Patterns of Ring Currents in Conjugated Molecules: A Few-Electron Model Based on Orbital Contributions

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In the CTOCD-DZ (continuous transformation of origin of current density-diamagnetic zero) formulation of coupled Hartree−Fock theory for magnetic response of closed-shell systems, induced current density at each point is calculated with the gauge origin at that point. In addition to its economy and accuracy for total current maps, CTOCD-DZ is shown to yield a unique and physically motivated definition of, and symmetry criteria for, orbital contributions to current density. This leads to a few-electron interpretation of ring currents. Only the four HOMO electrons of an aromatic ($4n+2$)-electron monocycle contribute significantly to the ring current, and in general only a small subset of the high-lying π electrons dominate the more complex patterns of current in polycyclic π systems. Benzene, naphthalene, hexacene, pyracylene, coronene, and corannulene are treated as examples.

1. Introduction

Ring currents play an important role in the interpretation of magnetic properties of conjugated and, in particular, aromatic systems.[1−5] They can now be visualized and quantitatively mapped for molecules of significant size with accurate and economical distributed-origin ab initio methods, which can be used to probe traditional models and explanations of magnetic properties.[6−15]

The purpose of the present paper is to show that a particular formulation of the distributed-origin approach, the CTOCD-DZ (continuous transformation of origin of current density-diamagnetic zero) method,[6,7] lends itself to ready interpretation of current density maps. It will be shown, first, that the definition of orbital contributions to the total induced current density is at its simplest for CTOCD-DZ, and second, that the derived sum-over-states formula for current density gives easily applied criteria for activity of an orbital. In particular, an analogue of the famous Hückel ($4n+2$) rule can be used to answer the question of how many and which electrons in a conjugated system are counted as responsible for ring currents. It can be proved that exactly *four* electrons produce the *whole* of the induced diatropic π current in a ($4n+2$)-electron monocycle, and just *two* are responsible for the induced paratropic π current of a $4n$-electron monocycle.[16] Similar simplifications apply to polycyclic systems such as naphthalene and coronene, where again four electrons produce the diamagnetic ring current. In corannulene, which exhibits counter-rotating paramagnetic and diamagnetic circulations,[14] the diamagnetic rim and paramagnetic hub currents arise from disjoint sets of four electrons each. It will be seen that differences between π systems in this respect can be rationalized by pictorial molecular-orbital arguments.

Within the orbital approximation, the total (first-order) current density distribution of a molecule can be formally partitioned into orbital contributions,[17]

$$\mathbf{j}(\mathbf{r}) = \sum_n \mathbf{j}_n(\mathbf{r})$$

For a molecule in a static uniform magnetic field, the total current density is invariant with respect to gauge transformations. In particular, apart from basis set effects, the current density is independent of the choice of gauge origin, the formal "center of rotation". This is not true for the individual orbital contributions, even in a complete basis. So far, the main interest in origin transformations has been concerned with their effects on the quality of current densities computed with finite basis sets. Apart from some early work,[18,19] orbital contributions have seldom been discussed, although partitioning into σ and π current densities has been found useful for planar conjugated systems.[12,19,20] The reason for this apparent lack of interest in orbital contributions may well be uncertainty relating to their status.

That orbital contributions do in fact depend on the choice of origin is illustrated in Figure 1 by maps of orbital and total π-electron current densities for the benzene molecule, computed in a large basis (see Appendix).[20] Maps are shown for two choices of gauge: (a) a single, fixed origin at the center of symmetry (the *monocentric* choice) and (b) the CTOCD-DZ distribution where the current density at each point is computed with that point as origin (the *ipsocentric* choice). In (a) all three occupied π orbitals, and therefore all six π electrons, make comparable contributions to the total π current density. On the other hand, in (b) the two $1a_{2u}$ electrons make almost no contribution and only the *four* electrons in the degenerate $1e_{1g}$ HOMO are mobile in the presence of a magnetic field normal to the molecular plane. Similar behavior will be described below for several aromatic systems. An explanation of these observations requires careful consideration of the definition of orbital contributions to total current density.

The structure of the present paper is as follows. The theory of the response of an N-electron system to an external magnetic field is summarized, and the ipsocentric (CTOCD-DZ) formulation is defined in section 2. Orbital current densities are defined as sums over states, and the unique physical status of the formulation is discussed in section 3. This leads to selection rules for contributing orbitals and a few-electron classification of ring-current systems in section 4. Section 5 shows how orbital contributions rationalize ring currents in a variety of π sys-

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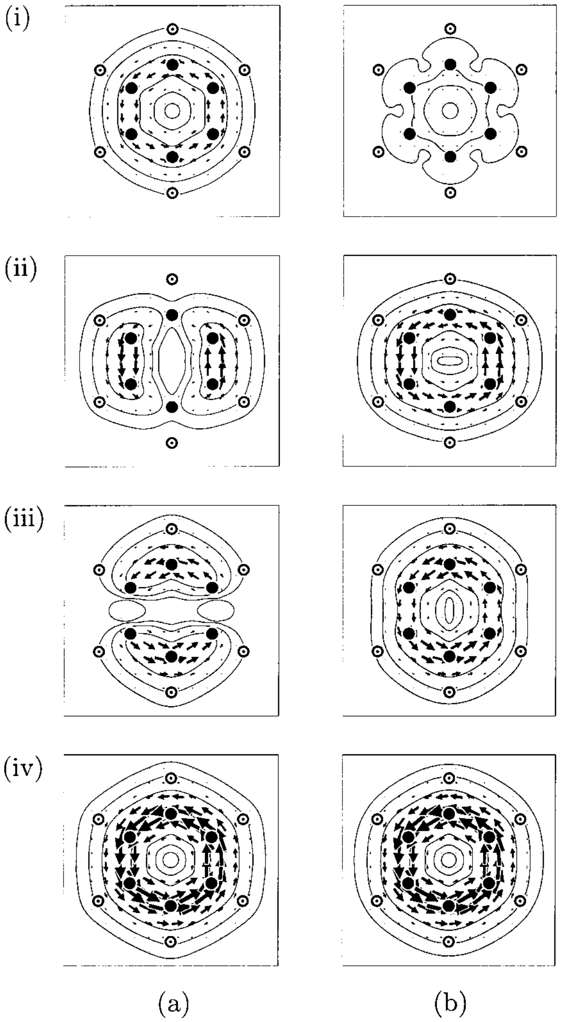


Figure 1. Orbital contributions to the π ring current in benzene. Maps are computed in (a) 1-center and (b) CTOCD-DZ methods. The orbital contributions are plotted for (i) $1a_{2u}$, (ii) $1e_{1g}(x)$, and (iii) $1e_{1g}(y)$ molecular orbitals, and (iv) shows the total computed π current. Computational details are given in the Appendix.

tems: benzene, naphthalene, hexacene, pyracylene, coronene, and corannulene. Section 6 draws some general conclusions. Technical details of the computations and current density maps are given in the Appendix.

