–6. As expected from the fact that we restrict the comparison of bond orders to homonuclear bonds, the agreement is better between DI and FBO values, whereas some points are off of the correlation in Figures 5 and 6 where MBO is correlated. However, again, one has to bear in mind that these points out of the trend may be due to the use of diffuse functions. It is also worth mentioning that the FBO values are systematically larger than MBO or DI ones. Nevertheless, the results are encouraging since all plots show good correlations (Pearson coefficient is always above $r = 0.96$) between the three methods. This opens up the possibility of using either the FBO or MBO procedures to construct reliable bond order-based indices instead

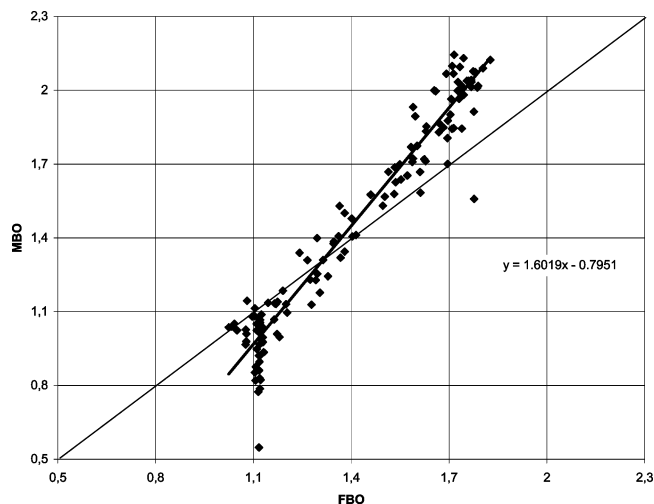


Figure 6. Correlation of Mayer bond order (MBO) with bond order from fuzzy partitioning (FBO) for the 179 different C–C bonds contained in our training set of molecules; correlation coefficient $r = 0.9646$.

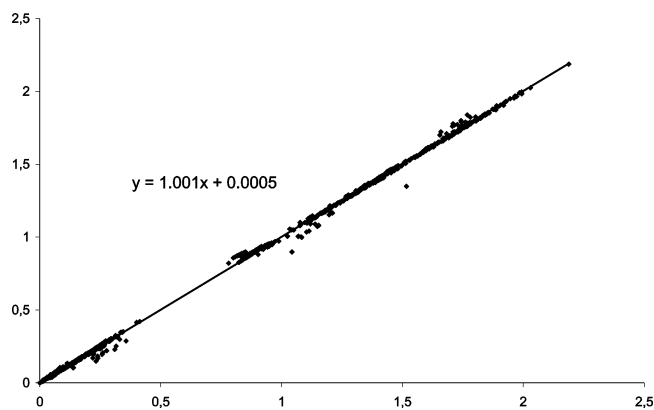


Figure 7. Correlation of bond order from fuzzy partitioning (FBO) calculated using Koga vs Slater–Bragg atomic radii sets; correlation coefficient $r = 1.0000$.

of the existing computationally demanding AIM-based ones. In particular, we plan to explore this possibility for PDI and FLU.^{37,39}

As aforementioned, the weight factors that control the shape and size of the fuzzy atoms are not uniquely defined. An exhaustive analysis of the effect of different weight factors upon the fuzzy atom derived indices probably deserves special attention, and it is out of the scope of the present work. Nevertheless, we have tested the effect of taking a different set of atomic radii that are used to determine the weight factor according to Becke's function. In particular, we have chosen the empirical set of Slater–Bragg.⁵² The comparison of the FBOs computed with both sets of atomic radii is shown in Figure 7. Both sets of values are practically coincident ($r = 1.000$), even for the “nonbonded pairs”. Indeed, contrary to electron populations, bond orders have been proved to be very stable with respect to dramatic changes in atomic radii of atoms, such as changing the value for a particular atom and keeping the rest invariant.⁵³

Conclusions

Three different sharing indexes, namely, the DI, the FBO, and the MBO have been compared for a large group of five-membered rings with a rich variety of bonds. In general, there is a good agreement with the exception of bonds involving P,

Al, B, and Be atoms. For the last three significant differences of the DI results and the FBO or MBO values are found. On the basis of previous results on the hydrides of Be, B, and Al,³ we consider that the DI values are underestimated for these systems because of the reduced size of the Be, B, and Al atomic basins within the AIM partitioning of the molecular space. As far as P bonds are concerned, the answers differ from index to index. For these bonds, the MBO suffers from strong basis set dependence (the use of diffuse functions dramatically decreases the bond order), although its values are closer to the FBO ones if *more atomic* (without diffuse functions) basis sets are used. With respect to the remaining types of bonds, good correlations are achieved between the three indexes, with most points following the expected trend despite some exceptions. This drives us to conclude that, in general, the three indexes predict the same electron pair distribution. The agreement between DI, FBO, and MBO results is particularly good for homonuclear bonds. In particular, noticeable trends are found for C–C bonds, encouraging the substitution of the DIs by the cheaper FBOs or even the MBOs in aromatic indexes based on DI such as the PDI and FLU. This issue is currently being investigated in our laboratory.

Note Added in Proof. Soon after the manuscript was accepted, a paper appeared in this journal by Torre et al. (Torre, A.; Alcoba, D. R.; Lain, L.; Bochicchio, R. C. *J. Phys. Chem. A* **2005**, *109*, 6587) that discusses the use of fuzzy atoms to determine three- and two-center bond indices.

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