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Current Densities of Localized and Delocalized Electrons in Molecules

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In the ipsocentric formulation of the response of a molecular charge cloud to an external magnetic field, each point is taken as its own gauge origin. Orbital contributions to induced current density can then be defined in both localized and delocalized pictures of electronic structure, and the mapping of these contributions exposes a physical criterion for the localizability of orbitals. It is found that intrinsically *localized* orbitals support local, closed-loop circulations, whereas attempts to impose localization on intrinsically *delocalized* orbitals yield unphysical, open-ended flowlines. This distinction is illustrated by current density maps for benzene, naphthalene, anthracene, tetracene, coronene, pyracylene, and borazine computed at the ab initio, coupled Hartree−Fock, CTOCD-DZ (continuous transformation of origin-diamagnetic zero) level. The computed maps recover the chemical intuition of a polycyclic aromatic hydrocarbon as comprising an intrinsically delocalized π-system atop a localized σ-valence system. When maximal localization is enforced, the local forms of π orbitals in the hydrocarbons all display open flowlines that build up into complex global patterns such as the counter-rotating ring currents in circulenes and the leaky perimeter circulations of the linear acenes. In contrast, the π system of borazine displays islands of closed circulation and is well represented by localized orbitals.

1. Introduction

A theory of ring currents in conjugated molecules, recently developed within the ipsocentric distributed gauge-origin formulation of current density in coupled Hartree−Fock theory,[1−4] has led to improved understanding of the factors that determine the existence of induced delocalized circulations of electronic charge for molecules placed in external magnetic fields.

It has been shown[3] that the definition of orbital contributions to the total induced current density is at its simplest in the ipsocentric formulation and that an analogue to the famous Hückel ($4n + 2$) rule answers the questions of how many and which electrons in a conjugated system are to be counted as responsible for ring currents. It has been proved[4] that, in Hückel theory, exactly four electrons account for the entire induced diatropic π current in a ($4n + 2$)-electron monocycle, and just two electrons dominate the induced paratropic π current of an ($4n$)-electron monocycle. It has been demonstrated that the Hückel-related rules are closely obeyed in actual cases and apply also to polycyclic systems such as naphthalene[3] and porphin[5] where, again, just the four HOMO electrons produce the global diamagnetic π ring current. The orbital model also accounts for the counter-rotating paramagnetic and diamagnetic circulations in wheel-like systems such as corannulene.[3,6] The diamagnetic rim- and paramagnetic hub-currents in this case arise from disjoint sets of four electrons (HOMO-1 and HOMO, respectively). In coronene on the other hand,[3,6] the four HOMO electrons are responsible for both the diamagnetic rim-current and the weaker paramagnetic hub-current. In all these cases, magnitude of current density and sense of circulation are explained by the relative energies of occupied and unoccupied orbitals, and by the electric- and magnetic-dipole selection rules, which, in the ipsocentric formulation, determine the details of the orbital current densities.

The few-electron model obtained in the ipsocentric formulation was developed in order to explain computed current densities of the delocalized π electrons in conjugated organic molecules. This model is closely akin to others in solid-state physics that interpret properties of metals in terms of the electrons lying close to the Fermi level.[7] Indeed, metallic behavior is already demonstrated by a planar molecule such as Al_4^{2-} in which all the valence electrons are delocalized, so that there is no conventional local bonding; in this particular example, the response to a magnetic field perpendicular to the molecular plane is a strong in-plane ring current that is dominated by the four electrons in the two highest-lying σ orbitals.[8,9]

The purpose of the present paper is to show that the ipsocentric formulation lends itself to the interpretation of current densities of localized as well as delocalized electrons and that it thereby provides new insights into the concept of localized orbitals on which much of the theory of the chemical bond is built.[10] It will be shown that the formal structure of orbital contributions to the current density is invariant under an orthogonal transformation of the orbitals. That is, the theory is as easily applied to the localized (or other) orbitals obtained by mixing canonical molecular orbitals as it is to the molecular orbitals themselves. It will be demonstrated by mapping orbital current densities that the concept of closed circulations of charge provides a magnetic criterion for the distinction between localized and delocalized electrons in molecules. For example (see section 4), whereas localization of the σ orbitals of benzene gives inner-shell and bond orbitals that support *closed local circulations*, the corresponding "localized" π orbitals support only *open-ended fragments* of the famous π ring current, with flowlines that cut through an orbital rather than circulating within it.

The structure of the present paper is as follows. In section 2, the theory of orbital current densities in the ipsocentric formulation is summarized, and the orthogonal transformation of orbitals is introduced. The theoretical and computational methods are

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detailed in section 3. In section 4, the essential difference between localized and delocalized electrons is demonstrated by means of orbital current density maps of the localized and delocalized σ and π orbitals in benzene, and a criterion for localization is proposed. In section 5, the criterion is demonstrated by the π structures of the conjugated hydrocarbons naphthalene, anthracene, pyracylene, and coronene, and in section 6, by the fully localizable structure of borazine. Some conclusions are drawn in section 7.

2. Orbital Current Densities and the Orthogonal Transformation

(i) Ipsocentric Formulation. We consider the closed-shell ground state of an N-electron system, with doubly occupied orbitals ψ_n ($n = 1, 2, ..., N/2$) and unoccupied orbitals ψ_p ($p > N/2$). We suppose that the orbitals are eigenfunctions of some appropriate one-electron Hamiltonian h_0 with corresponding eigenvalues (orbital energies) ϵ_n, ϵ_p. When the molecule is placed in constant uniform magnetic field $\mathbf{B}$, the Hamiltonian to first order in $\mathbf{B}$ is

$$h = h_0 + \frac{e^2}{2m_\mathrm{e}}\hat{\mathbf{l}}(\mathbf{d})\cdot\mathbf{B} \qquad (1)$$

where $\hat{\mathbf{l}}(\mathbf{d})$ is the angular momentum operator for rotation about the "gauge origin" $\boldsymbol{d}$ of the magnetic vector potential $\mathbf{A} = {}^1/_2\mathbf{B} \times (\mathbf{r} - \mathbf{d})$. Then $\hat{\mathbf{l}}(\mathbf{d}) = (\mathbf{r} - \mathbf{d}) \times \hat{\mathbf{p}}$ where $\hat{\mathbf{p}} = -i\hbar\nabla$ is the linear momentum operator.