2. Current Density and Origin Transformations

In the Schrödinger formulation of quantum theory the charge and current densities of an N-electron system in state Ψ are[8,21]

$$\rho(\mathbf{r}) = -eN\int \Psi^*\Psi \, d\tau' \tag{1}$$

and

$$\mathbf{j}(\mathbf{r}) = \frac{e}{m_e}\mathbf{A}\rho(\mathbf{r}) - \frac{e\hbar N}{2im_e}\int(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)d\tau' \tag{2}$$

where $\int \cdots d\tau'$ represents summation over all electron spins and integration over the spatial coordinates of all the electrons except one, for which the coordinates are set to $\mathbf{r}$, and $\mathbf{A}$ is the magnetic vector potential, related to the magnetic field by $\mathbf{B} = \nabla \times \mathbf{A}$. For a constant uniform field, the simplest form of $\mathbf{A}$ is

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{d}) \tag{3}$$

in which $\mathbf{d}$, the origin of vector potential, is explicitly included.

Let the Schrödinger equation in the absence of the magnetic field be

$$\hat{H}_0\Psi_I = \left(-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + V\right)\Psi_I = E_I\Psi_I \tag{4}$$

in which V is the usual potential energy function. The Hamiltonian to first order in the field $\mathbf{B}$ is[21]

$$\hat{H} = \hat{H}_0 + \frac{e}{2m_e}\hat{\mathbf{L}} \cdot \mathbf{B} \tag{5}$$

where $\hat{\mathbf{L}}$ is the angular momentum operator for rotation about $\mathbf{d}$ and is the sum of one-electron terms like $\hat{\mathbf{l}} = (\mathbf{r} - \mathbf{d}) \times \hat{\mathbf{p}}$, where $\hat{\mathbf{p}} = -i\hbar\nabla$ is the linear momentum operator for one electron.

We are interested here in systems with a closed-shell ground state Ψ_0. By perturbation theory, the first-order correction to Ψ_0 is

$${\Psi_0}^{(1)} = -\frac{e}{2m_e}\sum_{I>0}\Psi_I\frac{\langle\Psi_I|\hat{\mathbf{L}} \cdot \mathbf{B}|\Psi_0\rangle}{E_I - E_0} \tag{6}$$

and the current density to first order is

$$\begin{aligned}\mathbf{j}^{(1)}(\mathbf{r}) &= \frac{e}{2m_e}\mathbf{B} \times (\mathbf{r} - \mathbf{d})\rho_0(\mathbf{r}) + \frac{ie\hbar N}{m_e}\int[\Psi_0\nabla{\Psi_0}^{(1)} - \\ &\qquad {\Psi_0}^{(1)}\nabla\Psi_0]\, d\tau' \\ &= \mathbf{j}^{(d)}(\mathbf{r}) + \mathbf{j}^{(p)}(\mathbf{r}),\end{aligned} \tag{7}$$

The term $\mathbf{j}^{(d)}$ is the conventional "diamagnetic" current density, the classical response of a charge distribution to the applied field. This is the sole contribution to the current density in an atom with origin $\mathbf{d}$ at the nucleus. In general, the flow lines of $\mathbf{j}^{(d)}$ are circles in planes normal to the applied field, with the magnitude, $|\mathbf{j}^{(d)}|$, at each point proportional to both radius and local charge density. The term $\mathbf{j}^{(p)}$ is the "paramagnetic" current density and, by (6), is a typical quantum-mechanical "sum over states" , its value depending on the accessibility of excited states via rotational (magnetic dipole moment) transitions. It can be regarded as representing the interference to the free flow of $\mathbf{j}^{(d)}$ that is caused by the noncylindrical molecular field.

The exact total current density $\mathbf{j}^{(1)}$ is independent of the gauge origin $\mathbf{d}$, but its partitioning between $\mathbf{j}^{(d)}$ and $\mathbf{j}^{(p)}$ is not, as is clear from the above description of the "diamagnetic" circulation. It has long been recognized[21] that the distinction between diamagnetic and paramagnetic terms has no physical meaning, except for an atom with gauge origin on the nucleus, when $\mathbf{j}^{(p)}$ is zero. The choice of origin is less obvious in molecules. One approach has been to choose $\mathbf{d}$ at the center of charge, but this is theoretically arbitrary and it is neither necessary nor always computationally convenient to restrict the choice to just one center.

Choice of appropriate origin distribution has been a central preoccupation over the past 30 years in the development of practical methods of computing electron current densities and derived magnetic properties such as magnetizability and nuclear shielding tensors. Widely used methods that make use of a discrete distribution of origins include IGLO,[22,23] in which individual origins at the charge centroids of localized orbitals are used, and GIAO,[24] developed from London's extension of Hückel theory for molecules in a magnetic field.[2] On the other hand, Keith and Bader[6] pointed out that the origin distribution can be a continuous function, with the induced current density $\mathbf{j}^{(1)}(\mathbf{r})$ at each point $\mathbf{r}$ in space computed with respect to $\mathbf{d}(\mathbf{r})$ as origin, leading to the equivalent CSGT[6] and CTOCD[7] formulations, of which the simplest, the *ipsocentric* CTOCD-DZ formulation, is obtained by treating each point $\mathbf{r}$ as its own origin. From (7) it is seen that the diamagnetic component $\mathbf{j}^{(d)}$ vanishes when $\mathbf{d}$ is set equal to $\mathbf{r}$ and the *total* current density then reduces to

$$\mathbf{j}^{(1)}(\mathbf{r}) = \frac{ie\hbar N}{m_e}\left[\int(\Psi_0\nabla\Psi_0^{(1)} - \Psi_0^{(1)}\nabla\Psi_0)d\tau'\right]_{\mathbf{d}=\mathbf{r}} \tag{8}$$

With this equation, the concept of a classical diamagnetic response to the magnetic field has been subsumed into a single description in which both diamagnetic and paramagnetic effects can be interpreted in terms of the accessibility of excited states, through the perturbation expansion of the first-order wave function $\Psi_0^{(1)}$.

In 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. To do this, note that the angular momentum operator for rotation about any point $\mathbf{d}$ can be written $\hat{\mathbf{L}}(\mathbf{d}) = \hat{\mathbf{L}}(\mathbf{0}) - \mathbf{d} \times \hat{\mathbf{P}}$ where $\hat{\mathbf{L}}(\mathbf{0})$ now refers to rotation about the origin of coordinates and $\hat{\mathbf{P}}$, the N-electron linear momentum operator, has the symmetry of a translation. Thus, a rotation of charge about the point $\mathbf{d}$ has been replaced by a rotation about the origin $\mathbf{0}$ and a displacement term. For *any* choice of $\mathbf{d}$, the first-order wave function is then

$$\begin{aligned}\Psi_0^{(1)} &= \frac{e}{2m_e}\left[\sum_{I>0}\Psi_I\frac{\langle\Psi_I|\hat{\mathbf{L}}(\mathbf{0})|\Psi_0\rangle}{E_I - E_0}\right]\cdot\mathbf{B} + \frac{e}{2m_e}\left[\mathbf{d}\times\sum_{I>0}\Psi_I\frac{\langle\Psi_I|\hat{\mathbf{P}}|\Psi_0\rangle}{E_I - E_0}\right]\cdot\mathbf{B} \\ &= \Psi_0^{(\mathrm{p})} + \Psi_0^{(\mathrm{d})}\end{aligned} \tag{9}$$

