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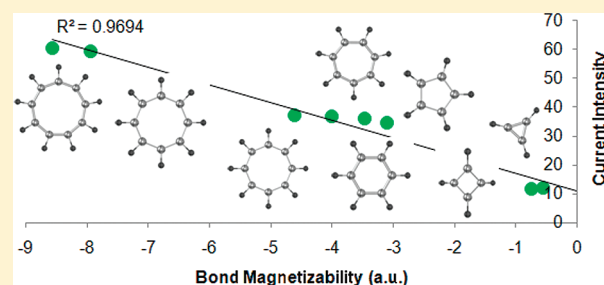
Interatomic Magnetizability: A QTAIM-Based Approach toward Deciphering Magnetic Aromaticity

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S Supporting Information

ABSTRACT: Interatomic magnetizability provides insight into the extent of electronic current density between two adjacent atomic basins. By studying a number of well-known aromatic, nonaromatic, and antiaromatic molecules, it is demonstrated that interatomic magnetizability (bond magnetizability) not only is able to verify the exact nature of aromaticity/antiaromaticity among different molecules, but also can distinguish the correct aromaticity order among sets of aromatic/antiaromatic molecules. The interatomic magnetizability is a direct measure of the current flux between two adjacent atomic basins and is the first QTAIM-derived index that evaluates aromaticity based on a response property, that is, magnetizability. Bond magnetizability is easy to compute, straightforward to interpret, and can be employed to evaluate the pure π - or σ -orbital contributions to magnetic aromaticity.



INTRODUCTION

The Quantum Theory of Atoms in Molecules, QTAIM,¹ has provided a unique approach for partitioning molecular properties into regional contributions arising from atoms, defined by the zero flux surfaces of the gradient of the one-electron density, embedded in the real space.

In recent years, topological characteristics of the gradient of the one-electron density and its critical points (CP), that is, points in which $\nabla\rho = 0$, as well as atomic properties, have been employed for the rationalization of many chemical concepts, particularly within bonding realm.² However, interpretation of such local characteristics is not always straightforward, and some of them have triggered ongoing controversies in the chemical community.³

Besides bonding, aromaticity⁴ is another chemical concept that has been studied in the context of the QTAIM by different indicators. A number of aromaticity indices have been developed based on the topological characteristics of CPs. Studying the topological characteristics among a diverse set of molecules has demonstrated that local relationships are indeed present between characteristics of (3, +1) critical points and other aromaticity descriptors,⁵ but a global relationship has not been established.⁶ Moreover, different aromaticity probes based on the topological characteristics of the (3, -1) critical points have been introduced.⁷ Apart from CP-based probes of aromaticity, a different class of aromaticity indices has been designed based on measuring the extent of electron delocalization between the atomic basins in molecules, that is, electron sharing indices of aromaticity.^{7a,8} The aforementioned indices should be classified beside the energetic⁹ and the structural¹⁰ indices of aromaticity as they all define and measure aromaticity based on different properties derived from *field-free ground state* molecular wave functions.

Another group of aromaticity indices measure the extent of aromaticity/antiaromaticity based on the response properties derived from *magnetic field-induced mixed ground-excited states* molecular wave functions, namely magnetic properties.¹¹ Although various magnetic indices of aromaticity have been developed in recent years,¹² to the best of author's knowledge, any QTAIM-derived magnetic index of aromaticity has not been proposed yet. Probably one reason is the limitations of the available commercial and user-friendly codes and the fact that the QTAIM-based magnetic properties of molecules are not as much well-known as the field-free atomic properties. To fill this gap, the present contribution deals with the interatomic magnetizability in detail.

