

The Leap-Frog Effect of Ring Currents in Benzene

Andrea Ligabue, Alessandro Soncini, and Paolo Lazzeretti*

Contribution from the Dipartimento di Chimica, Università degli Studi di Modena e Reggio Emilia, via G. Campi 183, 41100 Modena, Italy

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Abstract: Symmetry arguments show that the ring-current model proposed by Pauling, Lonsdale, and London to explain the enhanced diamagnetism of benzene is flawed by an intrinsic drawback. The minimal basis set of six atomic 2p orbitals taken into account to develop such a model is inherently insufficient to predict a paramagnetic contribution to the perpendicular component of magnetic susceptibility in planar ring systems such as benzene. Analogous considerations can be made for the hypothetical H₆ cyclic molecule. A model allowing for extended basis sets is necessary to rationalize the magnetism of aromatics. According to high-quality coupled Hartree–Fock calculations, the trajectories of the current density vector field induced by a magnetic field perpendicular to the skeletal plane of benzene in the π electrons are noticeably different from those typical of a Larmor diamagnetic circulation, in that (i) significant deformation of the orbits from circular to hexagonal symmetry occurs, which is responsible for a paramagnetic contribution of π electrons to the out-of-plane component of susceptibility, and (ii) a sizable component of the π current density vector parallel to the inducing field is predicted. This causes a waving motion of π electrons; streamlines are characterized by a “leap-frog effect”.

1. Introduction

According to previous findings,^{1–5} a number of unnecessary and unphysical hypotheses have been retained by Pauling,⁶ Lonsdale,⁷ and London^{8–10} (PLL) to construct the ring-current model (RCM) for interpreting the magnetic properties of benzene and other aromatic systems. The “revised ring-current model” that is presently being developed via computer experiments^{1–4} throws light on a number of questions which have been recently discussed at length in two papers reviewing the relevant literature.^{5,11} They are referred to for an outlook on the state of the art, including general problems which concern a reliable description of magnetic properties of planar cyclic hydrocarbons in connection with aromaticity. Hereafter, we will limit ourselves to recall a few basic facts useful for the present investigation.

For a molecule with n electrons, with mass m_e , charge $-e$, coordinates r_i , $i = 1, 2, \dots, n$, and N nuclei, the paramagnetic contribution to magnetizability is given by

$$\chi_{\alpha\beta}^p = \frac{e^2}{4m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \mathcal{R}(\langle a | L_\alpha | j \rangle \langle j | L_\beta | a \rangle) \quad (1)$$

and the corresponding diamagnetic contribution is written

$$\chi_{\alpha\beta}^d = -\frac{e^2}{4m_e c^2} \langle a | \sum_{i=1}^n (r^2 \delta_{\alpha\beta} - r_\alpha r_\beta)_i | a \rangle \quad (2)$$

according to a well-established notation.¹² The total magnetizability is evaluated as

$$\chi_{\alpha\beta} = \chi_{\alpha\beta}^p + \chi_{\alpha\beta}^d \quad (3)$$

An alternative expression is obtained¹³ in the form

$$\chi_{\alpha\delta} = \frac{1}{2c} \epsilon_{\alpha\beta\gamma} \int d^3 r r_\beta \mathcal{J}_\gamma^{B_\delta}(\mathbf{r}) \quad (4)$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita unit tensor, and $\mathcal{J}_\gamma^{B_\delta}$ is a second-rank tensor related to the current density induced by a spatially uniform, time-independent external magnetic field with flux \mathbf{B}

$$\mathbf{J}_\alpha^{\mathbf{B}}(\mathbf{r}) = \mathcal{J}_\alpha^{B_\beta}(\mathbf{r}) B_\beta \quad (5)$$

Sum over repeated Greek indices is implied throughout this paper according to standard tensor notation.

The first-order quantum mechanical current density can be expressed as the sum of a diamagnetic Larmor-type contribution, proportional to the unperturbed electron density, and a paramagnetic contribution which involves a sum over the unperturbed excited electronic states:

$$\mathbf{J}^{\mathbf{B}} = \mathbf{J}_d^{\mathbf{B}} + \mathbf{J}_p^{\mathbf{B}} \quad (6)$$

The diamagnetic contribution is

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$$\mathbf{J}_d^{\mathbf{B}}(\mathbf{r}) = -\frac{e^2}{2m_e c} \mathbf{B} \times \mathbf{r} \gamma(\mathbf{r}) \quad (7)$$

with

$$\gamma(\mathbf{r}) = n \int d\mathbf{x}_2 \dots d\mathbf{x}_n \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_n) \Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_n) \quad (8)$$

as the unperturbed electron density. The paramagnetic contribution is given by

$$\mathbf{J}_p^{\mathbf{B}}(\mathbf{r}) = -\frac{e}{m_e} n \int d\mathbf{x}_2 \dots d\mathbf{x}_n [\mathbf{B} \cdot \Psi_a^{\mathbf{B}*}(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_n) \mathbf{p} \Psi_a^{(0)}(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_n) + \Psi_a^{(0)*}(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_n) \mathbf{p} \mathbf{B} \cdot \Psi_a^{\mathbf{B}}(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_n)] \quad (9)$$