The term $\Psi_0^{(\mathrm{p})}$ gives rise to the conventional paramagnetic contribution $\mathbf{j}^{(\mathrm{p})}$ and is determined by the accessibility of states through *rotational* transitions. It follows that in the CTOCD-DZ formulation, $\Psi_0^{(\mathrm{d})}$ is responsible for the corresponding diamagnetic contribution and is determined by the accessibility of states through *translational* transitions. This sum-over-states representation of $\mathbf{j}^{(\mathrm{d})}$ can be derived directly from the commutator relation

$$\hat{H}_0\mathbf{r} - \mathbf{r}\hat{H}_0 = -\frac{\hbar^2}{m_e}\nabla \tag{10}$$

from which it follows, in the ipsocentric formulation ($\mathbf{d}$ replaced by $\mathbf{r}$ in the evaluation of the current density), that

$$\frac{ie\hbar N}{m_e}\left[\int(\Psi_0\nabla\Psi_0^{(\mathrm{d})} - \Psi_0^{(\mathrm{d})}\nabla\Psi_0)\,\mathrm{d}\tau'\right]_{\mathbf{d}=\mathbf{r}} = \frac{e}{2m_e}(B\times\mathbf{r})\rho_0(\mathbf{r}) \tag{11}$$

The right-hand side of (11) is the conventional diamagnetic contribution $\mathbf{j}^{(\mathrm{d})}$, with respect to the origin of coordinates as center of rotation.

Thus, *both* $\Psi_0^{(\mathrm{p})}$ and $\Psi_0^{(\mathrm{d})}$, and therefore $\mathbf{j}^{(\mathrm{p})}$ and $\mathbf{j}^{(\mathrm{d})}$, have the form of sums over states, although they obey different selection rules.

3. Orbital Current Densities

In the orbital approximation for a closed-shell ground state, the N-electron wave function Ψ_0 is a Slater determinant of $N/2$ doubly occupied orbitals, chosen to be real,

$$\Psi_0(1, 2, \ldots, N) = \det[\psi_1\alpha,\psi_1\beta,\psi_2\alpha,\psi_2\beta, \ldots ,\psi_{N/2}\alpha,\psi_{N/2}\beta] \tag{12}$$

with charge density

$$\rho_0(\mathbf{r}) = -2e\sum_{n=1}^{N/2}\psi_n(\mathbf{r})^2 \tag{13}$$

Since $\hat{\mathbf{L}}$ and $\hat{\mathbf{P}}$ are sums of one-electron operators, the first-order wave function $\Psi_0^{(1)}$ becomes a sum over states in which the Ψ_I are singly excited configurations Ψ_n^p obtained from Ψ_0 by excitation of one electron from an occupied orbital $\psi_n (n \leq N/2)$ to a virtual (unoccupied) orbital $\psi_p (p > N/2)$. The single sum over N-electron states can then be replaced by a double sum over orbitals and their excitations, i.e.,

$$\sum_{I>0}\Psi_I\cdots \rightarrow \sum_{n=1}^{N/2}\sum_{p>N/2}\Psi_n^p\ldots$$

and the first-order current density becomes a sum of *orbital* contributions

$$\mathbf{j}^{(1)}(\mathbf{r}) = 2\sum_{n=1}^{N/2}\mathbf{j}_n^{(1)}(\mathbf{r}) \tag{14}$$

with orbital current densities

$$\begin{aligned}\mathbf{j}_n^{(1)}(\mathbf{r}) &= -\frac{e^2}{2m_e}\mathbf{B}\times(\mathbf{r}-\mathbf{d})\psi_n^2 + \frac{ie\hbar}{m_e}[\psi_n\nabla\psi_n^{(1)} - \psi_n^{(1)}\nabla\psi_n] \\ &= \mathbf{j}_n^{(\mathrm{d})} + \mathbf{j}_n^{(\mathrm{p})}\end{aligned} \tag{15}$$

If, for simplicity, we neglect self-consistency corrections and suppose, at first, that the orbitals ψ_n are eigenfunctions of a one-electron Hamiltonian $\hat{H}_0$ with eigenvalues ϵ_n, the first-order correction to ψ_n becomes

$$\psi_n^{(1)}(\mathbf{r};\mathbf{d}) = -\frac{e}{2m_e}\left[\sum_{p>N/2}\psi_p(\mathbf{r})\frac{\langle\psi_p|\hat{\mathbf{l}}(\mathbf{0})|\psi_n\rangle}{\epsilon_p - \epsilon_n}\right]\cdot\mathbf{B} + \frac{e}{2m_e}\left[\mathbf{d}\times\sum_{p>N/2}\psi_p(\mathbf{r})\frac{\langle\psi_p|\hat{\mathbf{p}}|\psi_n\rangle}{\epsilon_p - \epsilon_n}\right]\cdot\mathbf{B} \tag{16}$$

where $\psi_n^{(1)}(\mathbf{r};\mathbf{d})$ indicates that the first-order wave function is a function of electron position $\mathbf{r}$ and depends parametrically on the displacement $\mathbf{d}$.

In the ipsocentric CTOCD-DZ formulation, the orbital current density $\mathbf{j}_n^{(1)}$ is therefore wholly determined by the accessibility of the virtual (unoccupied) orbitals from the occupied orbital ψ_n.

For other choices of gauge origin, however, it is only the *paramagnetic* current density $\mathbf{j}_n^{(\mathrm{p})}$ that is determined by (16). The simple occupied-to-virtual orbital interpretation is then lost for the diamagnetic contribution $\mathbf{j}_n^{(\mathrm{d})}$, because of the intrusion of nonphysical occupied-to-occupied orbital transitions. To see this we note that, as long as the potential energy function in $\hat{H}_0$ is a local operator, the orbital form of (11) is

$$\mathbf{j}_n^{(d)}(\mathbf{r}) = \frac{ie\hbar}{m_e}[\psi_n\nabla\psi_n^{(d)} - \psi_n^{(d)}\nabla\psi_n]_{\mathbf{d}=\mathbf{r}} = -\frac{e^2}{2m_e}(\mathbf{B}\times\mathbf{r})\psi_n^2 \tag{17}$$

where

$$\psi_n^{(d)} = \frac{e}{2m_e}\left[\mathbf{d}\times\sum_{\mathrm{m}\neq\mathrm{n}}\psi_m\frac{\langle\psi_m|\hat{\mathbf{p}}|\psi_n\rangle}{\epsilon_m-\epsilon_n}\right]\cdot\mathbf{B} \tag{18}$$