The second-rank magnetizability tensor, χ , of a system in an external magnetic field, B , is expressed in the terms of induced current density, $J(r)$,¹³ eq 1.¹⁴

$$\chi = \left(\frac{1}{2cB} \right) \int r \times J^{(1)}(r) dr \quad (1)$$

For an atomic basin defined by the zero-flux equation, $\nabla\rho \cdot n = 0$, magnetizability is expressed in the terms of induced current density, $J(r)$, flowing *within* the atomic basin, intra-atomic magnetizability, and the current density flux *through the interatomic surfaces* between the atom and its bonded neighbors, that is, interatomic magnetizability or bond magnetizability.^{13,14b,14c} It has been shown that in ionic and polar systems current density flow is localized in atomic basins and the contribution of the

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interatomic magnetizability to the magnetizability of the atom is minimal.¹⁵ On the other hand, in covalently bonded molecules, the contribution of bond magnetizability to the total atomic magnetizability is considerable and, in some cases, like aromatic molecules, even surpasses the intra-atomic magnetizability.¹⁵

In the present report, intra- and interatomic magnetizabilities as well as their out-of-plane components, which are in particular associated with the ring currents,^{11b,16} are studied for a number of well-known aromatic, nonaromatic, and antiaromatic molecules.

METHODS AND COMPUTATIONAL DETAILS

All of the structures were optimized by the Becke's three-parameter exchange¹⁷ and Lee–Yang–Parr's correlation non-local functional,¹⁸ usually denoted by B3LYP, combined with 6-311++G(d,p)¹⁹ basis set by Gaussian 03 suite of programs.²⁰ Studying the geometrical second derivatives of energy confirmed that all geometries correspond to the local minima. WFX files for the computation of magnetizabilities were obtained from NMR calculations by the Gaussian package using the GIAO²¹ method at the same level of theory through the fchk generated files by using the AIMAll program package.²² Intra- and interatomic magnetizabilities were computed by the Proaim integration approach, implemented in the AIMAll suite of programs; all magnetizabilities are directly tabulated in the AIMAll output (.sum file). The accuracy of the integration process was guaranteed by keeping the atomic integral of the one-electron density Laplacian below the 10^{-4} a.u. within all atomic basins. In addition, the summation of all basin energies was compared with the total electronic energy of the molecule, calculated independently at the above-mentioned computational level, to check that the differences remain below the $1 \text{ kcal} \cdot \text{mol}^{-1}$.

To study the exclusive contribution of π -electrons to the intra- and interatomic magnetizabilities, occupation numbers of orbitals in the WFX files were changed and the π -electrons were removed. This is possible because, within the contest of orbital approximation, the first order current density can be partitioned into its orbital contributions, eq 2.²³

$$J^{(1)}(r) = \sum_i J_i^{(1)}(r) \quad (2)$$

The difference between the total magnetizability and that of the remaining σ -framework represents the contribution of the π -electrons to the magnetizability. In the considered set of molecules, removing electrons from the π -MOs does not affect the position of the interatomic surfaces. On the other hand, because π -electron density is zero on the ring plane, where (3, −1) CP is placed, removing π -electrons does not affect the position of (3, −1) CP. Moreover, the high geometrical symmetry of the selected systems in this study guarantees that removing all electrons from a group of orbitals with the same symmetry label does not change the position of interatomic surfaces within the molecular space.

RESULTS AND DISCUSSION

The efficiency of the interatomic magnetizability for revealing the nature of aromaticity/antiaromaticity for a number of aromatic, antiaromatic, and nonaromatic molecules was studied; Figure 1 depicts the selected species, namely, aromatic, nonaromatic, and antiaromatic hydrocarbons as well as two inorganic species: borazine and Al_4^{2-} .