In these relationships, $\mathbf{x}_i = \mathbf{r}_i \otimes s_i$ is a space-spin coordinate, and the expression for the wave function perturbed by the magnetic field is obtained by the Rayleigh–Schrödinger perturbation theory

$$|\Psi^{\mathbf{B}}\rangle = -\frac{e}{2m_e c \hbar} \sum_{j \neq a} \omega_{ja}^{-1} |j\rangle \langle j | \mathbf{L} | a \rangle \quad (10)$$

The diamagnetic contribution to the current density vector field described by eq 7 is a Larmor-type term; the perturbed electrons flow in planes perpendicular to the inducing field. In the case of a diamagnetic atom, that is, a system even with respect to time-reversal, it is easy to see that the streamlines are circumferences with a common center on the nucleus. The current density can be expressed in classical terms, introducing the idea of London–Landau–Madelung local mean velocity $\mathbf{v} = \mathbf{v}(\mathbf{r})$:

$$\mathbf{J} = \rho \mathbf{v}, \quad \rho(\mathbf{r}) = -e\gamma(\mathbf{r}) \quad (11)$$

Assuming that the magnetic field lies in the z direction, the Larmor current density has purely transversal components

$$J_{dx}^{\mathbf{B}}(\mathbf{r}) = \frac{e^2}{2m_e c} B y \rho, \quad J_{dy}^{\mathbf{B}}(\mathbf{r}) = -\frac{e^2}{2m_e c} B x \rho$$

As the fields \mathbf{v} and \mathbf{J} are parallel, it is expedient to evaluate the streamlines of the former. Thus

$$\frac{v_y}{v_x} = \left(\frac{dy/dx}{dr/dr} \right) = -\frac{x}{y} \quad (12)$$

and the integral solutions of the elementary differential equation $x dx + y dy = 0$ are circumferences $x^2 + y^2 = r^2$; the diamagnetic current density flows around the nucleus of the atom, along circular circuits of constant electronic charge.

These results are obviously consistent with the invariance of a diamagnetic atom in a rotation of an arbitrary angle α about the direction of the magnetic field, represented by the operator

$$U_R(z, \alpha) = \exp\left(-\frac{i}{\hbar} \alpha L_z\right) \quad (13)$$

which transforms each circumference into itself.

Within coupled Hartree–Fock (CHF) perturbation theory,^{14–17} the relevant quantities defined via eqs 1–10 are rewritten

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allowing for the corresponding one-determinant form of the ground-state eigenfunction; in particular, the expressions for the diamagnetic and paramagnetic contributions to the current density tensor become

$$\mathcal{J}_{d\alpha}^{B\beta} = -\frac{e^2}{m_e c} \epsilon_{\alpha\beta\gamma} r_\gamma \sum_i^{\text{occ}} |\phi_i^{(0)}|^2 \quad (14)$$

$$\mathcal{J}_{p\alpha}^{B\beta}(\mathbf{r}) = -\frac{2e}{m_e} \sum_i^{\text{occ}} (\phi_i^{B\beta*} p_\alpha \phi_i^{(0)} + \phi_i^{(0)*} p_\alpha \phi_i^{B\beta}) \quad (15)$$

denoting respectively by $\phi_i^{(0)}$ and $\phi_i^{B\beta}$ the unperturbed and first-order perturbed molecular orbitals.

2. The Pauling–Lonsdale–London Model

We will first analyze the familiar ring-current model of Pauling,⁶ Lonsdale,⁷ and London,^{8–10} widely employed to interpret the magnetic properties of the benzene molecule. A spatially uniform and time-independent magnetic field is switched on parallel to the 6-fold symmetry axis of the molecule. The interacting system is studied assuming that the origin of the gauge is in the center of the molecule. Such a choice does not imply any loss of generality within the exact CHF method, which is gauge invariant.^{17,18} Choosing the C_6 axis along the z direction, the parallel paramagnetic component of the magnetizability tensor is readily obtained from eq 1 in the form

$$\chi_{||}^p = \chi_{zz}^p = -\frac{e^2}{m_e^2 c^2} \sum_i^{\text{occ}} \sum_m^{\text{vir}} \frac{|\langle \phi_i^{(0)} | L_z | \phi_m^{(0)} \rangle|^2}{\epsilon_i^{(0)} - \epsilon_m^{(0)}} \quad (16)$$

within a simple uncoupled Hartree–Fock (UCHF) perturbation theory. The one-electron angular momentum operator L_z is defined with respect to the origin, that is, the center of the molecule. In eq 16, $\phi_i^{(0)}$ and $\phi_m^{(0)}$ denote occupied and virtual unperturbed molecular orbitals respectively, with corresponding orbital energies $\epsilon_i^{(0)}$ and $\epsilon_m^{(0)}$. As the CHF iterative procedure is started from the UCHF Ansatz,¹⁷ no actual limitation is imposed on restricting our attention to the symmetry analysis of terms contributing to the simple UCHF relationship eq 16. The discussion for the higher-level CHF approximation would be essentially the same.