(degenerate orbitals are to be treated in blocks in the sum of orbital contributions). It follows that, for an electron in orbital ψ_n, *all* the other orbitals $\psi_m(m\neq n)$ must be deemed to be accessible for interpretation of the orbital diamagnetic current density, whereas only the *virtual* orbitals are required for the paramagnetic current density. As a result, although the total current density of the system remains independent of choice of origin **d**, the orbital current densities themselves do not, because choice of **d** fixes the diamagnetic and paramagnetic contributions to $\mathbf{j}_n^{(1)}$, and therefore, the weight of the nonphysical occupied-to-occupied transitions. Thus, if

$$\psi_n'(\mathbf{r};\mathbf{d}) = \frac{e}{2m_e}\left[\mathbf{d}\times{\sum_{m=1}^{N/2}}'\psi_m(\mathbf{r})\frac{\langle\psi_m|\hat{\mathbf{p}}|\psi_n\rangle}{\epsilon_m-\epsilon_n}\right]\cdot\mathbf{B} \tag{19}$$

is that part of $\psi_n^{(d)}$ containing the transitions from ψ_n to other *occupied* orbitals ψ_m, then, denoting the first-order current density calculated at **r** with gauge origin at **d** by $\mathbf{j}_n^{(1)}(\mathbf{r};\mathbf{d})$,

$$\mathbf{j}_n^{(1)}(\mathbf{r};\mathbf{d}) = \mathbf{j}_n^{(1)}(\mathbf{r};\mathbf{0}) - \frac{ie\hbar}{m_e}[\psi_n\nabla\psi_n' - \psi_n'\nabla\psi_n] \tag{20}$$

This is the equation that expresses the general origin dependence of the orbital current density. For an arbitrary choice of origin, (20) includes nonphysical terms. If, however, we make the ipsocentric choice, $\mathbf{d} = \mathbf{r}$, the term in square brackets on the RHS of (20) removes *all* occupied-to-occupied contributions from each separate orbital current density. It is this critical simplification that leads to the interpretation of current densities in terms of small numbers of electrons near to a molecular "Fermi level". Self-consistency corrections do not change this conclusion.

For any other choice of gauge origin, the nonphysical contributions vanish only when the orbital current densities (20) are summed, the contribution of a transition $\psi_n \rightarrow \psi_m$ in $\mathbf{j}_n^{(1)}$ canceling that of $\psi_m \rightarrow \psi_n$ in $\mathbf{j}_m^{(1)}$. Cancellation of nonphysical terms can also occur within well-defined blocks of orbitals even when $\mathbf{d} \neq \mathbf{r}$, perhaps most significantly in planar conjugated systems, where the symmetry separation between σ and π orbitals is maintained when the field is perpendicular to the molecular plane, and it is therefore permissible to make the traditional division into σ and π circulations, irrespective of the choice of gauge origin distribution.

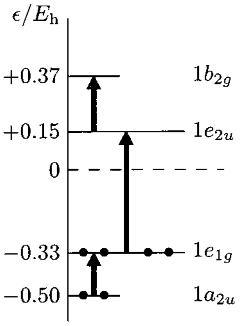


Figure 2. Orbital energy level diagram for benzene (RHF/6-31G** energies in hartree units). The arrows represent translational transitions, and the filled circles denote the occupancies.

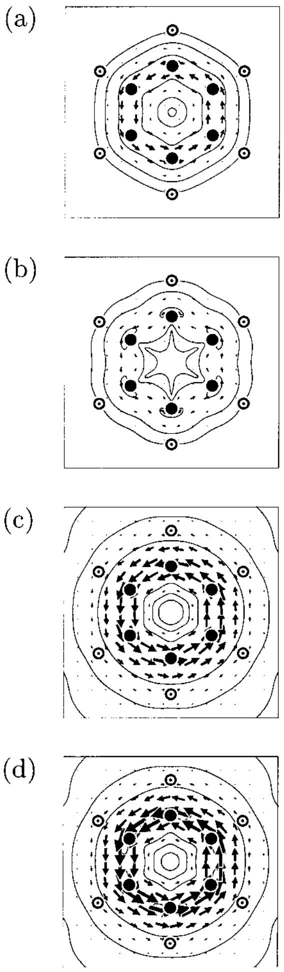


Figure 3. Orbital contributions to the π current densities in benzene ions. (a) The sole occupied orbital of the (4+) cation, $1a_{2u}$; (b) the (negligible) combined contribution of the $1a_{2u}$ and $1e_{1g}$ orbitals of the (4−) anion; (c) the (dominant) contribution of the four electrons in $1e_{2u}$ HOMO of the (4−) anion; and (d) the total π current in the (4−) anion. Computational details are given in the Appendix.

Self-consistency can now be considered briefly. In practice, the ψ_n are Hartree−Fock orbitals and the first-order orbital wave functions $\psi_n^{(1)}$ are calculated by means of coupled Hartree−Fock theory. The zeroth-order Hamiltonian is the Fock operator

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e}\nabla^2 + V + 2\hat{J} - \hat{K} \tag{21}$$

where V is the nuclear attraction energy, $\hat{J}$ is the coulomb operator and $\hat{K}$ is the nonlocal exchange operator. The presence of $\hat{K}$ means that the commutator relation for ∇, (10), is no longer strictly valid, and additional terms enter the representation of the diamagnetic current. The nonlocal operator also affects the first-order Hamiltonian, which now contains a first-order correction $\hat{K}^{(1)}$ to the exchange terms from the field-induced changes in the orbitals. However, $\hat{K}^{(1)}$ itself already depends on the $\psi_n^{(1)}$ and a recursive expansion of $\psi_n^{(1)}$ shows that the new terms are of order $(\Delta\epsilon)^{-2}$, and may normally be expected

