

Relative Weights of σ and π Ring Currents in a Few Simple Monocycles

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Abstract: By partitioning the bond current strength (current susceptibility) into plane symmetric and plane antisymmetric contributions, it is shown that 91% of the diatropic ring current of benzene is transported by the π electrons and the remaining non-negligible 9% is sustained by the σ electrons. In planar cyclooctatetraene 94% (6%) of the paratropic ring current is transported by the π (σ) electrons. In cyclopropane 95% (5%) of the diatropic ring current is transported by the σ (π -like) electrons. The 85% fraction of the diatropic ring current of Al_4^{2-} is transported by the σ valence electrons and 15% by the π valence electrons. In the nonaromatic borazine system the nitrogen-centered π electron circulations are surrounded by a weak diatropic “ring current” 6.5 times smaller than that of benzene.

1. Introduction

Within the orbital approximation, molecular properties result from a summation of orbital contributions, which can be conveniently classified according to their symmetry. If the properties under examination stem from the application of external fields, molecular orbitals are perturbed and their symmetry is not generally preserved. Orbital symmetry conservation is observed for plane symmetric molecules in the presence of a perpendicular magnetic field. In this case, plane symmetric and antisymmetric orbitals, hereafter referred to as σ and π orbitals, are only mixed among themselves and the first-order perturbed orbitals have the same symmetry as the unperturbed ones. Therefore, σ and π electrons give clearly distinguishable contributions to magnetic properties. This important feature, together with the assumption that σ electrons should give bond-localized circulations, has been exploited in past years to interpret the magnetic properties of a large class of (poly)cyclic conjugated hydrocarbons in terms of π ring current maps (see refs 1–4 for a few examples) and π contributions to the out-of-plane component of some molecular tensor properties, for

instance, magnetizability,⁵ magnetic shielding density,⁶ and magnetic shielding of either real⁷ or virtual nuclei. The latter properties are the target of the widespread computation of nucleus-independent chemical shift (NICS).^{8,9} Moreover, the delocalization of π ring currents is widely considered an indication of aromaticity.^{10,11} The dominant role of π electrons in determining the magnetic properties in polycyclic aromatic hydrocarbons (PAHs) is such a common tenet that it has been proposed even to recover *a posteriori* the strength of π currents from all-electron NICS grids.¹² This assumption is certainly questionable if both σ and π currents have appreciable magnitude. In this case, attention is readily paid to some quantification of the individual currents. The most used quantitative indicators are the just cited NICS and the “bond current strength” (current susceptibility).¹³ The latter is obtained by integrating the current density crossing a suitably chosen planar domain, which bisects a selected bond. When delocalization is present, a sizable net bond current flow is detected, whose strength can be used to make a direct comparison among different molecular systems. The retrieval of both contributions (σ and π) from the above all-electron indicators is certainly cumbersome. Indeed, a retrieval of σ and π currents in PAHs from an *a posteriori* analysis of NICS calculations had to introduce awkward saturated homologues,¹⁴ and the use of both NICS¹⁵ and bond current

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strengths¹⁶ led to conclusions on the relative weight of σ and π currents in aluminum clusters that were shown to be incorrect.¹⁷

The introduction of orbital contributions to the bond current strengths to be discussed here would certainly help in the matter, allowing a quantitative clear-cut separation of σ and π currents. In a recent study, analyzing current profiles, Fliegl et al.¹⁸ reported that “calculations of the ring-current profile show that the ring current of benzene is not transported by the π electrons on both sides of the molecular ring” and that their “...calculations challenge the widespread notion that the ring current is transported by the π electrons...”. This is a disputable result which demands attention and needs to be carefully re-examined to understand whether a number of previous investigations make sense.

In the present paper we provide the partitioning of the current density bond cross section into π and σ contributions for typical aromatic, antiaromatic, and nonaromatic systems (benzene, planarized cyclooctatetraene, borazine), allowing for the same choice made to show the ring current signature in proton shielding density maps,⁶ with the aim to elucidate which electrons actually transport the ring current. Moreover, we consider cyclopropane and Al_4^{2-} , which have recently attracted considerable attention in the attempt to disclose the nature of their recognized ring current.^{15–20} According to Walsh,^{21,22} cyclopropane can be portrayed as a perturbed ethylene donating its π electrons to a methylene unit. The superposition of the three contributing structures leads to in-plane electron delocalization, which can only be plane symmetric. Alternatively, cyclopropane can be seen as formed by three bent C–C bonds (banana bonds).²³ Moreover, hyperconjugation can result from resonating structures involving the set of three π -like CH_2 group orbitals and this provides an out-of-plane electron delocalization which can be split into plane symmetric and plane antisymmetric contributions. As formerly suggested by Dewar,²⁴ the application of a perpendicular magnetic field switches on a ring current,¹⁹ which retains the symmetry of the electron delocalization from which it stems. By our approach, in-plane and out-of-plane circulations can be readily resolved and weighted. This will be discussed in a separate section hereafter. The aluminum cluster Al_4^{2-} is perhaps even more appealing, as the distinction between σ and π ring currents, recently resolved in favor of the former kind,¹⁷ can now be given on quantitative grounds, as shown in the following.

2. Method

Within the orbital approximation, the first-order current density induced by a magnetic field \mathbf{B} in the electrons of a molecule can be formally partitioned into orbital contributions:²⁵

$$\mathbf{J}^{\mathbf{B}}(\mathbf{r}) = \sum_j \mathbf{J}_j^{\mathbf{B}}(\mathbf{r}) \quad (1)$$

It is well-known that the total current density $\mathbf{J}^{\mathbf{B}} = \mathbf{J}^{\mathbf{B}}(\mathbf{r})$ is only exactly gauge invariant if the basis set is complete. In particular, the current density is independent of the choice of the gauge origin. This is not true, in general, for the individual orbital contributions, even in a complete basis set.