By first-order perturbation theory, the current density induced in the electronic structure by field $\mathbf{B}$ is the sum of orbital contributions

$$\mathbf{j}^{(1)}(\mathbf{r}) = \sum_{n=1}^{N/2}\mathbf{j}_n^{(1)}(\mathbf{r}) \qquad (2)$$

where

$$\mathbf{j}_n^{(1)}(\mathbf{r}) = -\frac{e^2}{m_\mathrm{e}}\mathbf{B} \times (\mathbf{r} - \mathbf{d}){\psi_n}^2 + \frac{2ie\hbar}{m_\mathrm{e}}[\psi_n\nabla\psi_n^{(1)} - \psi_n^{(1)}\nabla\psi_n] \qquad (3)$$

is the contribution of the two electrons in orbital ψ_n. The first term on the right in (3) depends on the density of the unperturbed orbital and is the conventional diamagnetic component of current density. The second term, the paramagnetic component, depends also on the first-order correction to the orbital, $\psi_n^{(1)}$. When the Hamiltonian h_0 is a local operator, this first-order orbital is

$$\psi_n^{(1)}(\mathbf{r}) = -\frac{e}{2m_\mathrm{e}}\sum_{p>N/2}\psi_p(\mathbf{r})\frac{\langle\psi_p|\hat{\mathbf{l}}(\mathbf{d})\cdot\mathbf{B}|\psi_n\rangle}{\epsilon_p - \epsilon_n} \qquad (4)$$

Additional terms arising from nonlocal exchange interactions are included in $\psi_n^{(1)}$ when coupled Hartree–Fock theory is used, but these corrections do not affect the present arguments and can be expected to be relatively small.[3]

The exact total induced current density $\mathbf{j}^{(1)}(\mathbf{r})$, given by (2), is independent of the choice of gauge origin $\mathbf{d}$ (as we are not considering here the complications caused by the use of approximate wave functions). $\mathbf{d}$ may be chosen freely. It may be a fixed point or it may be a function of position.[1] In the latter case, $\mathbf{j}^{(1)}(\mathbf{r})$ at each point $\mathbf{r}$ in space is computed with respect to $\mathbf{d}(\mathbf{r})$ as the origin, leading to the equivalent CSGT and CTOCD formulations of current density. The partitioning between diamagnetic and paramagnetic contributions does, however, depend on $\mathbf{d}$, as do the individual orbital contributions $\mathbf{j}_n^{(1)}$. The simplest choice of gauge-origin distribution, the one that gives the ipsocentric (CTOCD-DZ) formulation, is to treat each point $\mathbf{r}$ as its own gauge origin. From (3) it is seen that the diamagnetic component of current density vanishes when $\mathbf{d}$ is set equal to $\mathbf{r}$, and the current density then reduces to

$$\mathbf{j}_n^{(1)}(\mathbf{r}) = \frac{2ie\hbar}{m_\mathrm{e}}[\psi_n\nabla\psi_n^{(1)} - \psi_n^{(1)}\nabla\psi_n]_{\mathbf{d}=\mathbf{r}} \qquad (5)$$

In this way, a unified description of the response to a magnetic field is obtained in which both diamagnetic and paramagnetic effects are interpreted in terms of the accessibility of excited states, through a single "sum-over-states" expansion, (4), of the first-order wave functions $\psi_n^{(1)}$. It is the simplification introduced by the ipsocentric choice that leads directly to the few-orbital model of delocalized systems.

For a system with elements of symmetry, the interpretation of current densities can make use of symmetry arguments as normally invoked in discussions of transitions between states in spectroscopy. The angular momentum operator for rotation about any point $\mathbf{d}$ is written $\hat{\mathbf{l}}(\mathbf{d}) = \hat{\mathbf{l}}(\mathbf{0}) - \mathbf{d} \times \mathbf{p}$, where $\hat{\mathbf{l}}(\mathbf{0})$ refers to rotation about the origin of coordinates, and hence has the symmetry of a rotation, and $\hat{\mathbf{p}}$, the linear momentum operator, has the symmetry of a translation. More generally, in preparation for the interpretation of local circulations, we write

$$\hat{\mathbf{l}}(\mathbf{d}) = \hat{\mathbf{l}}(\mathbf{r}_0) - (\mathbf{d} - \mathbf{r}_0) \times \hat{\mathbf{p}} \qquad (6)$$

in which $\hat{\mathbf{l}}(\mathbf{r}_0)$ now refers to rotation about $\mathbf{r}_0$. Then

$$\begin{aligned}\psi_n^{(1)}(\mathbf{r}) = {}& -\frac{e}{2m_\mathrm{e}}\left[\sum_{p>N/2}\psi_p(\mathbf{r})\frac{\langle\psi_p|\hat{\mathbf{l}}(\mathbf{r}_0)|\psi_n\rangle}{\epsilon_p - \epsilon_n}\right]\cdot\mathbf{B} + \\ & \frac{e}{2m_\mathrm{e}}\left[(\mathbf{d} - \mathbf{r}_0) \times \sum_{p>N/2}\psi_p(\mathbf{r})\frac{\langle\psi_p|\hat{\mathbf{p}}|\psi_n\rangle}{\epsilon_p - \epsilon_n}\right]\cdot\mathbf{B} \\ = {}& \psi_n^{(p)} + \psi_n^{(d)}\end{aligned} \qquad (7)$$

The term $\psi_n^{(p)}$ gives rise to the conventional paramagnetic contribution and is determined by the accessibility of unoccupied orbitals through *rotational* transitions. The term $\psi_n^{(d)}$ is the corresponding diamagnetic contribution and is determined by the accessibility of unoccupied orbitals through *translational* transitions.

(ii) Role of the Local Origin. It is important to distinguish between the *gauge origin* $\mathbf{d}$ and the local *origin of coordinates* $\mathbf{r}_0$. In the ipsocentric formulation $\mathbf{d}$ is set to $\mathbf{r}$, but the choice of $\mathbf{r}_0$ remains free. This allows a further flexibility in the interpretation of orbital current density, which is particularly useful for localized orbitals. Thus, although $\mathbf{d}(\mathbf{r})$ must be *common to all orbitals*, in order that the sum (2) over orbital current densities remain invariant to choice of gauge origin, different notional centers $\mathbf{r}_0$ can be chosen for different orbitals, or even for different regions of space. In contrast, $\mathbf{r}_0$ in some other formulations of current density is just the fixed origin of coordinates with respect to which position is defined, and the quantity $\mathbf{d}$ then acts as both gauge origin and local center of rotation. For example, in the popular IGLO method,[11,12] a single individual gauge origin is chosen at the centroid of charge for each localized orbital. The similarity between IGLO and the present approach is, however, more apparent than real, because in the ipsocentric approach each point is its own gauge origin, and the concept of local center of rotation has been introduced here only as an interpretative tool and does not play the necessary theoretical and computational role that defines the IGLO method.