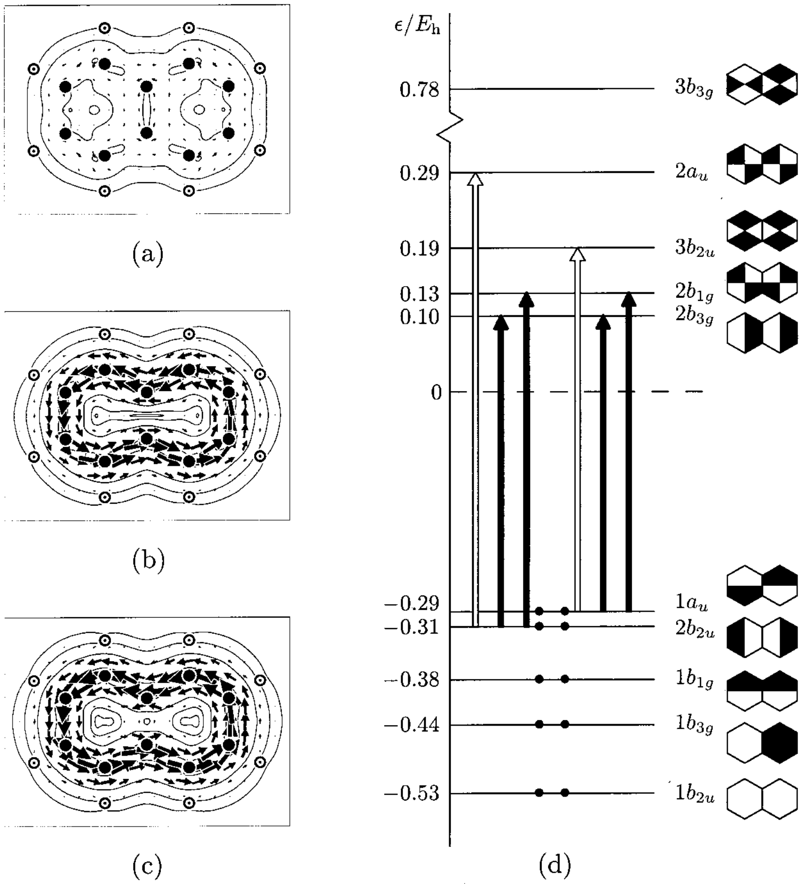


Figure 4. Orbital contributions to the current density in naphthalene. (a) The total current for the six electrons in the lower-lying orbitals $1b_{2u}$, $1b_{3g}$, and $1b_{1g}$; (b) the sum of orbital contributions of the four electrons in the near-degenerate pair $1a_u$ and $2b_{2u}$; (c) the complete π map; and (d) the orbital energy level diagram showing the $\pi-\pi^*$ transitions responsible for the orbital currents in (b). Black arrows represent translational transitions and white arrows rotational transitions from occupied levels. The nodal characteristics of the orbitals corresponding to the Hückel π manifold are indicated schematically on the right of (d); the broken scale indicates omission of high-lying $3b_{1g}$ and $4b_{2u}$ virtual orbitals. Computational details are given in the Appendix.

to be small (except in cases of near degeneracy of HOMO and LUMO when the simple orbital approximation, in any case, loses its validity).

4. Symmetry

To summarize, the primary conclusions of the analysis so far are

(a) orbital current densities are dependent on the choice of gauge origin **d**;

(b) in all but the CTOCD-DZ formulation, the orbital current densities contain nonphysical terms corresponding to transitions between occupied orbitals, canceling on summation;

(c) in this ipsocentric formulation, the current densities are expressed wholly as sums over states, and may be analyzed in terms of the accessibility of excited states via translational and rotational transitions.

This last conclusion can be exploited to give a simple few-electron model of ring currents in π systems.

Consider a planar conjugated system in which the ring currents are induced by a magnetic field at right angles to the molecular plane. In general, three factors will determine the existence and strength of the contribution of an occupied-to-unoccupied orbital transition $\psi_n \rightarrow \psi_p$. They are symmetry, spatial distribution, and energy.

Symmetry determines whether a transition contributes at all to the current density. If G is the point group of the field-free molecule, then a contribution can be classified as conventionally diamagnetic or paramagnetic (with respect to a position unshifted by all operations of G) using symmetries in G. Let $R_{||}$ represent rotation about the field direction, and $T_\perp$ translation at right angles to the field, and let the symbols $\Gamma(\psi)$, $\Gamma(R_{||})$, $\Gamma(T_\perp)$, and Γ_0, denote representations of an orbital (or degenerate set of orbitals), rotation around the field direction, translations at right angles to the field, and the totally symmetric representation in G, respectively. A transition $\psi_n \rightarrow \psi_p$ then has

(a) a contribution to $\mathbf{j}_n^{(1)}$ that is conventionally *diamagnetic* if the direct product of representations $\Gamma(\psi_n) \times \Gamma(\psi_p) \times \Gamma(T_\perp)$contains Γ_0,

(b) a contribution to $\mathbf{j}_n^{(1)}$ that is conventionally *paramagnetic* if $\Gamma(\psi_n) \times \Gamma(\psi_p) \times \Gamma(R_{||})$contains Γ_0,

otherwise, the transition has (c) exactly zero contribution.

A transition may obey (a) or (b), both (a) and (b), or neither (a) nor (b), depending on ψ_n, ψ_p, and G. In simple systems, such as those with only one conjugated circuit, the conventional dia/paramagnetic labels have clear and exclusive implications.[16]

The *spatial distribution* of a pair of orbitals affects the magnitude of a symmetry-allowed contribution. The two orbitals should occupy the same region of space and the functions ψ_p and $\hat{R}_{||}\psi_n$ or $\hat{T}_\perp\psi_n$ should have similar nodal structures if a transition is to be significant. For example, two orbitals with similar nodal surfaces related by rotation $\hat{R}_{||}$ will tend to give a large paramagnetic contribution, whereas an orbital ψ_p resulting from bisection of ψ_n by a single additional nodal surface

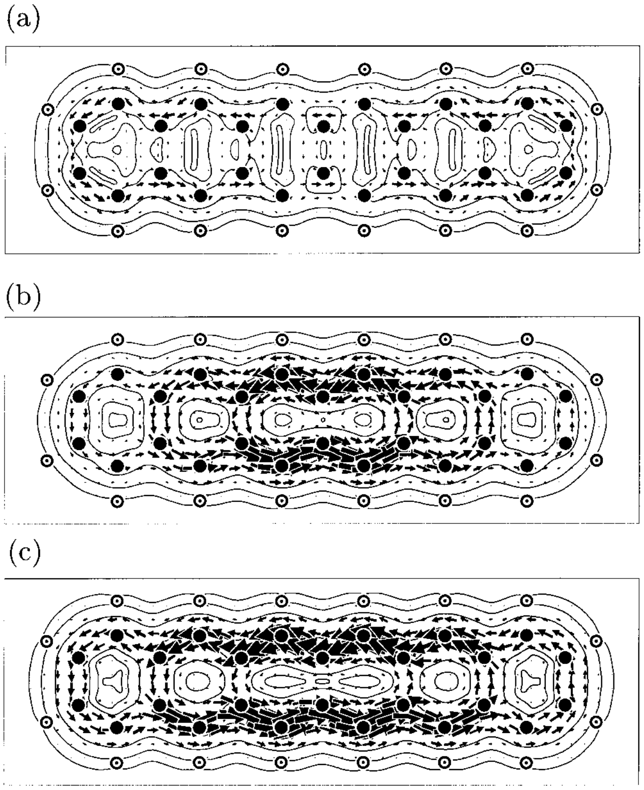


Figure 5. Orbital contributions to the current density in hexacene. (a) The total current for the 22 π electrons in the lower lying orbitals (total π except $3a_u$ and $4b_{2u}$); (b) the sum of orbital contributions of the four electrons in the near-degenerate pair $3a_u$ and $4b_{2u}$; and (c) the complete π map. Computational details are given in the Appendix.

perpendicular to the molecular plane will tend to give a large diamagnetic contribution, all other things being equal.

In addition to the above factors that act on the transition integrals in the numerators of the sum-over-states formulation, the transition energies in the denominators should be small. In conjunction with the requirement that ψ_n be occupied and ψ_p empty, this then suggests a major role for the HOMO−LUMO transition, symmetry permitting, and more generally implies that the total current density will be dominated by transitions from a few high-lying occupied orbitals into a small subspace of low-lying virtual orbitals. For large systems this can be an important simplification of the many-electron picture, as it shows that the number of mobile electrons need not scale with system size. When localized components are coupled by an interaction, their orbital energies spread out into bands, and the occupied−unoccupied gap typically decreases. The number of electrons with both symmetry- and energy-allowed access to virtual orbitals can then fall from a few per component to a few per assemblage.