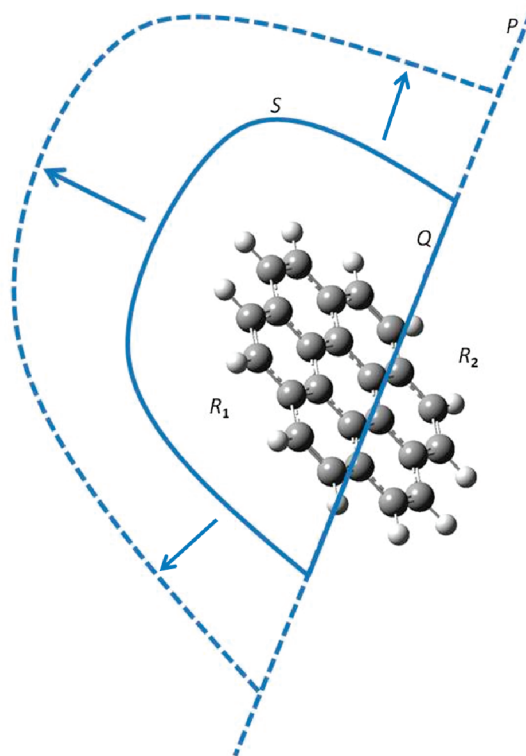


Figure 1

For practical applications with finite basis sets, methods have been devised to compute total origin-independent current densities. So far, mainly two strategies of calculation have been developed: one based on the continuous distribution of the origin of the current density^{26–29} and the other characterized by the use of gauge-including atomic orbitals (GIAO).^{13,30} The continuous transformation of the origin of the current density diamagnetic-zero (CTOCD-DZ) method, or *ipsocentric* method,^{31–33} is the simplest of the former kind.

In plane symmetric molecules in the presence of a perpendicular magnetic field, π and σ orbitals are symmetry distinct (see the Supporting Information for details). In this case the total current density is readily partitioned into π and σ contributions, regardless of the applied method. In particular, if the computed total current density is origin-independent, then also the π and σ current densities will be separately origin-independent.

Now let us consider the sketch in Figure 1, where a plane P , orthogonal to the plot plane, cuts the molecular space into two arbitrary regions, R_1 and R_2 . For any closed surface, formed by the portion Q of plane P and the surface S , enclosing the volume V of region R_1 , the Gauss theorem ensures that

$$\int_V \nabla \cdot \mathbf{J}^{\mathbf{B}} dv = \int_Q \mathbf{J}^{\mathbf{B}} \cdot d\mathbf{q} + \int_S \mathbf{J}^{\mathbf{B}} \cdot d\mathbf{s}$$

denoting by $d\mathbf{q}$ and $d\mathbf{s}$ the oriented element of area on Q and S , respectively. The intersection of plane P and the surface S with the plot plane is represented by a solid line in Figure 1. Since the divergence of the stationary current density vector vanishes everywhere, one finds that the sum of the two surface integrals on the right-hand side of the above relationship vanishes:

$$\int_Q \mathbf{J}^{\mathbf{B}} \cdot d\mathbf{q} + \int_S \mathbf{J}^{\mathbf{B}} \cdot d\mathbf{s} = 0$$

Expanding the volume V enclosing the region R_1 up to infinity, that is, taking an increasingly larger surface S and a wider portion Q of plane P , one has that $\lim_{Q \rightarrow P} \int_S \mathbf{J}^{\mathbf{B}} \cdot d\mathbf{s} = 0$, a condition satisfied for well-behaved molecular wave functions going smoothly to zero at infinity. Consequently, the integral of the current density crossing *any* arbitrarily chosen plane cutting a molecular domain vanishes, i.e.

$$\int_P \mathbf{J}^{\mathbf{B}} \cdot d\mathbf{q} = 0 \quad (2)$$

In practical calculations the field $\nabla \cdot \mathbf{J}^{\mathbf{B}}$ is not zero and eq 2 is not exactly fulfilled, except for symmetry reasons, as, for example, for every plane containing an even symmetry axis parallel to the inducing magnetic field \mathbf{B} , or when plane P is a symmetry plane perpendicular to \mathbf{B} . In all other cases the magnitude of the integral in eq 2 approaches zero on improving the quality of the calculation.

Let P be a plane bisecting at right angles a given bond between atoms K and L and let \mathbf{p} be a normal unitary vector

pointing from K to L. The cross section of the current density over P is given by

$$J_{\perp}^{\mathbf{B}} = \mathbf{J}^{\mathbf{B}}(\mathbf{r}) \cdot \mathbf{p} \quad (\mathbf{r} \in P) \quad (3)$$

The cross section $J_{\perp}^{\mathbf{B}}$ is a two-dimensional scalar field, having extremum points distributed around the center of the K–L bond. For each of these extrema a domain of integration of $J_{\perp}^{\mathbf{B}}$ can be defined as the area inside a contour line containing only that extremum point and no other point of maximum or minimum. The contour line value is set as close to zero as possible in agreement with the above condition. Then, if N is the number of domains, the net current strength for the selected bond is given by³⁴

$$\sum_{I=1}^N \int_I J_{\perp}^{\mathbf{B}} \cdot d\mathbf{p} \quad (4)$$

When the current flowing about a given bond is characterized by a substantially local vortical regime, the value of the integral in eq 4 for that bond will be vanishingly small.