If, allowing for the algebraic approximation, we adopt a minimal basis set of six $2p_z$ atomic orbitals, each centered on a carbon atom within the framework of the Hückel method,^{19,20} three occupied molecular orbitals are found. Assuming D_{6h} point group symmetry for benzene, there are one a_{2u} orbital, with lower energy, and two e_{1g} partners, spanning a doubly degenerate representation, at higher energy. The virtual orbitals are denoted by b_{2g} and e_{2u} according to their symmetry.

It is immediately evident that such a virtual molecular orbital basis, due to its reduced extension, cannot account for any paramagnetism of π electrons of benzene perpendicular to the

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skeletal plane, as none of the matrix elements $\langle \phi_1^{(0)} | l_z | \phi_m^{(0)} \rangle$ appearing in eq 16 is totally symmetric. In fact, applying the Wigner–Eckhart theorem²¹ and recalling that l_z transforms as A_{2g} , it is found that none of the direct products

$$\begin{aligned} A_{2u} \otimes A_{2g} \otimes E_{2u}, & \quad A_{2u} \otimes A_{2g} \otimes B_{2g} \\ E_{1g} \otimes A_{2g} \otimes E_{2u}, & \quad E_{1g} \otimes A_{2g} \otimes B_{2g} \end{aligned}$$

contains A_{1g} . Consequently, a description of the π electron system of benzene in terms of a Hückel minimal basis set necessarily implies an “effective invariance” with respect to a rotation about the C_6 axis, defined via eq 13, similar to the case of diamagnetic atoms. The physical limits of the minimal basis description are therefore evident; *the PLL model artificially constrains the benzene molecule to exhibit only out-of-plane diamagnetism.*

However, if an atomic basis set of two $2p_z$ orbitals per carbon atom were used according to a sort of improved “double- ζ Hückel scheme”, the virtual molecular orbital basis would also include functions transforming as the occupied MOs, that is, a_{2u} and e_{1g} .

Direct products $A_{2u} \otimes A_{2g} \otimes A_{2u}$, $A_{2u} \otimes A_{2g} \otimes E_{1g}$, and $E_{1g} \otimes A_{2g} \otimes A_{2u}$ do not contain A_{1g} , but nonvanishing matrix elements with symmetry $E_{1g} \otimes A_{2g} \otimes E_{1g} = A_{1g} \oplus A_{2g} \oplus E_{2g}$ would be obtained. Accordingly, *such a double- ζ ring-current model would predict a paramagnetic contribution of π electrons to the out-of-plane component of magnetic susceptibility of benzene via eq 16.*

3. The Cyclic H_6 System

Let us now consider the (unstable) six-membered ring H_6 in a D_{6h} spatial arrangement, in the presence of a magnetic field perpendicular to the molecular plane. This system was also discussed by London in his seminal paper on the RCM as a prototype of a diamagnetic molecule.⁹ In fact, theoretical current density maps show diamagnetic electron circulation delocalized all over the molecule and a striking similarity with benzene.⁵

Ab initio calculations of the magnetizability tensor at the coupled Hartree–Fock level of approximation, allowing for a minimal basis set, for example, STO-3G, or any larger primitive GTO basis contracted to a minimal CGTO basis, yield an identically vanishing component of the paramagnetic contribution parallel to the C_6 axis.⁵ However, the effective rotational invariance of the H_6 cycle arising from this description is only due to the limited size of the atomic basis set. This result is apparent from the symmetry analysis of the matrix elements which give a nonvanishing contribution to the property.

The STO-3G minimal basis set for the H_6 system consists of six s Gaussian type orbitals, centered on the H atoms. The unperturbed SCF calculation furnishes six MOs classified according to irreducible representations of the D_{6h} molecular point group, that is, three occupied a_{1g} and e_{1u} and three virtual b_{1u} and e_{2g} , the degenerate irreps contributing two partners each. The direct products

$$\begin{aligned} A_{1g} \otimes A_{2g} \otimes B_{1u}, & \quad A_{1g} \otimes A_{2g} \otimes E_{2g} \\ E_{1u} \otimes A_{2g} \otimes B_{1u}, & \quad E_{1u} \otimes A_{2g} \otimes E_{2g} \end{aligned}$$

do not contain A_{1g} ; the corresponding matrix elements vanish. Within a DZ calculation, that is, using two s atomic orbitals for each hydrogen atom, a_{1g} and e_{1u} MOs are added to the unperturbed virtual molecular orbital basis. Whereas $A_{1g} \otimes A_{2g} \otimes A_{1g}$, $A_{1g} \otimes A_{2g} \otimes E_{1u}$, and $E_{1u} \otimes A_{2g} \otimes A_{1g}$ do not contain the totally symmetric irrep, $E_{1u} \otimes A_{2g} \otimes E_{1u} = A_{1g} \oplus A_{2g} \oplus E_{2g}$.

Therefore, according to eq 16, a nonvanishing paramagnetic contribution to the out-of-plane component of magnetic susceptibility is obtained for H_6 , when the atomic basis set is flexible enough to span all the irreps of D_{6h} . This can be achieved by including atomic orbitals with higher quantum numbers. At any rate, a double- ζ of 12 s atomic orbitals is enough to yield a paramagnetic contribution to $\chi_{||}$.