In maps of current density within the ipsocentric formulation, the quantity $\mathbf{r}_0$ can be used to chart the points, such as centers of circulation, at which the current density vanishes. If, with respect to $\mathbf{r}_0$, the local paramagnetic contribution to the first-order wave function, $\psi_n^{(p)}$ in (7) for orbital ψ_n, is greater than the local diamagnetic contribution, $\psi_n^{(d)}$, then the local circulation around $\mathbf{r}_0$ *is* "paramagnetic" (clockwise in the maps). If the diamagnetic contribution is the greater than the local contribution *is* "diamagnetic" (anticlockwise in the maps). This "scanning" of the current density map corresponds to the visual perception of the global pattern of circulations that makes maps such useful tools for the visualization of data. It could be used as the basis for an automated "reading" of maps. These observations of course remain true in the exact gauge-independent *N*-electron theory of current density as they follow only from the definition of angular momentum as a moment of momentum.

(iii) Transformation of Orbitals. So far, it has been tacitly assumed that the current density is to be described in terms of contributions of canonical molecular orbitals. We now consider an orthogonal transformation that transforms the set of occupied molecular orbitals ψ_n to the new set of orthonormal orbitals ϕ_k. The *N*-electron one-determinant wave function is invariant under such a transformation of orbitals.[13] If the same transformation is applied to both unperturbed and first-order orbitals,

$$\phi_k = \sum_{n=1}^{N/2} U_{kn}\psi_n \qquad \text{and} \qquad \phi_k^{(1)} = \sum_{n=1}^{N/2} U_{kn}\psi_n^{(1)} \tag{8}$$

then the total current density is also invariant, and (2) and (3) are replaced by (9) and (10):

$$\mathbf{j}^{(1)}(\mathbf{r}) = \sum_{k=1}^{N/2} \mathbf{j}_k^{(1)}(\mathbf{r}) \tag{9}$$

where, in the ipsocentric formulation, the current density for the new orbital ϕ_k is

$$\mathbf{j}_k^{(1)}(\mathbf{r}) = \frac{2ie\hbar}{m_e}\left[\phi_k \nabla \phi_k^{(1)} - \phi_k^{(1)} \nabla \phi_k\right]_{\mathbf{d}=\mathbf{r}} \tag{10}$$

The significance of (10) is that it allows localized and delocalized descriptions of a system to be treated on an equal footing. Canonical molecular orbitals ψ_n are often delocalized over the whole molecular structure, but it is possible to calculate localized orbitals ϕ_k that may be more suitable for the description of inner-shell and σ-bond orbitals.[14,15] Even conventionally delocalized π systems support descriptions in terms of spatially localized π orbitals.[16,17]

After a summary of the technical details of the computational methods used in the present work, we examine in the following sections benzene and some other well-studied systems to discover how the alternative descriptions of electron distribution, localized and delocalized, perform in the interpretation of current density in terms of orbital contributions.

3. Methods

The geometries used in this paper are the theoretical 6-31G**/RHF equilibrium geometries, computed with the CADPAC program.[18] The 6-31G** basis was also used for all calculations of current densities, except for benzene and borazine for which the larger "Level V" basis (14s8p4d/8s3p) → [9s6p4d/6s3p][19,20] ensured the higher accuracy required for our discussion of current densities near nuclei in these molecules.

Localization of the molecular orbitals was performed by means of the population-localization method of Pipek and Mezey,[21] which makes use of Mulliken populations[22] and is therefore particularly appropriate for LCAO wave functions. Its results compare closely with those of the pioneering methods of Foster and Boys,[23] in which the distances between the orbital centroids are maximized, and of Edmiston and Ruedenberg[24] in which the total self-energy of the orbitals is maximized. The Pipek−Mezey method gives localized orbitals that are almost identical to those obtained by the Edmiston−Ruedenberg method and, like the latter, conserves $\sigma-\pi$ separation in conjugated planar systems.

The current density maps were computed within the ipsocentric CTOCD-DZ (continuous transformation of current density-diamagnetic zero) formulation of coupled Hartree−Fock theory with the Exeter version of the SYSMO suite of programs.[25] All the maps of orbitals, electron density, and current density for σ electrons are plotted in the molecular plane; those for the π electrons are plotted in a plane at distance 1 a_0 from the molecular plane. The current density maps show current $\mathbf{j}^{(1)}$ induced by a unit magnetic field perpendicular to the molecular plane, and the choices of plotting plane avoid problems associated with the component of current density parallel to the applied magnetic field.[26−29] This parallel component makes no contribution to the second-order energy or to integrated second-order magnetic properties such as mean magnetizability and nuclear shielding.[26,27] In the molecular plane, it is zero by symmetry; in the 1 a_0 plane, the parallel component is symmetry-allowed but is small at this height above the molecular plane,[28,29] so that the current flow lies essentially within the plane.

4. Localized and Delocalized Currents in Benzene

The electronic structure of the ground state of the benzene molecule is conventionally regarded as made up of three subsystems: localized inner shells on the carbons, localized σ-valence C−C and C−H bonds, and a delocalized π system. We consider the three separately.

Inner-Shell Orbitals. The six lowest-lying molecular orbitals of benzene, near degenerate at $\epsilon \approx -11.2\ E_h$, are essentially linear combinations of the carbon 1s atomic orbitals. They, and the corresponding localized orbitals, display tight circles of current density (not shown here) with total maximum current density $j_{\max} \approx 1.7$ au (au $= e\hbar/m_e a_0^4$) close to the nuclei (compare with 0.1 au typical of the interatomic regions of the molecule).

Each localized inner-shell orbital, ϕ_k, is essentially an atomic orbital centered on a carbon at $\mathbf{r}_k$. With respect to the theory presented in section 2, the choice $\mathbf{r}_0 = \mathbf{r}_k$ then closely mimics the conventional single-center description of the diamagnetic circulation in atoms. The "paramagnetic" component $\phi_k^{(p)}$ of the first-order wave function is small (zero in the isolated atom) and $\phi_k^{(1)}$ is determined almost wholly by the remaining "diamagnetic" component $\phi_k^{(d)}$; that is, by the accessibility of unoccupied orbitals through translational transitions. As the inner-shell orbital has mainly s-character, all unoccupied orbitals with local p-character contribute to $\phi_k^{(1)}$, which determines the current density of the electrons in ϕ_k.