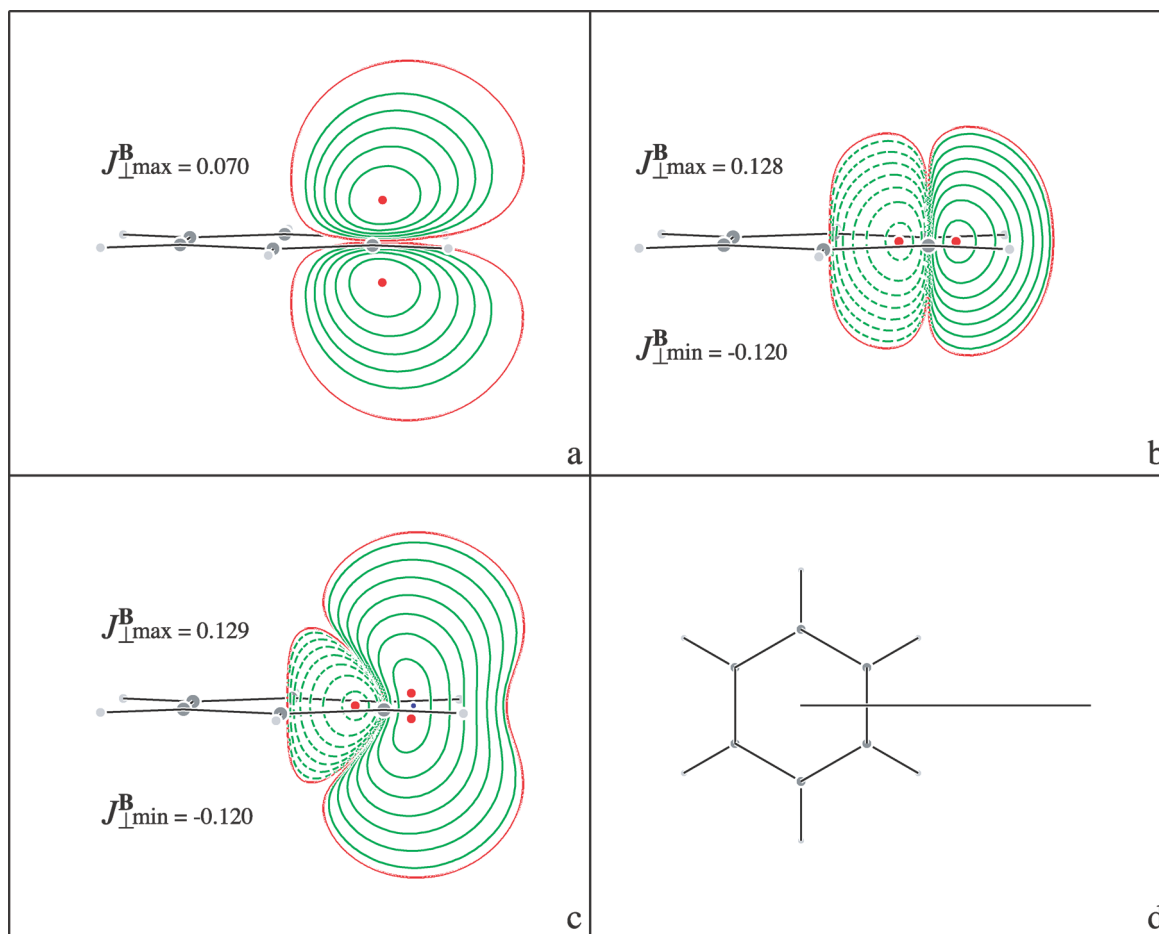


Figure 2. Current density cross sections for a plane perpendicular to a C–C bond in benzene and passing through the bond center: (a) π electron contribution; (b) σ electron contribution; (c) all electrons; (d) top view showing the profile of the cutting half-plane. The perturbing magnetic field of unitary magnitude is perpendicular to the molecular plane and in (a)–(c) is pointing from bottom to top. Solid (dashed) contour lines denote positive (negative) values of $J_{\perp}^{\mathbf{B}}$ corresponding to the outgoing (incoming) direction of the current density. Red dots locate a maximum of the cross section (within regions bound by solid contour lines) or a minimum (within regions bound by dashed contour lines), whose values are reported in atomic units. The small blue dot in (c) locates a saddle point in the outgoing current region. Green contour values are halved step by step, starting from the 80% inner extremum. The red contour at 10^{-3} au encloses the domain used to compute current strengths.

Table 1. Current Strengths (nA/T) Computed for Benzene^a

contribution	out	in	net
π	5.9 + 5.9	0	11.7
σ	7.9	-6.8	1.1
all-electron	17.7	-4.9	12.8

^a For each row, the sum of “out” and “in” terms matches the “net” result within numerical integration errors. This is also true for the sum of the σ and π contributions in the last column, but not for the columns labeled “out” and “in”, since the “out” and “in” integration domains in the all-electron cross section differ from those of the σ and π cross sections, as can be clearly observed in the figures.

Conversely, a value different from zero is a measure of current delocalization.

Calculations have been carried out for benzene, planarized cyclooctatetraene, borazine, cyclopropane, and Al_4^{2-} . For all the molecules but Al_4^{2-} , optimized geometries have been obtained at the RHF level using the (13s10p5d2f/8s4p1d) basis set of uncontracted Gaussian functions (see the Supporting Information for details). For Al_4^{2-} the optimal equilibrium geometry has been obtained at the RHF level using the 6-311+G(3df) basis set, as in ref 17. Origin-independent CTOCD-DZ current densities, computed at the coupled Hartree–Fock (CHF) level, using the same basis set adopted for the geometry optimization, have been

obtained and partitioned into π and σ contributions. Bond cross sections for π , σ , and total current densities have been computed via eq 3. Integration domains have been determined according to the above algorithm; π , σ , and total current strengths have been calculated via eq 4. Throughout this study, a magnetic field with a strength of 1 au is assumed within the linear approximation.