It is important to recall that *further improvement of the basis set beyond the DZ level cannot reduce the paramagnetic contribution to the susceptibility component parallel to the 6-fold symmetry axis*; coupled self-consistent field (CSCF) calculations within the algebraic approximation provide a lower bound to the true Hartree–Fock value of $\chi_{||}^p$, corresponding to a complete atomic basis set, as proven by Moccia.²² In other words, although its size is quite small, the paramagnetism of H_6 , systematically underestimated in actual CSCF calculations, should be considered physically meaningful. The value estimated via a noncontracted (8s) GTO basis set from van Duijneveldt’s compilation²³ is $\chi_{||}^p = 1.37$ cgs ppm au. The prediction obtained via the (6s/4p) \rightarrow [3s/2p] Sadlej’s basis set²⁴ rises to 5.55 cgs ppm au.

4. The Benzene Molecule

Quite similar considerations can be made for the real molecule of benzene. In a minimal basis set common origin (CO) CSCF ab initio calculation, 36 molecular orbitals are obtained, 21 of which are occupied. The 15 virtual orbitals are classified as a_{1g} , a_{2g} , b_{2g} , $2e_{2g}$, $2b_{1u}$, $2e_{1u}$, and e_{2u} according to their symmetry. Again, observing that l_z transforms as A_{2g} , it is readily checked that the π MOs of symmetry a_{2u} and e_{1g} do not contribute to the parallel component of magnetic susceptibility, eq 16, as all the matrix elements between these occupied orbitals and the 15 virtual orbitals are zero by symmetry.

However, theoretical predictions arrived at via extended Gaussian basis sets,^{25,26} providing a higher-quality description of the virtual MO space, unequivocally demonstrate that the paramagnetic contribution of π electrons to $\chi_{||}$ cannot be neglected. This contribution is physically meaningful, and its magnitude is systematically underestimated in CSCF calculations. For a fixed molecular geometry, it increases with atomic basis set quality. A lower bound obtained in ref 26 is 62.65 cgs ppm au. This is only 9% of the corresponding diamagnetic contribution, -668.18 , but is large enough to show that pure Larmor circulation of π electrons cannot take place in benzene; the current streamlines are expected to deviate substantially from the PLL picture. In any event, we can conclude that a minimal basis set ab initio calculation of benzene is unsuitable to develop a reliable model for the π electron flow induced by a magnetic field perpendicular to the molecular plane.

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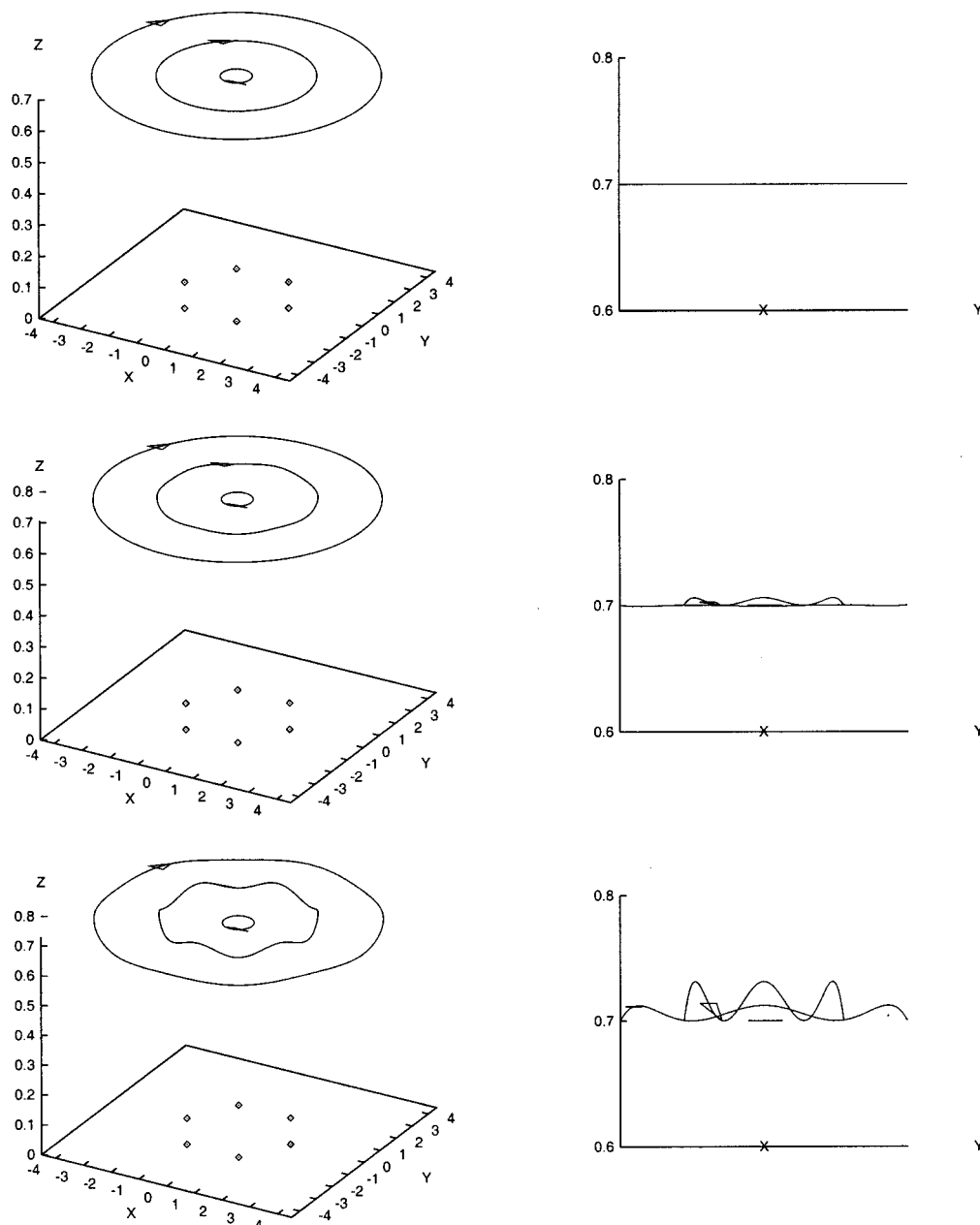