***σ*-Valence Orbitals.** The total current density induced in the σ-valence structure by a magnetic field at right angles to the

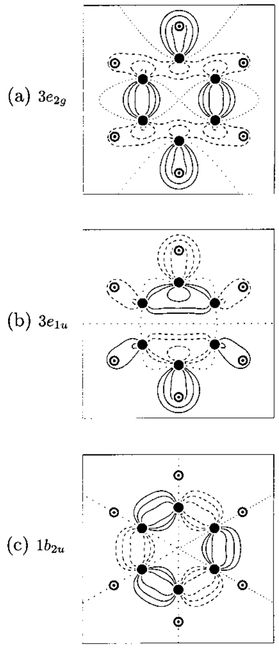

Figure 1. Three highest-lying σ molecular orbitals of benzene. Orbital contour maps for (a) the degenerate pair $3e_{2g}$, (b) the $3e_{1u}$ pair, and (c) $1b_{2u}$. Contours are $\pm 0.07 \times 1.5^n\ a_0^{-3/2}$, $n = 1, 2, 3, ...$ Carbon and hydrogen centers are denoted by filled and dotted circles, respectively.

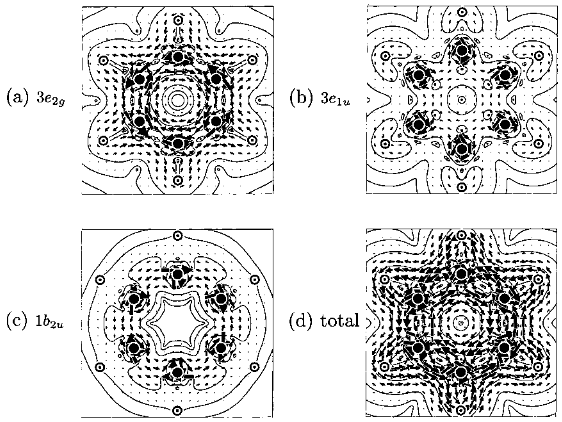

Figure 2. σ-Valence orbital and total current density maps for benzene. The maps are plotted in the molecular plane and show the current density induced by the unit magnetic field perpendicular to the plane for (a) the degenerate pair $3e_{2g}$, (b) the $3e_{1u}$ pair, (c) $1b_{2u}$, and (d) the total σ-valence distribution (the direction of flow near the carbon nuclei is reversed when inner-shell densities are included). Diamagnetic circulation is anticlockwise, paramagnetic circulation is clockwise. The contours show the modulus of current density with contour values 0.001×4^n au (au $= e\hbar/m_e a_0^4$), for $n = 0, 1, 2, ...,$ and the vectors (arrows) show the magnitude and direction of current density. For clarity, the length of arrows representing the large current densities near nuclei (see text) has been restricted to that corresponding to density 0.15 au. Atomic symbols as in Figure 1.

molecular plane in benzene is dominated by that of the 10 electrons in the three highest-lying σ molecular orbital levels: $3e_{2g}$ (the σ-HOMO), $3e_{1u}$, and $1b_{2u}$. The individual canonical orbitals are shown in Figure 1. The corresponding orbital current densities in the molecular plane are shown in Figures 2a and 2b for the degenerate orbital pairs $3e_{2g}$ and $3e_{1u}$, and Figure 2c for $1b_{2u}$.

The total σ-valence current density distribution in the plane, given in Figure 2d, can be regarded as made up of two distinct components: (i) strong local paramagnetic (clockwise) circulations around the carbons ($j_{\max} \approx 0.4$ au) and (ii) local diamagnetic (anticlockwise) circulations in C−C and C−H bonds ($j_{\max} \approx 0.12$ au). Note that the global diamagnetic circulation around the perimeter of the molecule and paramagnetic circulation inside the hexagon of carbons arise here from the superposition of the local circulations.

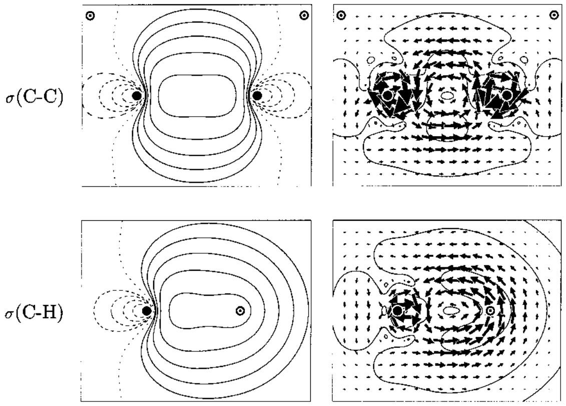

Figure 3. Localized σ-bond orbitals and orbital current densities in benzene. The orbital contours are as in Figure 1; the current density contours are as in Figure 2, with the same restriction on arrow length. Atomic symbols as in Figure 1.

The strong local paramagnetic circulation around each carbon is made up of circulations that are paramagnetic in the "inner" regions in orbitals $3e_{1u}$ and $1b_{2u}$ and diamagnetic in orbitals $3e_{2g}$. These can be explained within the ipsocentric formulation in terms of the accessibility of virtual orbitals with the appropriate local orbital symmetry. In particular, Figure 1 shows that the three sets of orbitals have atomic p-like structure at each carbon and that *only one* of the two in-plane p components is involved in $3e_{1u}$ and $1b_{2u}$, radial in $3e_{1u}$ and tangential in $1b_{2u}$. The second component in each case is accessible by local rotation. In contrast, both p-type components are involved in the $3e_{2g}$ orbital pair so that local rotation is inhibited. The direction of the net circulation around the carbons is reversed when the diamagnetic inner-shell circulations are included.

This interpretation of currents complements traditional pictures that involve the redistribution of charge that accompanies the formation of covalent bonds.[30−33] For a first-row atom such as carbon in which σ bonding can be interpreted in terms of the overlap of sp-hybridized orbitals, the build-up of charge between the nuclei is accompanied by a charge depletion close to the nucleus. This "positive hole" in the unperturbed electron distribution facilitates the paramagnetic rotation of charge in the presence of the magnetic field.