3. Results and Discussion

3.1. Benzene. Cross sections of the first-order current density induced by a unitary magnetic field perpendicular to the molecular plane of benzene are shown in Figure 2. These cross sections have been computed via eq 3 for the half-plane bound by the C_6 axis of symmetry, extending toward the tail molecular regions and bisecting one of the C–C bonds, as shown in panel (d).

As can be observed, the cross section of the total current density in panel c is in good agreement with the cross section reported in Figure 5 of ref 18. However, it should be remarked that (i) the total cross section is equal to the sum of the π and σ cross sections shown in panels (a) and (b), respectively, (ii) a substantial fraction of the outgoing total current returns through the region bound by the dashed contours as a result of the local diatropic vortex circulation

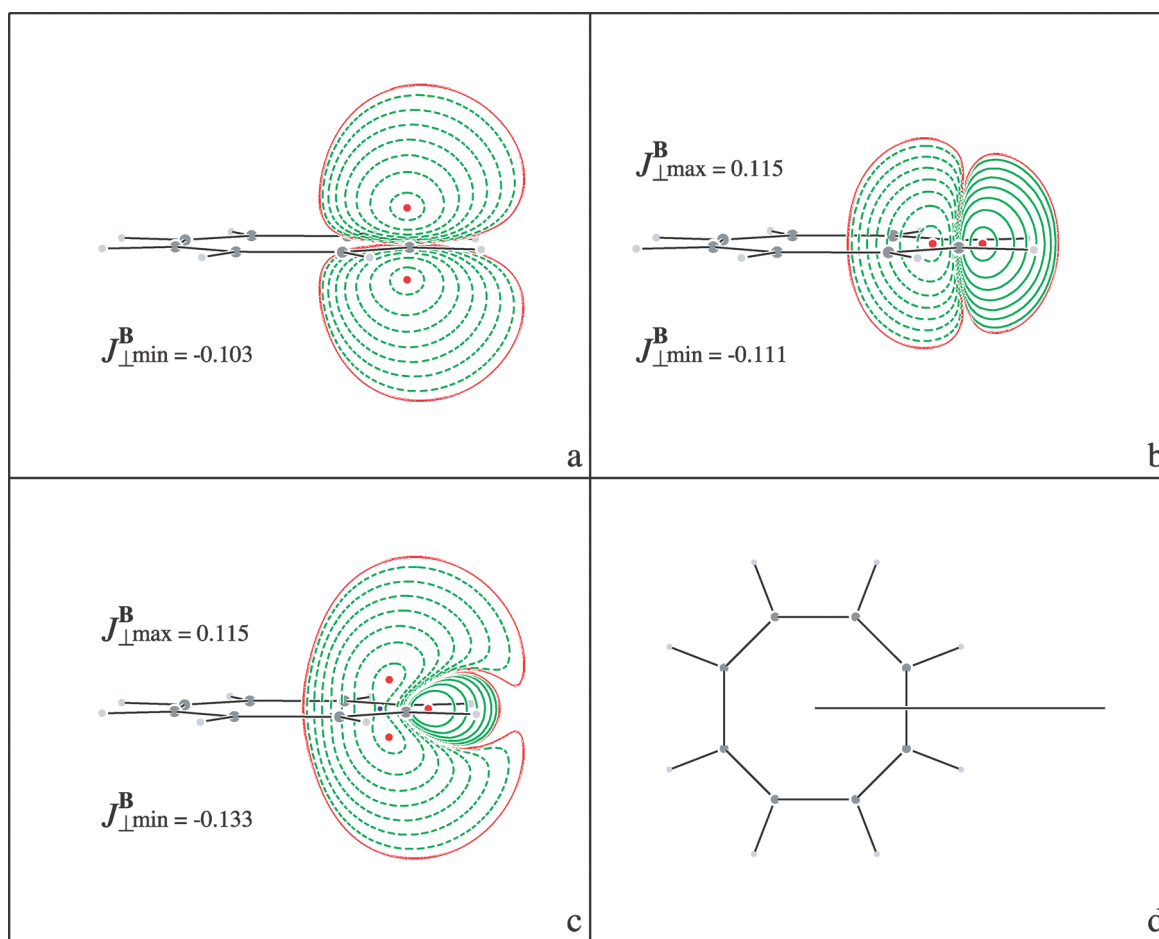


Figure 3. Current density cross sections for a plane perpendicular to a C–C single bond in planarized cyclooctatetraene and passing through the bond center: (a) π electron contribution; (b) σ electron contribution; (c) all electrons; (d) top view showing the profile of the cutting half-plane. See the Figure 2 caption for other details. The small blue dot in (c) locates a saddle point in the incoming current region.

Table 2. Current Strengths (nA/T) Computed for Planar Cyclooctatetraene^a

contribution	out	in	net
π	0	-9.0 - 9.0	-18.0
σ	6.5	-7.6	-1.1
all-electron	3.6	-22.8	-19.2

^a See footnote ^a of Table 1.

about the selected C–C bond (see Figure S1 of the Supporting Information), (iii) this localized regime of current is sustained only by the σ electrons, and (iv) the π current is fully delocalized as documented by the absence of incoming current in the cross section shown in panel (a).

In panel (c), the two red dots outside the carbon ring, on both sides of the molecular plane, correspond to maximum values of the total cross section. They result from the superposition of the two outgoing π current distributions, having maxima above and below the molecular plane, with the outgoing σ current distribution, having a single maximum over the molecular plane. Since the π current is vanishing over the molecular plane, the maximum value of the σ cross section becomes a *saddle point* in the total cross section, which is marked with a small blue dot in the figure. The superposition of the two outgoing π current distributions with the incoming σ current distribution inside the carbon ring does not alter the position of the minimum, which is the same in both σ and total cross sections.