Figure 1. Streamlines of the current density vector field induced in the H_6 cyclic molecule by a magnetic field in the z direction, normal to the xy molecular plane. The position of the hydrogen nuclei is marked with dots. The plots display (left) a perspective view in the region at $z_0 = 0.7$ bohr and (right) the projection of the streamlines onto the yz plane. From top to bottom, results obtained via STO-3G, 8s, and (6s4p) \rightarrow [3s2p] basis sets are shown.

It is worth mentioning that the individual orbital contributions to the total current density field may have a limited physical significance. For instance, the continuity equation for the stationary state

$$\nabla \cdot \mathbf{J}^B = 0 \quad (17)$$

valid for the total field $\mathbf{J}^B(\mathbf{r})$ for any \mathbf{r} all over the molecular domain, is not necessarily satisfied by the “components” defined via a resolution into orbital terms analogous to eq 15. In fact, one could add transverse terms $\mathbf{j}_{i,ADD}$ to individual components \mathbf{j}_i , with the constraint $\sum_i^{occ} \mathbf{j}_{i,ADD} = \mathbf{0}$, leaving eq 17 invariant. However, the exchange currents $\mathbf{j}_{i,ADD}$ would not alter the general pattern of the total $\mathbf{J}^B(\mathbf{r})$ field. The quite general symmetry analysis of eq 16 could also not be modified.

5. Current Density Maps

The streamlines of the current density vector field of H_6 , induced by an external magnetic field perpendicular to the molecular plane, are shown in Figure 1. They have been obtained in CO CSCF calculations with the gauge of the vector potential in the center of the hydrogen ring. When the minimal STO-3G basis²⁷ is used, the streamlines are circumferences fully contained in planes parallel to that of the molecule. The flow is purely diamagnetic, in agreement with the London model,⁹ and the corresponding CHF estimate for the paramagnetic contribution to the out-of-plane component of magnetic susceptibility vanishes identically. The situation for one of these planes, 0.7 bohr above the hydrogen ring, is visualized in 3-D

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perspective on the top of Figure 1. Accordingly, the projection of the flow onto the yz plane, on the right of the same figure, is a straight line.

A small improvement of the Gaussian basis set is sufficient to provide a different description of the current density field. The streamlines obtained via an 8s primitive GTO basis²³ contracted to DZ describe a more realistic regime. The effective rotational symmetry is lost. The orbits lying on the molecular plane, a σ_h locus that cannot be crossed by any streamline due to magnetic symmetry constraint,⁵ have a vanishing component in the direction perpendicular to the plane. Orbits outside σ_h are not planar. A stationary oscillation takes place due to the fact that the flow has a component in the direction of the external magnetic field and rises to a local maximum distance from σ_h in the H–H “bond” regions. A local minimum distance is found in the proximity of each hydrogen nucleus.

These features become more evident when higher-quality basis sets are adopted, according to the visualization in the bottom of the same figure, obtained via a (6s4p) \rightarrow [3s2p] basis set from Sadlej’s tables.²⁴

Such a behavior of the trajectories, which we referred to as “leap-frog effect”, is fully consistent with the $D_{6h}(C_{6h})$ magnetic point group symmetry of the H_6 system in the presence of a perpendicular magnetic field; the $R\sigma_v$ and $R\sigma_d$ planes (where R denotes the time-inversion operator) through the hydrogen nuclei and the midpoint of bonds can only be crossed perpendicularly, whereas no constraint on direction occurs in the intermediate regions.⁵ A symmetric distribution of trajectories can be observed on the plane for $z = -0.7$ au, below that of the molecule, owing to the σ_h mirror of the $D_{6h}(C_{6h})$ magnetic group.

These results are also entirely consistent with the symmetry analysis of section 3, confirming that the London model for H_6 is correct only within a minimal basis approximation. Its pure diamagnetism depends on the essential inadequacy of minimal basis sets for rationalizing molecular magnetic properties.

The modulus of the current density field is shown in Figure 2, using 3-D perspective views and corresponding contours of $|\mathbf{J}|$. Within the minimal basis description, the intensity along a given closed circuit lying in the plane of the H_6 ring is not uniform; local maxima (minima) are found over the nuclei (bonds).