The essentially paramagnetic nature of the σ-valence current density around each carbon nucleus, and its origin in the unidirectional asymmetry of the bonding orbitals, is seen even more clearly in Figure 3 of the *localized* orbitals and corresponding current density maps. In both the C−C and C−H orbitals the current density is a superposition of a paramagnetic circulation around each carbon and a diamagnetic circulation around a point at or close to the centroid of the bond. In the ipsocentric formulation it is therefore appropriate to consider more than one formal center of rotation $\mathbf{r}_0$ in each localized orbital, one for the inner circulation around each carbon and one for the primary circulation in the bond. We note that all 24 σ-valence electrons contribute fully to the current density in the localized orbital picture.

***π* Orbitals.** It is well-known that although localized π orbitals can be calculated for benzene, they contain substantial contributions from atomic orbitals on more than two carbons and are not unique.[16,17] There is, in fact, a one-parameter family

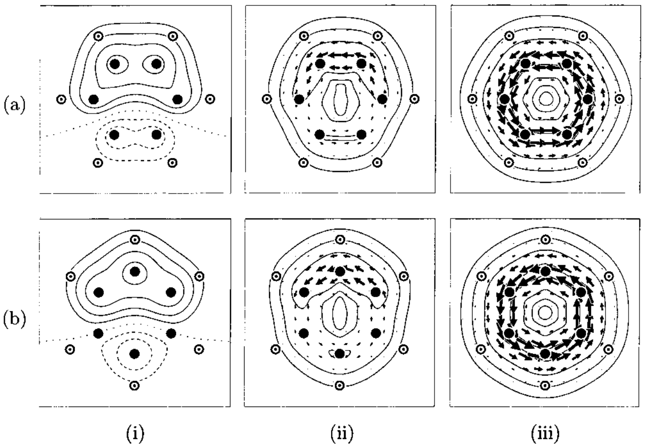

Figure 4. Localized π orbitals in benzene. Alternative localization schemes (see text): (a) $\alpha = 0$, (b) $\alpha = \pi/3$. In each case, (i) is a representative orbital, (ii) is the corresponding orbital current density, (iii) is the total π current density. The maps are plotted in the 1 a_0 plane. Orbital contours are $\pm 0.02 \times 2^n\, a_0^{-3/2}$, $n = 1, 2, 3, ...$ Current density contours are as in Figure 2 (no restriction on arrow length required). Atomic symbols as in Figure 1.

comprising an infinite number of sets of equally localized equivalent orbitals of type

$$\phi_1 = \frac{1}{\sqrt{3}}[1a_{2u} + \sqrt{2}(1e_{1g}(x)\cos\alpha + 1e_{1g}(y)\sin\alpha)]$$

$$\phi_2 = C_3\phi_1 \qquad \phi_3 = C_3^{\,2}\phi_1 \qquad (11)$$

where C_3 is the operation of rotation through $2\pi/3$ about the principal axis and α is an arbitrary angle. The set with $\alpha = 0$, illustrated by one representative orbital in Figure 4a(i), spans one of the Kekulé structures of benzene; the set with $\alpha = \pi/3$ gives the complementary Kekulé structure. Another set, with $\alpha = \pi/2$, is illustrated by the representative orbital in Figure 4b(i); each orbital in this set has maximum π density on one carbon.

The *essential* nonlocalizability of the benzene π orbitals is demonstrated in dramatic fashion by the current densities shown in Figure 4a(ii),b(ii). Each "localized" orbital contributes an open-ended fragment of current density to the total ring current (Figure 4a(iii),b(iii)), and the center of circulation remains at the center of the carbon hexagon, *outside* the region of greatest orbital density. The invariance to parameter α is demonstrated by the identical total current densities obtained from the two sets of orbitals.

Such fragmentation patterns are not unique to benzene, and it is demonstrated in section 5 that nonlocalizability of current density is a property of many conjugated π systems, even those for which a unique set of localized π orbitals exists.

This discussion prompts the question: *when should an orbital be treated as localized?* The present analysis of orbital current density suggests that a magnetic criterion for the physical significance of an orbital is that the orbital should support closed flowlines of current density. By this criterion, the inner-shell and localized σ-valence orbitals of benzene have physical reality as localized orbitals, but the π orbitals are necessarily delocalized.

5. Conjugated Hydrocarbons

The localized σ-valence orbitals of planar conjugated hydrocarbons, and of their associated current densities, are similar to those shown in Figure 3 for benzene, with only minor variations with position in the molecule, and they are not considered further here. Of primary interest in these systems is the π structure.

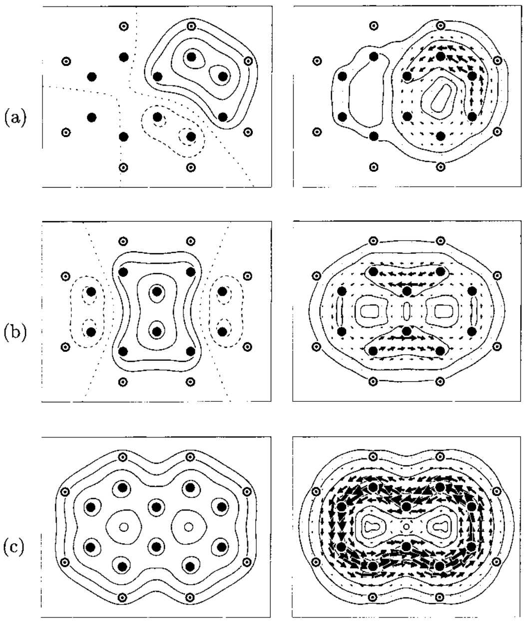

Figure 5. Localized π orbitals and total π distribution in naphthalene. (a) and (b) are the two distinct localized orbitals with corresponding orbital current densities. (c) is the total π distribution. Mapping details as in Figure 4.

It has been proposed by England and Ruedenberg (ER)[17] that the localized π structures of planar conjugated hydrocarbons can be constructed from just four basic types of localized orbitals. Two of these, labeled πl2 and πl3 by ER, are the orbitals (a) and (b), respectively, shown in Figure 4 for benzene. England and Ruedenberg used a method based on Hückel π molecular orbital theory with inclusion of overlap to calculate the molecular orbitals and invoked the Mulliken approximation for two-electron integrals[34] in the implementation of the classic Edmiston−Ruedenberg localization procedure.[24] Despite the very great differences between the semiempirical and the present ab initio methods, they give broadly similar localized orbitals and structures. We revisit here some well-studied molecules[3] in order to compare the patterns of orbital current density in both localized and delocalized desciptions.