In light of the above analysis, the claim made in ref 18 that “the strongest diatropic ring current flows on the outside of the ring and in the ring plane” cannot be justified by the current profile along a unique direction. Actually, starting from the maximum value of the σ cross section and moving perpendicularly to the molecular plane, the total cross section becomes greater, as required by the presence of the π ring current.

The current strengths collected in Table 1 provide a quantitative confirmation. They have been computed via eq 4, integrating the current density cross sections shown in Figure 2 over the domains enclosed within the red contour lines at 10^{-3} au. A smaller contour line value, i.e., larger integration domains, does not produce a significant effect on the computed current strengths. First of all, we observe a fairly good agreement between the all-electron current strengths and the results of ref 18 despite the different methods of calculation. Then we observe that the π contribution is fully delocalized, giving a net current strength of 11.7 nA/T, equally partitioned on both sides of the molecular plane.

The calculated σ current strengths are 7.9 nA/T for the outgoing current and -6.8 nA/T for the incoming current. A large fraction of these two current strengths is provided by the local diatropic vortex circulating about the C–C bond. Surely, the net current strength of 1.1 nA/T of the σ electrons

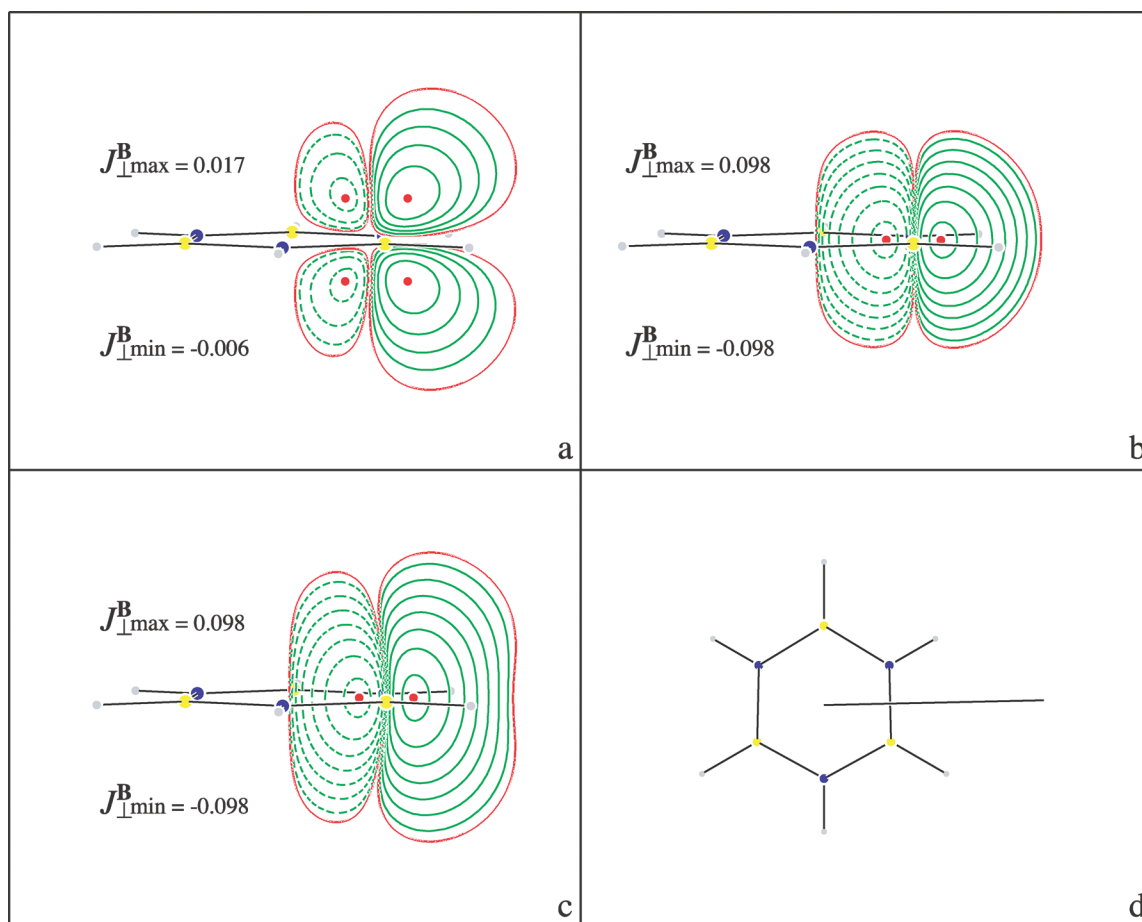


Figure 4. Current density cross sections for a plane perpendicular to a B–N bond in borazine and passing through the bond center: (a) π electron contribution; (b) σ electron contribution; (c) all electrons; (d) top view showing the profile of the cutting half-plane. B/N atoms are in yellow/blue. See the Figure 2 caption for other details.

Table 3. Current Strengths (nA/T) Computed for Borazine^a

contribution	out	in	net
π	1.2 + 1.2	-0.3 - 0.3	1.8
σ	6.2	-5.9	0.3
all-electron	8.5	-6.4	2.1

^a See footnote ^a of Table 1.

is delocalized, and therefore, it contributes to the diatropic ring current. The computed all-electron net current strength is 12.8 nA/T, which provides a quantitative measure of the diatropic ring current in benzene. From these figures, we can conclude that 91.4% of the diatropic ring current of benzene is transported by the π electrons and the remaining non-negligible 8.6% is sustained by the σ electrons.