Such a pattern, observable on top of the figure, is at variance with the London model, based on the assumption of fully delocalized, freely flowing electrons,⁹ which would imply equal modulus in every point of a closed orbit. Allowing for the 8s basis set, the distance between minima and maxima gets smaller, as can be observed in the center of Figure 2. Further increase of basis quality causes the maximum peaks to disappear. According to the results obtained by the (6s4p) \rightarrow [3s2p] Sadlej’s basis set, the contours in the bottom of Figure 2 are topological circumferences with the same center in the midpoint of the molecule. The maximum intensity diminishes when larger basis sets are used, as can be seen from the top to the bottom of Figure 2.

Visualizations of the current density field induced in the π cloud of benzene by a magnetic field perpendicular to the molecular plane are very similar, as shown in Figures 3 and 4. Three calculations were carried out, using STO-3G, 6-31G, and the large (13s8p4d/8s3p) \rightarrow [8s6p4d/6s3p] basis set from ref 26. A fully diamagnetic circulation in the plane 0.7 bohr above

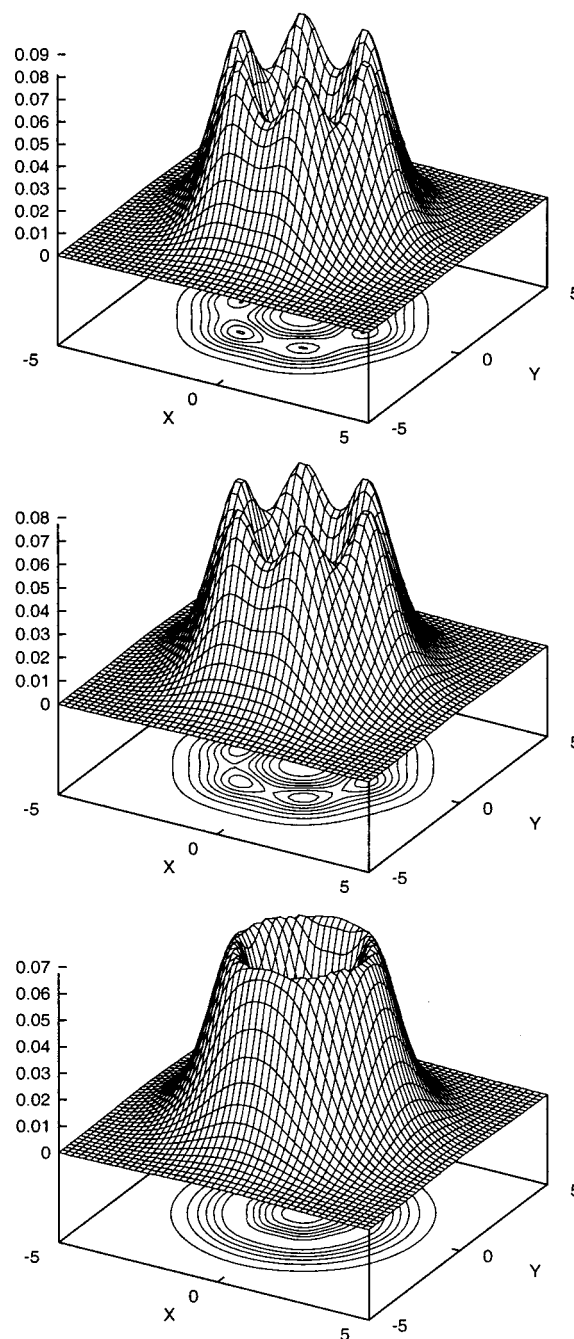


Figure 2. 3-D perspective representation of $|\mathbf{J}|$, the modulus of the current density induced in the H_6 ring, corresponding to Figure 1. Maximum intensity is ~ 0.08 (~ 0.06) au within the STO-3G ((6s4p) \rightarrow [3s2p]) calculation, on the top (on the bottom) of the figure. The contour values on the plane at $z_0 = 0.7$ bohr increase in steps of 0.01 from the outermost contour at 0.01 au.

that of the molecule, that is, in the vicinity of maximum π electron density, is predicted via the CO CSCF approach with the STO-3G basis, as shown on top of Figure 3.

A small leap-frog effect can be detected at the 6-31G level of accuracy. However, the stationary oscillation of π electrons predicted by our most accurate calculation has an amplitude of ~ 0.15 bohr for the innermost streamline in the bottom of Figure 3.