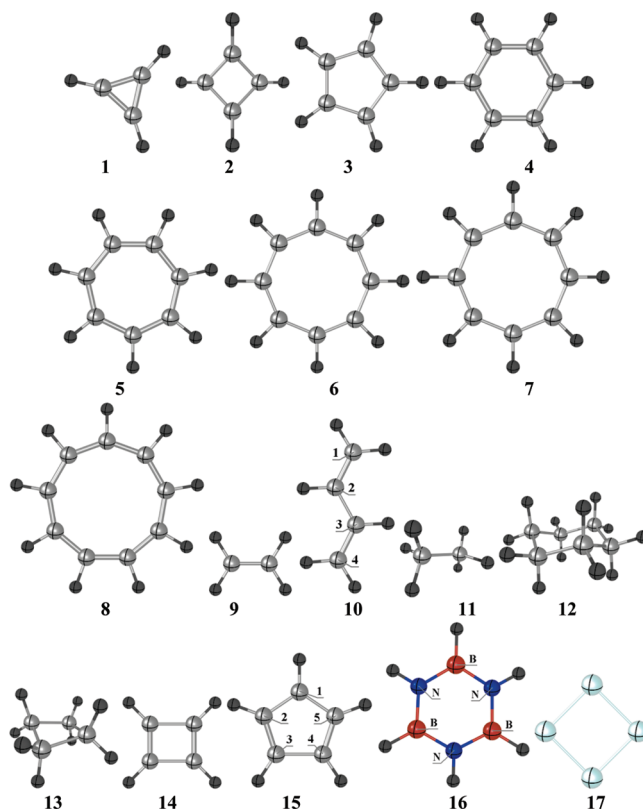


Figure 1. Structures of studied molecules in this work: (1) cyclopropenyl cation, (2) cyclobutadiene dication, (3) cyclopentadienyl anion, (4) benzene, (5) tropylium cation, (6) cyclooctatetraene dication, (7) cyclooctatetraene dianion, (8) cyclononatetraenyl anion, (9) ethylene, (10) butadiene, (11) ethane, (12) cyclohexane, (13) cyclobutane, (14) cyclobutadiene, (15) cyclopentadienyl cation, (16) borazine, and (17) Al_4^{2-} .

Aromatic Hydrocarbons. The magnetic aromaticity order of the selected aromatic hydrocarbons is well-founded based on various probes.^{12k,24} It has been shown that the extent of magnetic aromaticity among these molecules is related to two factors: the number of π -electrons and the ring size. Increasing the ring size or the number of electrons increases the magnetic aromaticity, that is, the strength of current density, $J(r)$. The isotropic as well as out-of-plane intra- and interatomic magnetizabilities of the hydrogen and carbon atoms in the aromatic hydrocarbons are listed in Table 1.

It is worth noting that intra-atomic magnetizabilities show a fair correlation with the molecular charge. It is evident that, among 2π -, 6π -, and 10π -electron species, the isotropic as well as the out-of-plane intra-atomic magnetizabilities of both carbon and hydrogen generally are decreased by increasing the total positive molecular charge. The same trend is also evident for the contribution of the interatomic magnetizability between carbon and hydrogen basins. Accordingly, the contribution of the bond magnetizabilities between hydrogen atoms and carbon atoms to the magnetizabilities of the carbon atoms is decreased as the molecular charge becomes more positive. These trends are expected because by increasing the molecular (positive) charge, the electron population in the hydrogen basins and consequently its contribution to the magnetizability decreases.

On the other hand, the isotropic and in particular the out-of-plane bond magnetizabilities between adjacent carbon atoms are perfectly in line with the ring current intensity, as it was

Table 1. Isotropic and Out-of-Plane Intra-Atomic ($\chi(\Omega)^{\text{intra}}$ and $\chi_{zz}(\Omega)^{\text{intra}}$) and Interatomic ($\chi(\text{C}|\Omega)$ and $\chi_{zz}(\text{C}|\Omega)$) Magnetizabilities for the Aromatic Hydrocarbons in cgs-ppm Units^a