Naphthalene. The localized π orbitals of naphthalene, the total π-electron density, and the associated current densities are shown in Figure 5. Orbital (a) is similar to that in benzene (ER type πl2) and, as in benzene, the current traverses the orbital as an open-ended fragment of the total π circulation (c). The central-bond orbital (b), labeled πl2′ by ER, contributes further fragments to the total current, but this time at right angles to the bond; by symmetry current cannot flow along the central bond. The naphthalene π system is therefore again intrinsically delocalized and closely follows the four-electron rule for monocycles,[3,4] whereby only the four electrons in the two highest-lying molecular orbitals make significant contributions to the total (diamagnetic) ring current.

A molecule containing only localized π orbitals of types πl2 and πl2′, (a) and (b) in Figure 5, has been defined by England and Ruedenberg as of Kekulé-type, since each orbital then appears to describe a "double bond". In agreement with ER, the computed localized π structure of naphthalene corresponds to the unique Kekulé structure with a central double bond. On the other hand, the total π-electron density distribution shows a largely uniform pattern throughout the system and provides few clues to the expected current density.

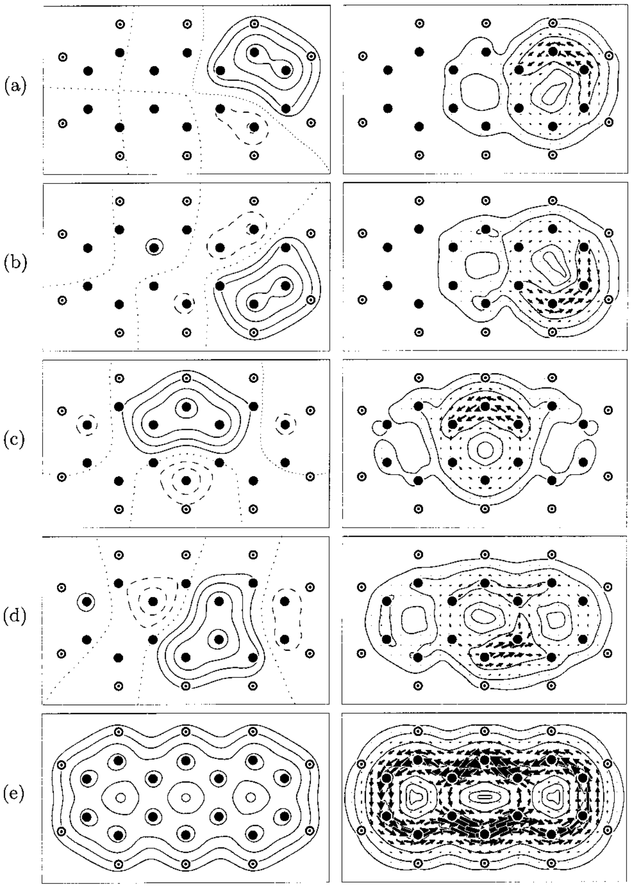

Figure 6. Localized π orbitals and total π distribution in anthracene. (a) to (d) are the four distinct localized orbitals with corresponding orbital current densities. Each of (a), (b), and (d) has an equivalent partner obtained by left-right reflection. (e) is the total π distribution. Mapping details as in Figure 4.

Anthracene. The complex pattern of localized orbitals in anthracene (Figure 6), particularly in the central ring, reflects the absence of a unique totally symmetric Kekulé structure for this molecule. Orbital (c), of ER type πl3, is similar to the alternative orbital for benzene shown in Figure 4b, while orbitals (d) are hybrids of πl3 and πl4, the latter having one dominant carbon at the center of a triangle of three others. The nonsymmetrical localized structure of the central ring gives rise to two different, but similar, pairs of orbitals (a) and (b), of almost pure ER type πl2, in the outer rings.

All the localized orbitals of anthracene contribute fragments of current density to the total π current that flows largely around the perimeter of the carbon structure, but with some cross-linking.[35] In the localized description the cross-links of current around the central ring are associated with the complex multicenter structure of orbital (d) and the consequent bifurcation of the current. Once more, the (delocalized) π molecular orbitals are essentially nonlocalizable, and anthracene follows the four-electron rule. There is a single center of circulation, although the leakage of current around the central ring reflects the partial breakdown of the full delocalization of the simple monocycle.

Linear Acenes. With the localization procedure used in the present work, linear acenes with even numbers of rings have the unique Kekulé-type structure found in naphthalene, with type πl2 bonds on the perimeter and a πl2' central bond. The distinct localized orbitals for tetracene (naphthacene) are shown in Figure 7. In this case a partial breakdown of full delocalization is reflected by cross-links of current around the central naphthalenic unit, with contributions from both (a) and (b). In the same way, linear acenes with odd numbers of rings have the anthracene pattern, with πl3 and πl3/l4 hybrids in the central ring, (c) and (d) in Figure 6, and type πl2 on the perimeter. The essential nonlocalizability of the π orbitals in the linear acenes is observed in all cases studied[35] and is in full agreement with the observation by ER that the localized π orbitals suffer from “local delocalization” (sic).

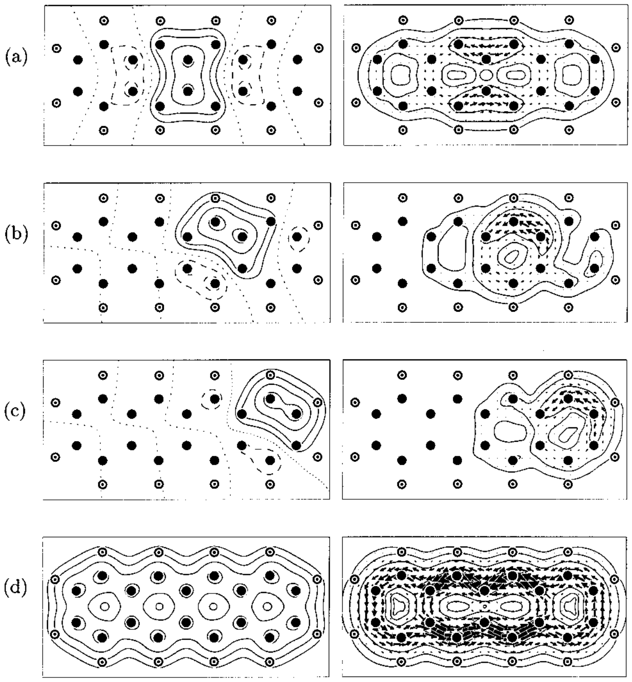

Figure 7. Localized π orbitals and total π distribution in tetracene. (a) to (c) are the three distinct localized orbitals with corresponding orbital current densities. (d) is the total π distribution. Mapping details as in Figure 4.