3.2. Planarized Cyclooctatetraene. Cross sections of the first-order current density induced by a unitary magnetic field perpendicular to the molecular plane of planarized cyclooctatetraene are shown in Figure 3. These cross sections have been computed via eq 3 for the half-plane bound by the C_4 axis of symmetry, extending toward the tail molecular regions and bisecting one of the single C–C bonds, as shown in panel (d).

As can be observed in panel (a), the π electron cross section is reversed with respect to benzene and the absence of outgoing π current is consistent with a large paratropic

ring current. The σ cross section in panel (b) is similar to that in benzene, except that the incoming current seems to extend on a bit larger area than that of the outgoing current (see Figure S2 of the Supporting Information). The total cross section in panel (c) can be discussed much in the same way as in benzene. In this case the two red dots on both sides of the molecular plane appear inside the carbon ring and originate from the superposition of the incoming π and σ currents. The distance of these points from the molecular plane is larger than in benzene, documenting the larger effect of the paratropic π ring current.

Current strengths are reported in Table 2. Also in this case we observe a substantial agreement between the all-electron current strengths evaluated here and those of ref 18. The π contribution is fully delocalized, giving a net current strength of -18.0 nA/T, equally partitioned on both sides of the molecular plane.

The calculated σ current strengths are 6.5 nA/T for the outgoing current and -7.6 nA/T for the incoming current. In this case, the incoming current prevails over the outgoing current, giving a negative net current strength for the σ electrons of -1.1 nA/T, which contributes to the total paratropic ring current. The computed all-electron net current strength is -19.2 nA/T, which shows that the paratropic ring current of planar cyclooctatetraene is, in absolute value, 50%

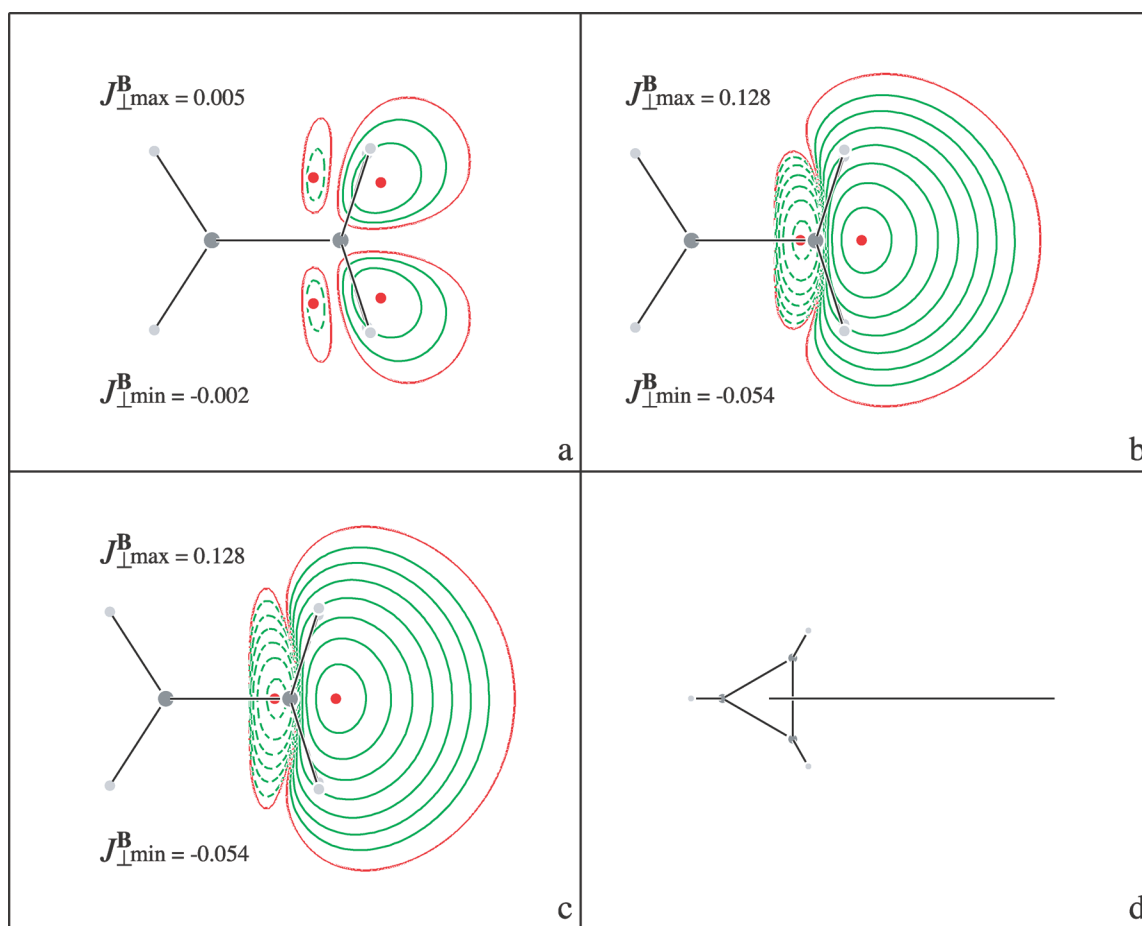


Figure 5. Current density cross sections for a plane perpendicular to a C–C bond in cyclopropane and passing through the bond center: (a) π -like contribution computed as the sum of plane antisymmetric current density orbital contributions; (b) σ contribution computed as the sum of plane symmetric current density orbital contributions; (c) all electrons; (d) top view showing the profile of the cutting half-plane. See the Figure 2 caption for other details.

Table 4. Current Strengths (nA/T) Computed for Cyclopropane^a

contribution	out	in	net
π -like	0.3 + 0.3	-0.0 - 0.0	0.5
σ	11.0	-1.3	9.7
all-electron	11.5	-1.4	10.2

^a See footnote ^a of Table 1.

stronger than in benzene. From these figures, we conclude that 94% of the paratropic ring current of planar cyclooctatetraene is transported by the π electrons and the remaining 6% is sustained by the σ electrons.