molecule	$\chi(\text{C})^{\text{intra}}$	$\chi(\text{H})^{\text{intra}}$	$\chi(\text{C} \text{C}')$	$\chi(\text{C} \text{H})$	$\chi_{zz}(\text{C})^{\text{intra}}$	$\chi_{zz}(\text{H})^{\text{intra}}$	$\chi_{zz}(\text{C} \text{C}')$	$\chi_{zz}(\text{C} \text{H})$	I_{π}^b
C ₃ H ₃ ⁺	−1.646	−0.857	−1.192	−0.689	−4.959	−1.028	−2.362	−1.467	11.97
C ₄ H ₄ ²⁺	−0.924	−0.703	−1.339	−0.642	−3.955	−0.777	−2.657	−1.008	11.77
C ₅ H ₅ [−]	−3.667	−1.491	−2.234	−0.972	−4.056	−1.760	−5.020	−1.645	34.56
C ₆ H ₆	−2.550	−1.239	−2.213	−0.802	−3.368	−1.239	−4.973	−1.291	36.04
C ₇ H ₇ ⁺	−1.782	−1.037	−2.340	−0.712	−3.116	−0.998	−5.538	−1.167	36.85
C ₈ H ₈ ²⁺	−1.226	−0.893	−2.540	−0.636	−3.050	−0.849	−6.346	−1.082	37.24
C ₈ H ₈ ^{2−}	−2.607	−1.528	−3.223	−0.959	−3.379	−1.516	−9.274	−1.267	59.34
C ₉ H ₉ [−]	−3.117	−1.299	−3.764	−0.791	−3.033	−1.104	−9.871	−1.070	60.43

^a I_{π} values, which show π -ring current intensity, are also presented for comparison. ^b Taken from ref 24c; please also see ref 24d.

Table 2. Contributions of Isotropic $\chi_{\pi}(\text{C}|\text{C}')$ and Out-of-Plane $\chi_{\pi zz}(\text{C}|\text{C}')$ π -Interatomic, Magnetizability, to the Magnetizability of the Carbon Atoms for Aromatic Hydrocarbons in cgs-ppm Units

	C ₃ H ₃ ⁺	C ₄ H ₄ ²⁺	C ₅ H ₅ [−]	C ₆ H ₆	C ₇ H ₇ ⁺	C ₈ H ₈ ²⁺	C ₈ H ₈ ^{2−}	C ₉ H ₉ [−]
$\chi_{\pi}(\text{C} \text{C}')$	−0.354	−0.355	−1.102	−1.392	−1.668	−1.966	−2.35	−3.069
$\chi_{\pi zz}(\text{C} \text{C}')$	−0.566	−0.756	−3.102	−3.474	−4.002	−4.619	−7.942	−8.564

expected.^{24c,d} The out-of-plane bond magnetizabilities is increased regularly by increasing the number of π -electrons, it also increases by increasing the ring size, in line with the other magnetic aromaticity probes.^{12k,l,24a,24c} Only one flaw in the aromaticity order is found between the benzene and cyclopentadienyl anion; all other aromaticity probes suggest that π -ring current of benzene is more intense than its five-membered homologue.^{12k,l,24a,24c} The bond magnetizabilities in Table 1 reflect the role of both σ - and π -electrons in the magnetizability; the net effect of π -electrons were also measured by modifying the occupation numbers of MOs and the number of electrons in WFX file. Table 2 presents the π -bond magnetizability for the aromatic hydrocarbons; the contribution of the σ -framework to the magnetizabilities of these molecules is presented in Table S-1.

Studying the π -magnetizabilities demonstrates that the higher bond magnetizability in cyclopentadienyl anion originates from its σ -framework of the molecule and benzene sustains a stronger π -current, as demonstrated before.^{12k,l,24a,24c}

Nonaromatic Hydrocarbons. To verify the efficiency of the bond magnetizability as a reliable aromaticity index, a number of nonaromatic molecules were studied and their bond magnetizabilities were compared with that of the aromatic species, Table 3.