Symmetry, spatial distribution and node count, and energy are of course linked in π systems, but the three-fold division gives a handy set of rules of thumb for interpretation and prediction of computed currents. They are applied in the following section to some illustrative examples.

The rules also suggest a useful shorthand for describing the physical origins of ring currents in π systems. If the magnetic response is dominated by n_1, n_2, and n_3 electrons with transitions allowed, respectively, under translational only, rotational only and both selection rules, we will label it (n_1d + n_2p + $n_3$dp), for diamagnetic, paramagnetic, and mixed response. In the same way that many closed-shell π systems obey a (4n+2) Hückel rule, it turns out that many are (4d) ring-current systems, and (n_1 + n_2 + n_3) is generally significantly smaller than the total π-electron count.

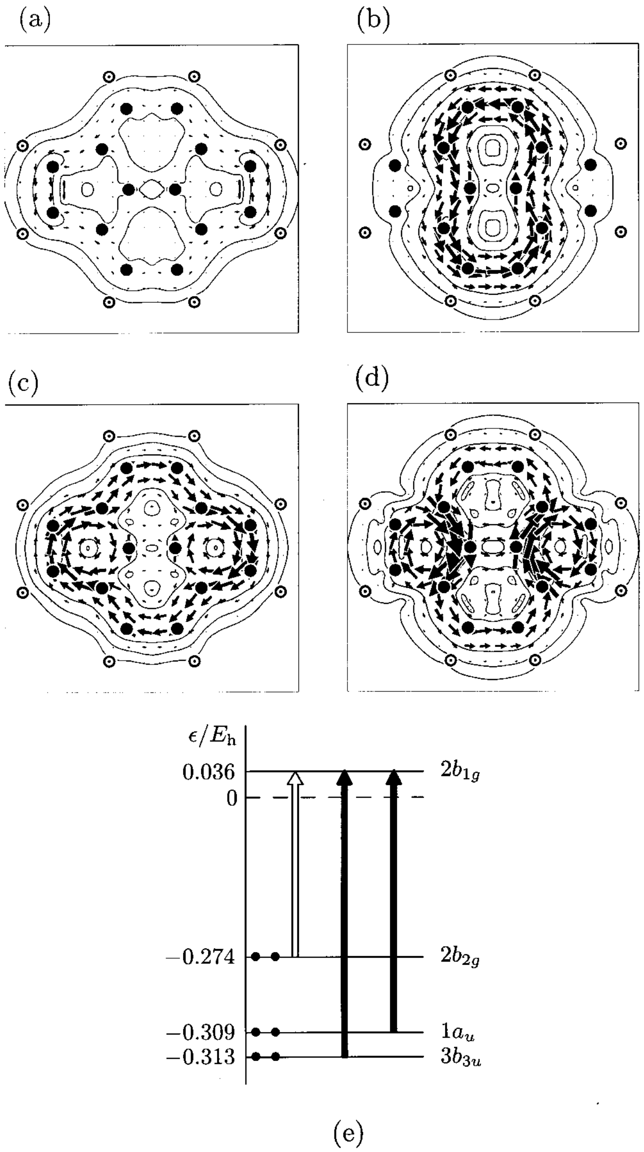
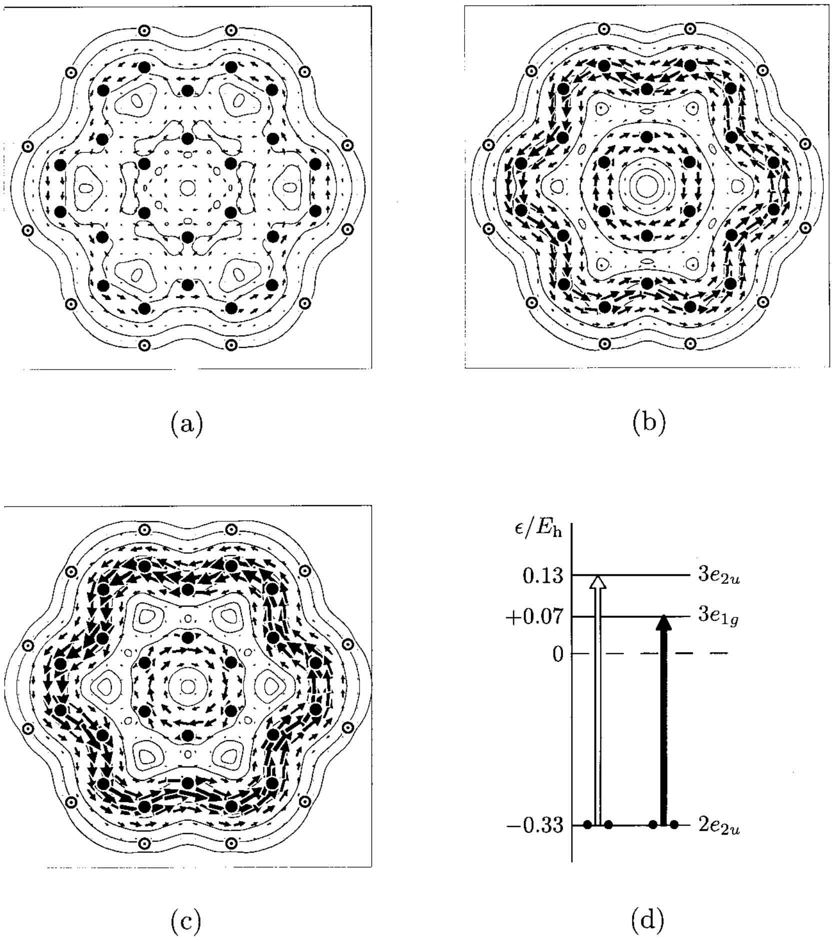


Figure 6. Orbital contributions to the current density in pyracylene. (a) The total current for the eight electrons in the lower lying orbitals (total π except $1a_u$, $3b_{3u}$, and $2b_{2g}$); (b) the sum of orbital contributions of the four electrons in the near-degenerate pair $1a_u$ and $3b_{3u}$; (c) the contribution of the HOMO, $2b_{2g}$; (d) the complete π map; and (e) the orbital energy level diagram showing the π−π* transitions responsible for the orbital currents in (b) and (c). Black arrows represent translational transitions and white arrow rotational transition from occupied levels. Computational details are given in the Appendix.

5. Examples

(i) Benzene (4d). In the Hückel theory of π-electron systems, the molecular orbitals of a conjugated hydrocarbon are represented as linear combinations of 2pπ atomic orbitals forming an "active space" which is usually rich enough in symmetry to represent the orbital excitations that dominate the magnetic response properties of the system. Figure 2 shows the π-orbital energy level diagram for benzene, with RHF/6-31G** orbital energies added to show the scale.

The Figure also shows the transitions between orbital levels allowed by the selection rules. In the point group D_{6h}, the rotation R_z belongs to representation a_{2g} so that *no* purely rotational transitions are allowed within the π manifold. All π



(a) (b)

(c) (d)

Figure 7. Orbital contributions to the current density in coronene. (a) The current arising from all but the four electrons in the HOMO $2e_{2u}$; (b) the contribution of the four electrons in the HOMO $2e_{2u}$; (c) the complete π map; and (d) the orbital energy level diagram showing the $\pi-\pi^*$ transitions responsible for the orbital currents in (b). The black arrow represents translational transition and the white arrow rotational transition from the HOMO. Computational details are given in the Appendix.

ring currents are therefore purely diamagnetic. The translations (T_x, T_y) belong to e_{1u}, and transitions are allowed only between *neighboring* orbital levels of benzene.