3.3. Borazine. Cross sections of the first-order current density induced by a unitary magnetic field perpendicular to the molecular plane of borazine are shown in Figure 4. These cross sections have been computed via eq 3 for the half-plane bound by the C_3 axis of symmetry, extending toward the tail molecular regions and bisecting one of the B–N bonds, as shown in panel (d).

Borazine represents an interesting example, as the non-aromatic character of the molecule is well documented by the π cross section shown in panel (a). In this case, a large fraction of the outgoing π current is connected to the incoming π current on both sides of the molecular plane, as a consequence of the substantially local vortical regime of

the π circulation. The σ cross section shown in panel (b) is almost identical to that of benzene. Owing to the much weaker π contribution, the total cross section in panel (c) does not show the red dot pair.

Current strengths are displayed in Table 3. As expected, the π contribution is small and partially reduced owing to the local character of the flow of the π current. Nonetheless, a net π current strength of 1.8 nA/T has been computed.

The calculated σ current strengths are 6.2 nA/T for the outgoing current and -5.9 nA/T for the incoming current. Therefore, the net current strength for the σ electrons is negligible, documenting an almost completely local regime of the current sustained by the σ electrons (see Figure S3 of the Supporting Information). The computed all-electron net current strength is 2.1 nA/T, which is typical of a weak diatropic ring current.

3.4. Cyclopropane. The nine valence molecular orbitals of cyclopropane can be split into six plane symmetric and three plane antisymmetric orbitals with respect to the σ_h plane of the carbon atoms. For a magnetic field perpendicular to that plane, the plane symmetric orbitals provide the σ contribution to the induced current density while the plane antisymmetric orbitals give a π -like contribution.

Cross sections of the first-order current density induced by a unitary magnetic field perpendicular to the molecular

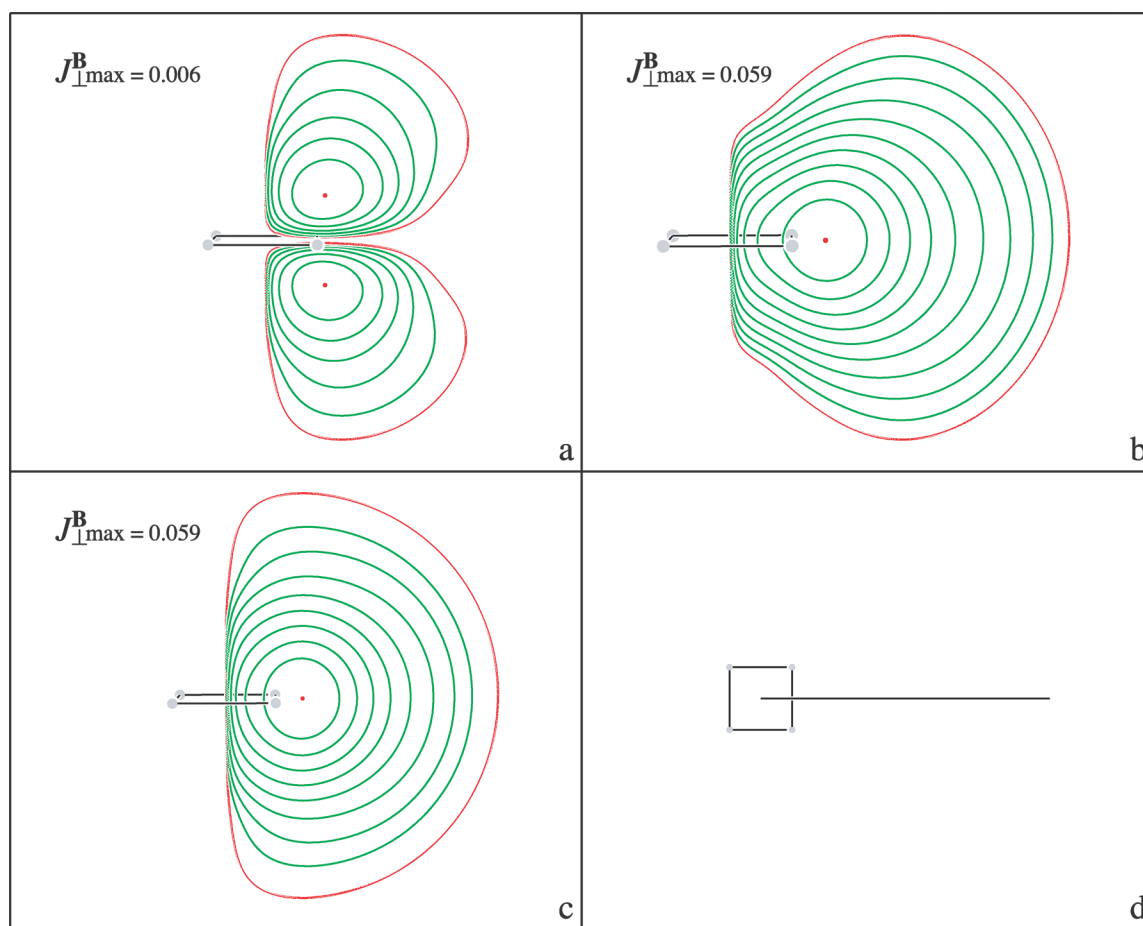


Figure 6. Current density cross sections for a plane perpendicular to an Al–Al bond in Al_4^{2-} and passing through the bond center: (a) contribution from the $2a_{2u}$ π HOMO; (b) contribution from the $5a_{1g} + 2b_{2g} + 4b_{1g} + 5e_u + 4a_{1g}$ σ valence orbitals; (c) all electrons; (d) top view showing the profile of the cutting half-plane. The red contour at 10^{-4} au encloses the domain used to compute current strengths. See the Figure 2 caption for other details.