Remarkable differences between magnetizabilities of carbon atoms of the molecules in Table 3 and those in Table 1 are found. The isotropic and out-of-plane intra-atomic magnetizabilities of nonaromatic species (especially in sp^3 hybridized carbon atoms) are almost similar, but among aromatic species, the out-of-plane components are larger than the isotropic values. The out-of-plane bond magnetizabilities of the nonaromatic hydrocarbons are smaller than those of aromatics. The bond magnetizability of π -bonds among nonaromatic hydrocarbons are less than 2.2 (less than 2π -electron hydrocarbons) in cgs-ppm units and that of σ -bonds is close to unity. In addition, the ratio of the out-of-plane to isotropic magnetizability in alkane molecules are less than unity; this ratio increases among alkenes, but still remains lower than that of aromatic hydrocarbons. Intra-atomic magnetizabilities of hydrogen atoms and C–H bond magnetizability for nonaromatic species are similar and close to that of benzene, the only neutral aromatic species in the Table 1.

Antiaromatic Hydrocarbons. A successful aromaticity index must be able to characterize antiaromatic trait as well. In antiaromatic molecules it is well-known that paratropic ring currents affect the magnetizability and chemical shifts of the atoms in molecule; Table 4 presents atomic and bond contributions to the magnetizability of two antiaromatic species.

Even among the antiaromatic molecules intra- and interatomic magnetizabilities of hydrogen atoms are not different from that of their aromatic and nonaromatic counterparts, but the intra-atomic magnetizabilities of carbon atoms are decreased. The net effect of paratropic currents is manifested in the C–C bond magnetizabilities as they are *positive*; particularly, out-of-plane components are much more affected by the paratropicity. Although both cyclobutadiene and cyclopentadienyl cation have 4π -electrons, the difference between their C–C bond magnetizabilities is considerable. This is mainly due to the fact that small HOMO–LUMO gaps intensify paratropicity; the energy gap between HOMO and LUMO of cyclobutadiene is one and a half times more than that of cyclopentadienyl anion (the energy gap between HOMO and LUMO orbitals of cyclobutadiene and cyclopentadienyl anion are 3.541 and 2.007 eV, respectively, at B3LYP/6-311++G(d,p) computational level).

Inorganic Molecules. To examine the validity of the newly introduced index, two inorganic species were studied, Table 5.

Borazine, which is also known as inorganic benzene, is characterized as a nonaromatic species by studying its current density map.^{24a,25} Intra-atomic magnetizability of the hydrogen basins in this molecule are in line with the rest of studied species; the isotropic and out-of-plane magnetizabilities of the hydrogen atoms which are bonded to the boron atoms (electropositive and hence electron donating element) are more than the hydrogen atoms that are bonded to the nitrogen atoms (electronegative and electron withdrawing element). The average out-of-plane bond magnetizabilities of the borazine ring are quite low (−1.939 in cgs-ppm units) and in the range of nonaromatic molecules (less than 2.2 cgs-ppm).

Al_4^{2-} is the first observed bare all-metal aromatic species; this molecule was first assigned as a 2π -electron aromatic species,²⁶ but a subsequent study demonstrated that this species is a double,

Table 3. Isotropic and Out-of-Plane Intra-Atomic, $\chi(\Omega)^{\text{intra}}$ and $\chi_{zz}(\Omega)^{\text{intra}}$ and Interatomic $\chi(\text{C}|\Omega)$ and $\chi_{zz}(\text{C}|\Omega)$ Magnetizabilities for Nonaromatic Hydrocarbons in cgs-ppm Units