Other conjugated systems demonstrate that the simple patterns of local current densities can combine to give complex and surprising totals.

Coronene. The ipsocentric orbital analysis of the π current density of coronene shows that the diamagnetic-rim-plus-paramagnetic-hub pattern of ring currents is dominated by the contributions of the four electrons in the degenerate HOMO pair of orbitals. Figure 8 shows that the localized structure is of Kekulé-type, made up of six local orbitals of type πl2 on the rim and six radial of type πl2'. Those of the first type contribute only to the diamagnetic circulation in the rim, but the radial orbitals contribute also to the counter-circulation in the hub. Neither the localized orbitals nor the total π electron distribution provide any hint of the rim/hub nonlocalizable circulation when coronene is placed in a magnetic field at right angles to the molecular plane.

Pyracylene. Figure 9 shows that that the localized π structure of pyracylene is made up of the types πl2 and πl2' local orbitals of the parent naphthalenic unit, with two additional local orbitals of types πl2 that define the paramagnetic circulations in the pentagons. In this case, however, the resultant multicenter pattern of circulations shows that some partial localization of the π structure may be possible.

Subsets of the individual localized orbitals can be combined to provide an analysis of the current density in terms of localized structural motifs. Addition of the current densities of the four equivalent orbitals 9a recovers a diatropic naphthalenic ring current (Figure 10a), while orbital 9b with the pair of equivalent orbitals 9c gives the pair of disjoint paratropic pentagonal circulations (Figure 10b).

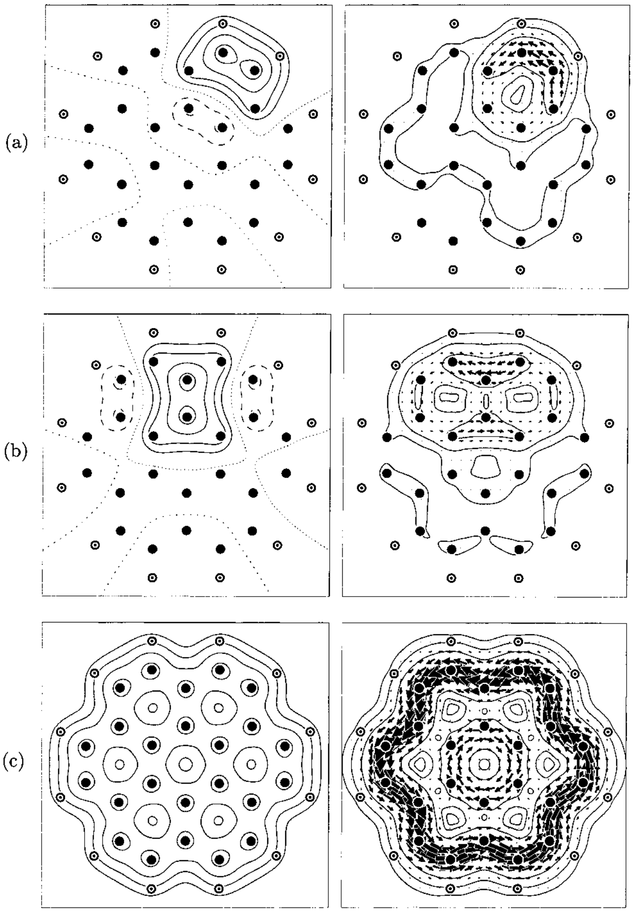

Figure 8. Localized π orbitals and total π distribution in coronene. (a) and (b) are the two distinct localized orbitals with corresponding orbital current densities. (c) is the total π distribution. Mapping details as in Figure 4.

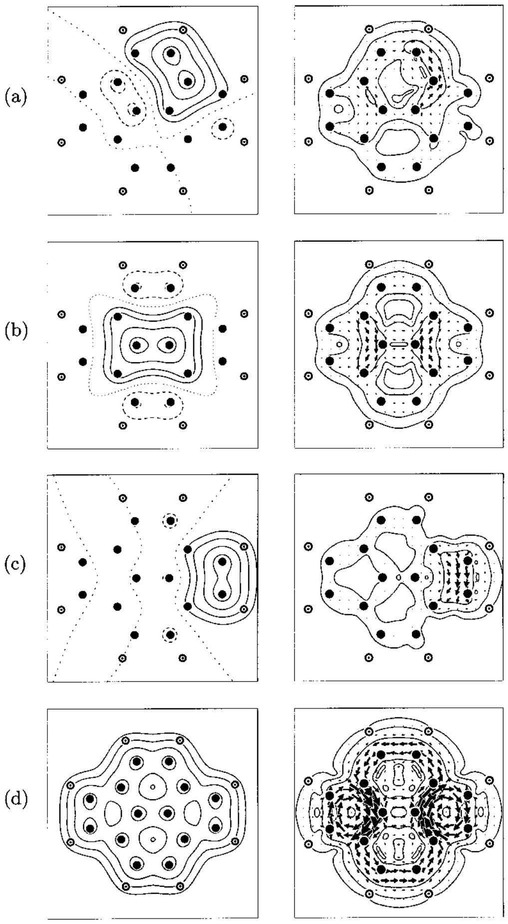

Figure 9. Localized π orbitals and total π distribution in pyracylene. (a) to (c) are the three distinct localized orbitals with corresponding orbital current densities. (d) is the total π distribution. Mapping details as in Figure 4.

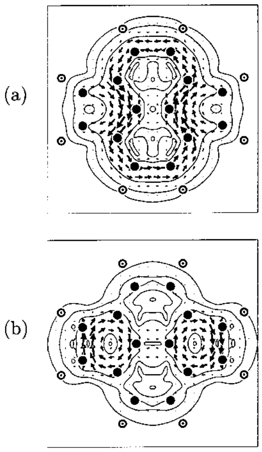

Figure 10. Partial localization of the π distribution in pyracylene. Mapping details as in Figure 4.

6. Borazine

From the nonlocalizable systems exemplified by the planar conjugated hydrocarbons, we turn now to an example in which homonuclear CC pairs are replaced by isoelectronic heteronuclear pairs BN.