Table 5. Current Strengths (nA/T) Computed for the Al_4^{2-} Cluster

contribution	out = net
π	2.1 + 2.1
σ	24.0
all-electron	28.4

plane of cyclopropane are shown in Figure 5. These cross sections have been computed via eq 3 for the half-plane bound by the C_3 axis of symmetry, extending toward the tail molecular regions and bisecting one of the C–C bonds, as shown in panel (d).

As can be observed in panel (a), the π -like cross section is weak and shows an outgoing current connected to a smaller incoming current on both sides of the molecular plane. The σ cross section displayed in panel (b) is much larger and, as in all previous cases, shows an outgoing current outside the carbon cycle and an incoming current inside the carbon cycle. Quite remarkably, for cyclopropane, incoming and outgoing σ currents are very different in regard to magnitude and extension, the external current largely prevailing over the internal current (see also Figure S4 of the Supporting Information). It should also be noted that the σ cross section is rather elongated on both sides of the σ_h plane of the carbon atoms up to the region about the hydrogen atoms. This fact, together with the bifurcation of the cyclopropane ring current in proximity of the methylene unit,^{20,35} suggests that both in-plane and out-of-plane circulations take place. The comparison of the total cross section in panel (c) with the σ cross section in panel (b) shows only minimal differences, thus revealing the very low importance of the π -like current.

Current strengths are reported in Table 4. As can be seen, the π -like current strength is negligible, its net value being as small as 0.5 nA/T. The calculated σ current strengths are 11.0 nA/T for the outgoing current and –1.3 nA/T for the incoming current. The large difference accounts for a net diatropic σ ring current whose strength (9.7 nA/T) is comparable to that of the π ring current of benzene.

The calculated all-electron current strengths given in the last row of Table 4 are in good agreement with the results of ref 18. Considering the all-electron net current strength of 10.2 nA/T, we can conclude that 95% of the diatropic ring current of cyclopropane is transported by the σ electrons and the remaining 5% is sustained by the π -like electron distribution. There is convincing evidence that the cyclopropane σ ring current is composed by in-plane and out-of-plane circulations.

3.5. Al_4^{2-} . The Al_4^{2-} subunit was initially indicated to be a π aromatic species, allowing for its detection by photoelectron spectroscopy.³⁶ On the other hand, direct calculation of the induced current density in Al_4^{2-} , using the ipsocentric method, confirmed the existence of a diatropic ring current, but almost entirely attributed to σ electrons.³⁷ This result was contradicted by CMO-NICS(0) calculations,¹⁵ which yield a π contribution to the NICS (–17.8) larger than the σ one (–11.1), and by bond current strength calculations, performed with the GIMIC method,¹⁶ which show substantially equal π and σ contributions. In a successive analysis,¹⁷ both the CMO-NICS(0) and the GIMIC conclusions were

shown to be largely incorrect and the prevailing role of σ electrons with respect to a (however) nonvanishing contribution from π electrons was reaffirmed. It is now interesting to check the validity of the latter result against the quantitative predictions provided by our approach.

Cross sections of the first-order current density induced by a unitary magnetic field perpendicular to the molecular plane of Al_4^{2-} are shown in Figure 6. These cross sections have been computed via eq 3 for the half plane bound by the C_4 axis of symmetry, extending toward the tail molecular regions and bisecting one of the Al–Al bonds, as shown in panel (d).

The absence of incoming currents in both π and σ cross sections, shown in panels (a) and (b), respectively, is consistent with a complete delocalization of the currents sustained by the valence electrons of Al_4^{2-} . However, the σ cross section is much larger, by nearly 1 order of magnitude.

Current strengths are reported in Table 5. As can be seen, the π current strength is not negligible, its value being 4.2 nA/T. The calculated σ current strength is 24.0 nA/T. The total current strength of 28.4 nA/T is in rather nice agreement with the value reported in ref 16 of 28.1 nA/T, despite the different method and basis set.

From these figures, we conclude that 85% of the diatropic ring current of Al_4^{2-} is transported by the σ valence electrons and the remaining 15% is sustained by the two π valence electrons. This result is in good agreement with the conclusion reported in refs 37 and 17 depicting Al_4^{2-} as a σ aromatic molecule.

4. Conclusions

Origin-independent CTOCD-DZ current densities induced by a magnetic field perpendicular to the σ_h planes of benzene, planarized cyclooctatetraene, borazine, cyclopropane, and Al_4^{2-} have been partitioned into π and σ contributions. In benzene and planar cyclooctatetraene, current density bond cross sections show that the π electrons sustain fully delocalized currents whereas the σ electrons sustain largely localized currents. These results confirm the widespread notion that the ring current in aromatic benzene and antiaromatic cyclooctatetraene is transported by the π electrons on both sides of the ring. A small fraction of the total ring current is transported also by the σ electrons. In the nonaromatic borazine the π electron current is mainly localized around nitrogen atoms; however, a small fraction circulates all over the ring. The ring current of cyclopropane has a net σ character. The Al_4^{2-} cluster is confirmed to be mainly σ aromatic on the magnetic criterion.

In the present paper we show that within the orbital approximation the π and σ contributions to the current can be quantitatively estimated, which will be helpful in all cases in which the two contributions are of comparable magnitude.

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Supporting Information Available: Proof of the clear-cut partition of the first-order magnetic field induced current

density distribution into π and σ contributions for systems containing a symmetry plane immersed in a perpendicular magnetic field, optimized Cartesian coordinates of the investigated molecules, sum rules for charge conservation, and current density maps on the molecular planes for a unitary and perpendicular magnetic field. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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