molecule	$\chi(\text{C})^{\text{intra}}$	$\chi(\text{H})^{\text{intra}}$	$\chi(\text{C} \text{C}')$	$\chi(\text{C} \text{H})$	$\chi_{zz}(\text{C})^{\text{intra}}$	$\chi_{zz}(\text{H})^{\text{intra}}$	$\chi_{zz}(\text{C} \text{C}')$	$\chi_{zz}(\text{C} \text{H})$
ethene butadiene	−3.492	−1.286	−1.633	−0.816	−3.968	−1.308	−2.180	−1.339
(C ₁)=C ₂	−3.558	−1.296 ^a	−1.544	−0.857 ^b	−3.859	−1.342 ^c	−2.179	−1.399 ^d
(C ₂)−C ₃	−2.209	−1.209	−1.062	−0.778	−2.673	−1.233	−1.927	−1.283
ethane	−4.331	−1.445	−1.227	−1.018				
cyclobutane	−3.545	−1.370	−0.928	−0.932	−2.990	−1.280 ^e	−0.913 ^e	−1.179 ^e
cyclohexane	−3.237	−1.347	−1.230	−0.915	−3.031	−1.248 ^e	−1.076 ^e	−1.098 ^e

^a The reported value is the average of magnetizabilities of the two terminal hydrogen atoms. The magnetizabilities of the Z and E terminal hydrogens are −1.290 and −1.302, respectively. ^b The reported value is the average of the contribution of the bonds between carbon and hydrogen atoms to the magnetizability of carbon. The contributions of the bonds of Z and E terminal hydrogens to the magnetizability of the carbon are −0.859 and −0.855, respectively. ^c The reported value is the average of magnetizabilities of two terminal hydrogen atoms. The magnetizabilities of Z and E terminal hydrogens are −1.366 and −1.317, respectively. ^d The reported value is the average of the contribution of the bonds between carbon and hydrogen atoms to the magnetizability of carbon. The contributions of the bonds of Z and E terminal hydrogens to the magnetizability of the carbon are −1.441 and −1.356, respectively. ^e The values are reported along the main axis of symmetry, C₂ and C₃ in cyclobutadiene and cyclohexane, respectively.

Table 4. Isotropic and Out-of-Plane Intra-Atomic, $\chi(\Omega)^{\text{intra}}$ and $\chi_{zz}(\Omega)^{\text{intra}}$ and Interatomic $\chi(\text{C}|\Omega)$ and $\chi_{zz}(\text{C}|\Omega)$ Magnetizabilities for Antiaromatic Hydrocarbons in cgs-ppm Units

molecule	$\chi(\text{C})^{\text{intra}}$	$\chi(\text{H})^{\text{intra}}$	$\chi(\text{C} \text{C}')$	$\chi(\text{C} \text{H})$	$\chi_{zz}(\text{C})^{\text{intra}}$	$\chi_{zz}(\text{H})^{\text{intra}}$	$\chi_{zz}(\text{C} \text{C}')$	$\chi_{zz}(\text{C} \text{H})$
C ₄ H ₄								
C=C	−2.068	−1.189	−0.238	−0.710	−1.847	−1.211	+1.766	−1.107
C−C			+0.587				+2.455	
C ₃ H ₅ ⁺								
(C ₁ ⁺)−C ₂	+1.774	−0.887	+3.777 ^a	−0.541	−1.176	−0.942	+12.402 ^a	−1.079
(C ₂)=C ₃	−2.697	−1.035	+3.200 ^a	−0.764	−3.013	−1.068	+11.610 ^a	−1.221
(C ₃)−C ₄	−0.734	−0.973	+4.389	−0.654	−1.966	−1.001	+13.609	−1.097

^a The reported value is the average of mutual contributions of the bond between atom A and B to the magnetizabilities of the atom A and atom B.