In the ipsocentric formulation, therefore, the four electrons in the degenerate $1e_{1g}$ HOMO contribute to the current density of the π electrons via transitions to the $1e_{2u}$ LUMO. The two electrons in $1a_{2u}$ are inactive because the only symmetry-accessible states, $1e_{1g}$, are occupied.

By contrast, as demonstrated by Figure 1a, the interpretation of the π current density is quite different in the single-center formulation. All three occupied orbitals make significant contributions to the total current density. The patterns and magnitudes are consistent with Lenz's-law diamagnetic circulation around the center of the ring, with orbital current densities given by $\mathbf{j}_n^{(d)}$. As we have seen, such a response is possible only if all orbitals are deemed to be accessible in $\mathbf{j}_n^{(d)}$. Thus, in this formulation, level $1e_{1g}$ is accessible to the electrons in $1a_{2u}$ despite being fully occupied, and $1a_{2u}$ is accessible to the electrons in $1e_{1g}$, providing a paramagnetic contribution from a *downward* translational transition. These contributions in to and out of $1a_{2u}$ cancel in the sum over orbitals.

The nature of the current densities of closed-shell ions of benzene can also be predicted from the orbital diagram (Figure 2). Removal of the four electrons of $1e_{1g}$ makes these orbitals available to two π electrons in $1a_{2u}$, providing a two-electron diamagnetic ring current in the tetracation. Addition of four electrons to the $1e_{2u}$ LUMO of neutral benzene blocks the transitions from $1e_{1g}$, but the four electrons in the $1e_{2u}$ HOMO of the *tetraanion* then have access to $1b_{2g}$, so that a four-electron diamagnetic ring current is maintained. These predictions are confirmed by ab initio CTOCD-DZ calculations at the frozen geometry of neutral benzene (Figure 3). The cation is a (2d) system and the anion is a (4d) system. Addition of two further electrons to give the hexaanion would fill the available Hückel active space, removing the $\pi-\pi^*$ ring currents. In this case, however, computation shows that the hypothetical 12π system has a small HOMO−LUMO gap to several low-lying virtual levels. There is an appreciable total diamagnetic ring current which is a superposition of small contributions from the electrons in the $1b_{2g}$, $1e_{2u}$, and $1e_{1g}$ occupied orbitals via transitions to virtual orbitals which are outside the scope of the strict Hückel model.

General symmetry considerations show that all aromatic ($4n$+2) monocycles can be expected to be (4d) systems, and that the splitting of HOMO and LUMO in antiaromatic ($4n$) monocycles leads to generic (2p) paratropicity. This is discussed in detail elsewhere.[16]

(ii) Naphthalene (4d). The differences in the monocentric and ipsocentric interpretations of the ring currents become more interesting for systems with larger numbers of π electrons. Figure 4 shows the π current density maps for naphthalene in the ipsocentric formulation: (a) the total current for the six electrons of the lower-lying orbitals $1b_{2u}$, $1b_{3g}$, and $1b_{1g}$ and (b) the sum of orbital contributions of the four electrons in the

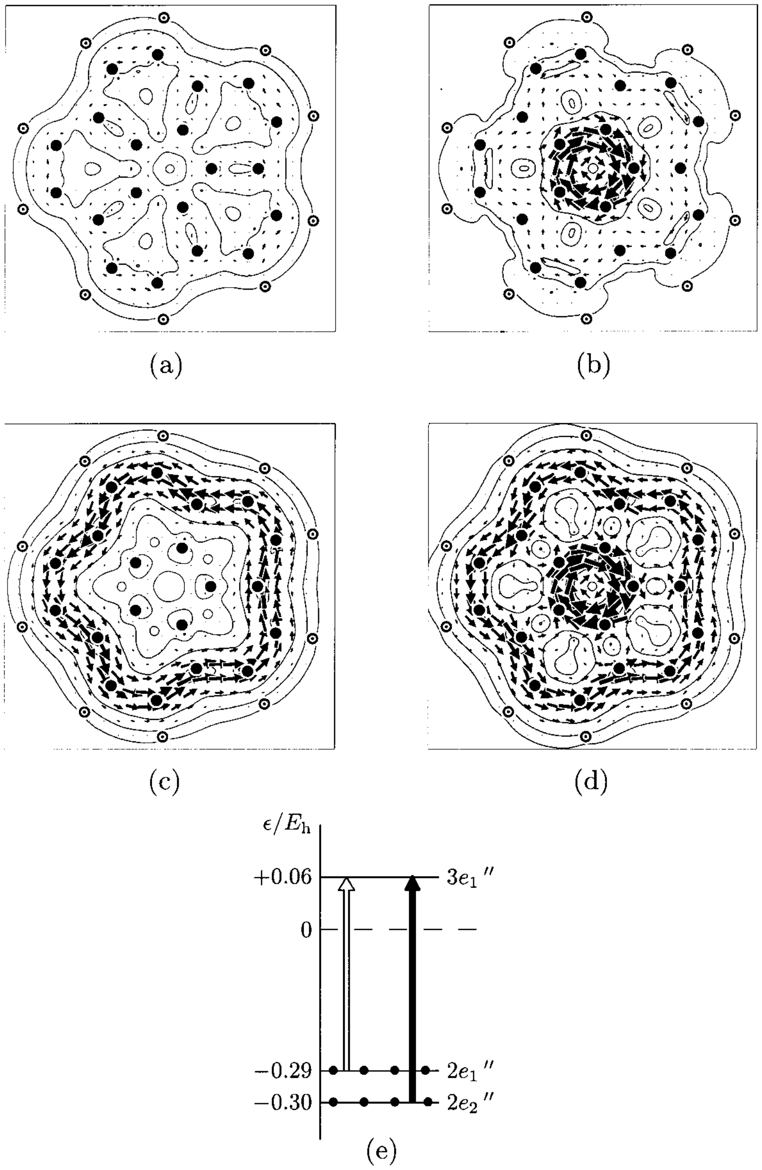


Figure 8. Orbital contributions to the current density in corannulene. (a) The current arising from all but the eight electrons in the near-degenerate $2e_1''$ and $2e_2''$; (b) the contribution of the four electrons in the HOMO $2e_1''$; (c) the contribution of the four electrons in the HOMO-1 $2e_2''$; (d) the complete π map; and (e) the orbital energy level diagram showing the $\pi-\pi^*$ transitions responsible for the orbital currents in (b). The black arrows represent translational transitions and the white arrows rotational transitions. Computational details are given in the Appendix.

near-degenerate pair $1a_u$ and $2b_{2u}$, which is visually indistinguishable from (c), the full π map. It is clear from the maps that only the four electrons in the near-degenerate HOMO pair make significant contributions to the total π current density.