The peaks observable in the region of the carbon nuclei in the 3-D plots of Figure 4, displaying a magnitude of the π electron contribution to the current field, are quite sharp when

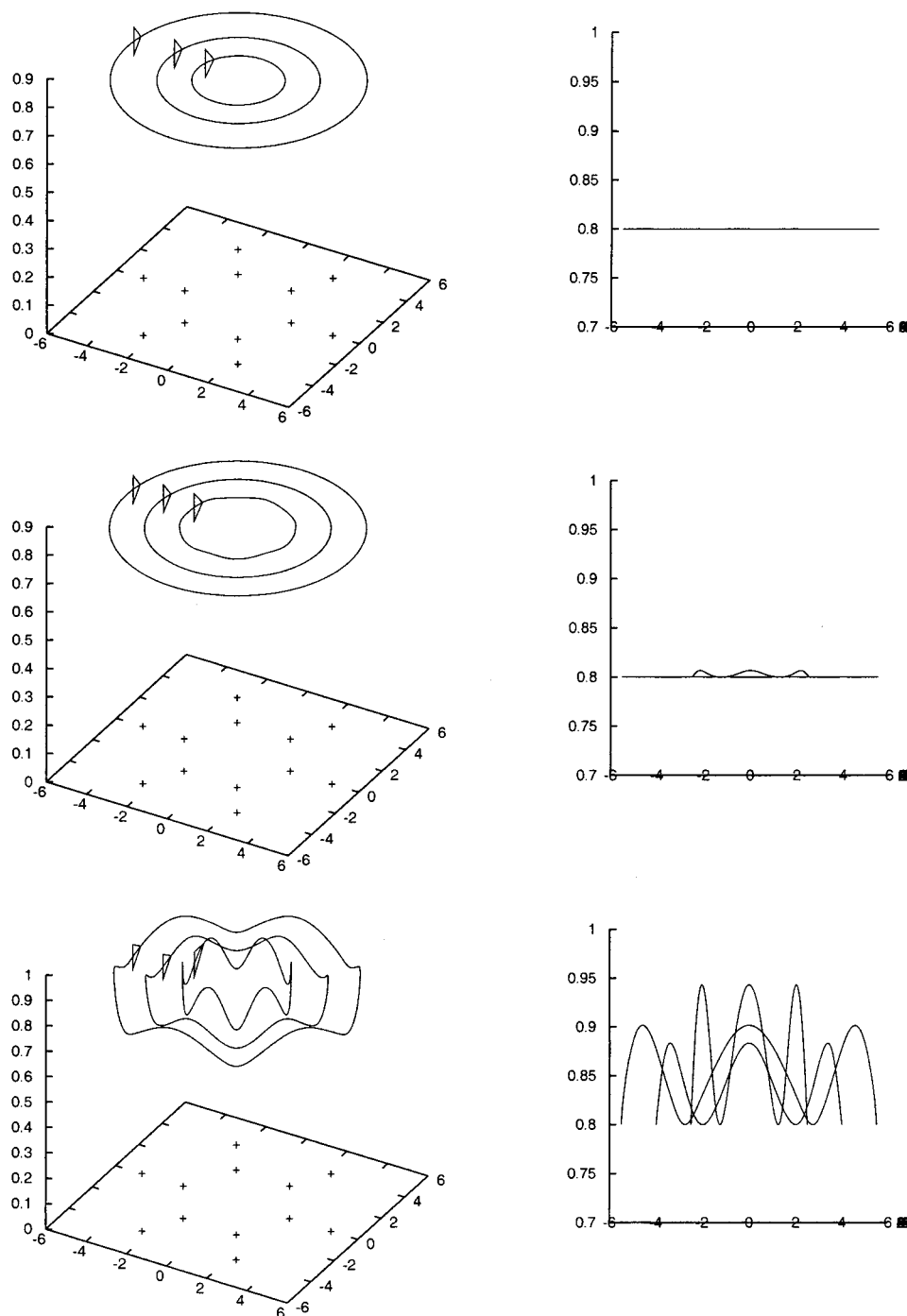


Figure 3. Streamlines of the current density vector field induced in the π electron of benzene by a magnetic field in the z direction, normal to the xy molecular plane. The position of the nuclei is marked with crosses. The plots display (left) a perspective view in the region at $z_0 = 0.8$ bohr and (right) the projection of the streamlines onto the yz plane. From top to bottom, results obtained via STO-3G, 6-31G, and (13s8p4d/8s3p) \rightarrow [8s6p4d/6s3p] basis sets are shown.

minimal basis sets are used. They tend to flatten on increasing basis set quality. The maximum values decrease from ~ 0.25 to ~ 0.09 au from the top to bottom of Figure 4. The extended basis calculation predicts a more uniform intensity of the field in the plane of the plot.

6. Concluding Remarks

The Pauling–Lonsdale–London model for π electron ring currents in benzene, and the analogous London model for the H_6 ring, can only predict fully diamagnetic circulation induced

by a magnetic field perpendicular to the molecular plane. This feature is an unavoidable consequence of the low quality of minimal basis sets of atomic orbitals.^{6,7,9} A minimal basis lacks the flexibility needed to correctly describe the paramagnetic contribution to the out-of-plane component of magnetic susceptibility.