Table 5. Isotropic and Out-of-Plane Intra-Atomic, $\chi(\Omega)^{\text{intra}}$ and $\chi_{zz}(\Omega)^{\text{intra}}$ and Interatomic $\chi(\Omega|\Omega')$ and $\chi_{zz}(\Omega|\Omega')$ Magnetizabilities for Inorganic Species in cgs-ppm Units

molecule	$\chi(\Omega)^{\text{intra}}$	$\chi(\text{H})^{\text{intra}}$	$\chi(\Omega \Omega')$	$\chi(\Omega \text{H})$	$\chi_{zz}(\Omega)^{\text{intra}}$	$\chi_{zz}(\text{H})^{\text{intra}}$	$\chi_{zz}(\Omega \Omega')$	$\chi_{zz}(\Omega \text{H})$
borazine								
B N'	+4.601	−2.372	−0.555	−0.396	−0.090	−2.129	−1.282	−0.826
N B'	−8.776	−0.780	−1.124	−0.812	−8.238	−0.815	−2.596	−1.157
Al ₄ ^{2−}	−15.114		−9.224		−36.220		−23.124	
Al ₄ ^{2−} (σ) ^a	−9.383		−6.539		−32.736		−20.013	
Al ₄ ^{2−} (core) ^b	−2.974		−0.096		−2.974		−0.352	

^a Sum of contributions of the σ -framework and core electrons of the molecule to the magnetizability. ^b Pure contribution of the core electrons of the molecule to the magnetizability.

σ -, and π -aromatic cluster.²⁷ Both the absolute values of the intra- and interatomic magnetizabilities of this cluster are considerably large. It is interesting to note that bond magnetizabilities of the Al₄^{2−} are less than intra-atomic magnetizabilities of the molecule; the ratio of the bond magnetizabilities to intra-atomic magnetizabilities of Al₄^{2−} is almost comparable, with the same ratio for the 2 π -electron hydrocarbons, see Table 1.

The relative π - and σ -aromaticity of Al₄^{2−} are defined by studying the magnetizabilities of σ -framework and core electrons of this species. Pure π -magnetizability is defined as the difference between the total magnetizability and the magnetizability of the σ -framework, which is −3.111 ppm. Similarly, the difference between the magnetizabilities of the σ -framework and core electrons reveals

the pure contribution of the valence σ -electrons (−19.661 ppm). These values show that π -electrons are responsible for 13.7% of the electronic current in the molecule; this is in line with a recent study that suggests a 14.8% π -currents contribution to the aromaticity of the molecule.^{24b} Besides, Table 5 demonstrates that only a small portion of magnetizability in Al₄^{2−} is related to the core electrons, ~1.5%.

CONCLUSIONS

Studying both intra- and interatomic magnetizabilities for a diverse set of hydrocarbons and two inorganic species demonstrates that intra-atomic magnetizabilities are not much affected

by the so-called ring current in aromatic/antiaromatic systems. It seems that intra-atomic magnetizability is more affected by the total charge of the molecules as well as the population of the atomic basins; however, a straightforward relationship between these two factors was not found because the ring current partially affects the basin magnetizabilities. On the other hand, interatomic magnetizability (bond magnetizability) reflects the strength of aromatic/antiaromatic ring currents exclusively; it is demonstrated that the out-of-plane bond magnetizabilities are capable to verify the extent of magnetic aromaticity, that is, the strength of ring current, among both hydrocarbons and inorganic species. Moreover, pure contributions of the π - and σ -electrons to the magnetizability can be recovered from the total magnetizability.

In summary, bond magnetizability is the first QTAIM-based index for measuring the aromaticity by response properties, that is, magnetic aromaticity; this index is easy to compute by the user-friendly AIMAll package and is straightforward to interpret. Compared with the usual magnetic indices of aromaticity, for example, NICS,¹²ⁱ ARCS,^{12j} and NICS scan,^{12f,g} bond magnetizability is much more reliable, as its results are in line with refined indices such as electron density versus NICS_{zz} scan,^{12k} ring current intensity,^{24c} and current density analysis. This advantage is due to the fact that bond magnetizability is a direct result of the current intensity flux between two adjacent atoms in a cyclic molecule.

■ ASSOCIATED CONTENT

S Supporting Information. The σ -framework magnetizabilities of aromatic hydrocarbons and details of the approach for separation of the π -electron contributions to the magnetizability by modifying WFX files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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