The localized σ-valence orbitals of borazine, the total σ-valence electron density, and the associated current densities are shown in Figure 11. The orbitals are superficially similar to those in benzene (Figure 3), but the total current densities are very different. The σ-bond circulations in benzene, seen in the total density map (Figure 2d), are characteristic of nonpolar covalent bonds. In borazine, however, there is a significant shift of the center of "interatomic" circulation toward the electronegative nitrogen in both B−N and N−H bonds, with the result that the individual orbital contributions combine to give a single diamagnetic circulation around each nitrogen, leaving the borons isolated within their local atomic circulations. The B−H bond is polarized toward the hydrogen and its identity is preserved in the total current density (Figure 11d).

Figure 12 for the localized π orbital shows that the total π current density of borazine is made up of distinct islands of circulations around the nitrogen centers[36] and confirms that the soubriquet "inorganic benzene" is entirely inappropriate, despite the presence of six π electrons. The pattern of localization is indeed close to that expected of three noninteracting distributions. Thus, if the three localized orbitals are ϕ_1, ϕ_2, and ϕ_3, in the absence of overlap the corresponding canonical orbitals are the nondegenerate $1a_2''$, $\psi_1 = (1/\sqrt{3})[\phi_1 + \phi_2 + \phi_3]$, and the degenerate $1e''$ pair, $\psi_2 = (1/\sqrt{2})[\phi_1 - \phi_2]$ and $\psi_3 = (1/\sqrt{6})[2\phi_3 - \phi_1 - \phi_2]$. The current density associated with ψ_1 near nitrogen 1 would have strength equal to one-third that of ϕ_1, that of ψ_2 would be one-half, and that of ψ_3 would be one-sixth. The computed maximum current densities for the canonical orbitals follow these proportions. The maximum total density is 0.044 au: the corresponding computed values (in au) at site 1 for the canonical orbitals are 0.014 for ψ_1, 0.023 for ψ_2, and 0.007 for ψ_3, compared with 0.015, 0.022, and 0.007, respectively, for noninteracting local distributions.

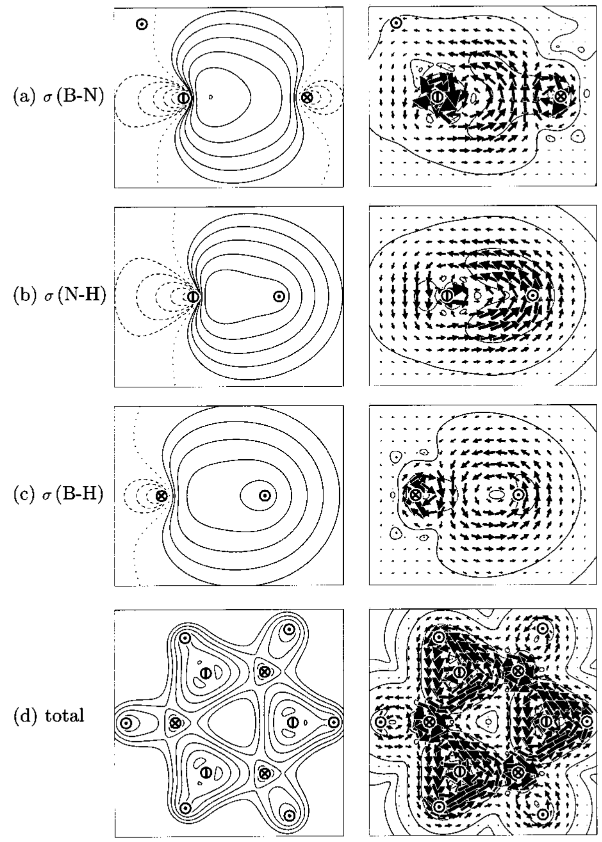

Figure 11. σ-Bond orbitals and total σ-valence distribution in borazine. Mapping details as in Figure 2. Nitrogen, boron, and hydrogen centers are denoted by barred, crossed, and dotted circles, respectively.

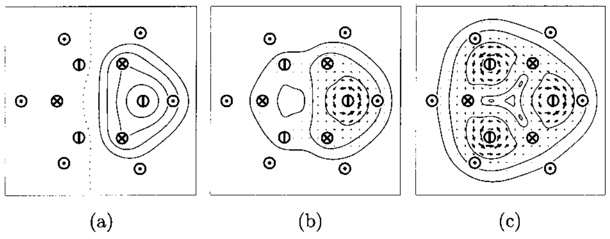

Figure 12. Localized π orbitals and total π distribution in borazine: (a) representative localized orbitals; (b) the corresponding orbital current density; (c) the total π current density. Mapping details as in Figure 4 with atomic symbols as in Figure 11.

All three π orbitals make significant contributions to the π current density in borazine, in contrast to benzene in which the current is dominated by the four electrons in the degenerate HOMO pair. This difference in the *number* of electrons that are deemed to contribute can be interpreted in terms of the different degrees of localizability of the two systems. In borazine, the π molecular orbitals are fully localizable, and the total current density is the sum of disjoint local circulations each involving two electrons and determined by the accessibility of virtual orbitals with the correct *local* symmetries. All six π electrons therefore appear as contributors in both localized and delocalized (canonical) descriptions of the system. The π structure of benzene, on the other hand, is essentially nonlocalizable, and the number of contributing electrons is determined by the accessibility of virtual orbitals with the correct *global* symmetries. This results in a decrease in the number of contributing electrons from six in the localized description to four in the delocalized description.

7. Conclusions

The ipsocentric formulation of the theory of current density has been extended to provide a visualization of the patterns of current flow in systems with several centers of circulation. It has been shown that the formal structure of orbital contributions to the total current is invariant under an orthogonal transformation of the orbitals, and the orbital analysis can therefore be applied in a uniform way to both localized and delocalized description of the electronic structure.

The analysis of the patterns of current flow in localized orbitals suggests that a magnetic criterion for the physical significance of an orbital is that it should support closed flowlines of current density. By this criterion the inner-shell orbitals and the σ-valence orbitals of benzene and related conjugated hydrocarbons and the π orbitals of borazine have physical reality as localized orbitals. Localized π orbitals for the hydrocarbons, on the other hand, contribute open-ended fragments of current density to the total, with flowlines that cut through the orbital rather than circulating within it. The π orbitals in these systems are therefore intrinsically delocalized, whereas borazine exemplifies a structure that is intrinsically localized, the total π current being the sum of disjoint local circulations.

In all the systems studied here, the number of electrons counted as contributing to the current density is related to the degree of localizability of the electron distribution. The few-electron picture of aromatic systems[3,4] is shown to be a consequence of the delocalized nature of their π structure.

The way is now open to exploration of localization and magnetic response in extended systems.

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