The π orbital energy level diagram of naphthalene, Figure 4d, shows the transitions from the near-degenerate HOMO pair, $1a_u$ and $2b_{2u}$, to low-lying virtual orbitals allowed by R (rotational) and T (translational) selection rules. The symmetry of the system is $\mathbf{D}_{2h}$ and the pattern of energy levels is closely related to that of the 10-membered monocyclic ring, with near-degenerate HOMO and LUMO pairs. Symmetry forbids current along the central bond, and the HOMO−LUMO transitions of type T give rise to the four-electron diamagnetic circulation around the perimeter of the carbon structure, as in the monocycle itself. The formally allowed R transitions from $1a_u$ to $3b_{2u}$ and $2b_{2u}$ to $2a_u$ are evidently of less importance, as would be expected from their larger energy denominators and the high degree of cancellation in the transition moment caused by the more complex nodal structure of the target orbital, as illustrated by the orbital diagrams in Figure 4d.

Neutral naphthalene is therefore an essentially diamagnetic system. Diamagnetism and the dominance of just four electrons are features common to the whole family of linear acenes.

(iii) Hexacene (4d). Figure 5 shows π current densities for hexacene, including (a) the contribution of the 22 electrons in orbitals below the ($3a_u$, $4b_{2u}$) HOMO pair and (b) the four-electron diamagnetic circulations of the HOMO pair and (c) total π.

The total π current is again dominated by the HOMO contribution, which exhibits the characteristic concentration, or "clustering" , of current density in the central region,[12] with the other 22 electrons providing only a uniform and weak perimeter circulation. Hexacene and the other linear acenes are therefore simple (4d) systems.

(iv) Pyracylene (4d+2p). The pictorial interpretation of orbital contributions can also shed light on polycyclic systems that exhibit coexisting diamagnetic and paramagnetic ring currents. In pyracylene, the pentagonal rings are known to be paratropic[25−31] and Figure 6 shows that just three orbitals determine the π current map for this molecule.

The near-degenerate $1a_u$, $3b_{3u}$ pair gives rise to a diamagnetic circulation around the perimeter of the naphthalenic subunit, and the $2b_{2g}$ HOMO gives a circulation that is totally paramagnetic both within each pentagon and around the molecular perimeter. Superposition of the currents from these six electrons yields the familiar pattern for pyracylene in which two paratropic pentagons lie on either side of the diatropic central naphthalenoid motif. This pattern is reinforced when the circulation of the σ electrons is included in the total picture,[30,32] and is consistent with the NICS values calculated for the pentagons and hexagons of this molecule.[31]

The orbital energy level diagram, Figure 6e, shows that the current density maps are consistent with the allowed *T* and R transitions from the higher occupied orbitals to the LUMO. The LUMO $2b_{1g}$ can be accessed by *T* transition from the near-degenerate pair $1a_u$ and $3b_{3u}$ to give four-electron diamagnetic circulations, and by R transition from the HOMO $2b_{2g}$ to give two-electron paramagnetism. In the shorthand notation, pyracylene is a (4d+2p) system.

(v) Coronene (4dp) and Corannulene (4d+4p). The patterns of π currents in both coronene and corannulene have been shown[14] to consist of a superposition of a diamagnetic circulation around the outer rim with a paramagnetic counter-circulation on the inner hub. The outer circulation is the stronger in coronene, whereas in corannulene it is the inner circulation that is the stronger. This difference is explained when the orbital analysis is invoked. The maps in Figure 7 demonstrate that *both* the inner and outer circulations in coronene come from the *four* electrons in the degenerate $2e_{2u}$ pair. The pattern of relevant orbital levels illustrated in Figure 7d shows that the currents can be interpreted in terms of *T* and R transitions from the HOMO to the two low-lying degenerate pairs of virtual orbitals.

In contrast, the maps in Figure 8 demonstrate that *eight* electrons are responsible for the π ring currents in corannulene (the planar structure is discussed here, but no significant differences are expected for the bowl ground state[14]). The orbital level diagram in Figure 8e shows that the $3e_1''$ LUMO pair can be accessed via R transition by the four electrons in the $2e_1''$ HOMO, and via T transition by the four electrons in the near-HOMO $2e_2''$ (the two occupied pairs are almost degenerate in 6-31G**, and their relative disposition is sensitive to basis set). Thus, coronene is (4dp) but corannulene is (4d+4p). The annulene-within-an-annulene model, which is disproved by the ab initio calculation,[14] would presumably have ranked both systems as (4d+4d) $\equiv$ (8d), with con-rotating diamagnetic rim and hub currents.

The new orbital description also provides an interpretation of the reversal of direction of ring current on the hub when four electrons are added to give the 4-anion of corannulene. The added electrons occupy the $3e_1''$ LUMO of the neutral molecule, thereby blocking access to the lower-lying electrons. The R transition, which enables the inner paramagnetic circulation in the neutral molecule, is now disabled, and the new pattern of orbital levels in the anion leads to *con*-rotatory diamagnetic rim and hub currents.[14]

Many more examples can be quoted. Ring current maps are currently available for carbon monocycles,[33] the polyacenes up to heptacene,[12] the fused tetracycles acepleiadylene and dipleiadiene,[13] some polycyclic aromatic hydrocarbons based on naphthalene,[32] hexaethynylbenzene,[34] and kekulene,[15] and the orbital description gives a tool for classifying the calculated patterns in all of them.

6. Conclusion

Use of orbital contributions to electron current density has been held back by difficulties in obtaining a unique definition. It has been shown here that the ipsocentric gauge distribution of the CTOCD-DZ (CSGT) method leads to a unique and physically motivated definition, and hence to a few-electron interpretation of ring currents. Rationalizations and predictions of ring currents can now use arguments based on orbital symmetry, spatial distribution, and energy to classify π systems. As the magnetic response is attributed to a few mobile electrons in high-lying orbitals, significant simplifications can be expected for the large π systems encountered in biology and material science.

Appendix

The geometries used in this paper are the theoretical 6-31G**/SCF equilibrium geometries, computed with the CADPAC program.[35] The 6-31G** basis was also used for all calculations of current densities except for those for benzene and its ions, which used the larger "level 5" basis (12s8p4d /8s3p) → [9s6p4d/6s3p].[20] The computation of the maps was performed with the Exeter version of the SYSMO suite of programs.[36]

The maps show the π current density induced by unit magnetic field acting at right angles to the molecular plane and are, in all cases, plotted in the plane $1a_0$ above that of the nuclei. This plane is close to the maximum of π current and electron density and at this height there is little difference between computed maps in the small and large bases. The contours show the modulus $|\mathbf{j}|$ of current density with values $0.001 \times 4^n\, e\hbar/m_e a_0^4$ (au) for $n = 0, 1, 2, ...$, and the vectors represent in-plane projections of current. In all plots the diamagnetic circulation is shown anticlockwise, the paramagnetic circulation clockwise.

For benzene and its ions, the plotting area is a square of side $12a_0$, and the vectors are centered on the points of a 16×16 grid. All the other maps are drawn to this scale except for hexacene (Figure 5), for which a slightly smaller scale has been used.

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