The Hückel ground-state electronic wave function of the π electrons in the benzene molecule, and the minimal basis set wave function of the H_6 cyclic structure, provide an incorrect description of the electron cloud perturbed by a perpendicular

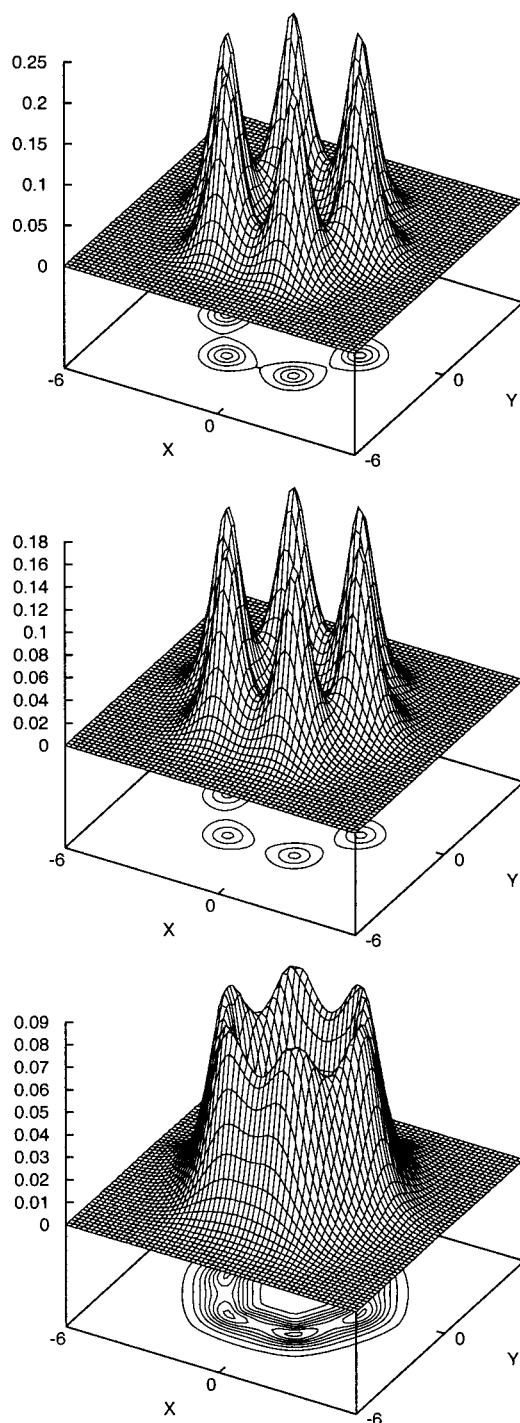


Figure 4. 3-D perspective representation of the modulus of the current density induced in benzene corresponding to Figure 3. Maximum intensity is ~ 0.25 au from the STO-3G and ~ 0.09 au from the $(13s8p4d/8s3p) \rightarrow [8s6p4d/6s3p]$ calculations, respectively. From top to bottom, the corresponding contour values on the plane at $z_0 = 0.7$ bohr increase in steps of 0.05, 0.02, and 0.01 au from the outermost contour.

magnetic field as a geometrical object effectively invariant to an arbitrary rotation about the 6-fold symmetry axis. The unphysical features implicit in the minimal basis set descriptions are readily evinced by group-theoretical procedures, see section 2. It could be argued that the diamagnetism of the London models is an a priori feature, a sort of tautological implication intrinsically related to “his poor and arbitrary guess”, in the

words of Musher.²⁸ Therefore, the minimal basis set representation of these molecules, leading perforce to a picture in terms of purely diamagnetic Larmor circulation, is basically inadequate to rationalize their magnetic response.

The adoption of extended basis sets at the CHF level of accuracy provides more reliable ab initio models for the magnetic properties of these molecular systems, confirming that the hypotheses made in the conventional Pauling–Lonsdale–London model are too restricted. According to the maps of current density field reported in this paper, the flow induced by a magnetic field perpendicular to the molecular plane in the π electrons of benzene and σ electrons of the H_6 ring is remarkably similar.

At variance with the London picture in terms of pure Larmor regime, the current is characterized by two striking features: (i) the streamlines have a paramagnetic component parallel to the perturbing magnetic field \mathbf{B} , so that the circulation exhibits a peculiar “leap-frog effect”, and (ii) the local deviations from rotational symmetry toward $D_{6h}(C_{6h})$ magnetic symmetry observed for the projections of the flow on planes perpendicular to \mathbf{B} are significant. The latter may be enough to explain the quite large paramagnetic contribution of π electrons to the out-of-plane susceptibility of benzene, 62.65 cgs ppm au, estimated in extended ab initio calculations assuming the origin of the gauge in the midpoint of the molecule.²⁶ Its magnitude is roughly 9% of the theoretical average magnetic susceptibility from the same source, -692.49 , and 10% of the corresponding experimental value, -614 cgs ppm au.²⁹

Furthermore, the modulus of the current density field along a given orbit displayed in the maps reported in the present work is by no means uniform, as would be in the typical case of a fully delocalized London flow, but increases substantially in the vicinity of the nuclei when reduced basis sets are employed. Moreover, the intensity is comparable to that of the currents observed in noncyclic molecules, which suggests that superconducting behavior of aromatic π electrons in a magnetic field³⁰ is unlikely to occur.⁵

Eventually, it should be emphasized that the leap-frog effect is not responsible for the nonvanishing paramagnetic term $\chi_{||}^p$. As it is evident from relationships 4 and 5, the paramagnetic component of the current density in the direction of the magnetic field does not contribute to $\chi_{||}$; it is the distortion from rotational to hexagonal symmetry which gives rise to nonvanishing paramagnetism of the out-of-plane component of magnetic susceptibility.

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