

Delocalized magnetic currents in benzene

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Results of *ab initio* calculations of the magnetic properties of cyclic, conjugated hydrocarbons are analyzed for the delocalized current. They fit well into earlier models for localized and delocalized currents, suggesting that an important delocalized current exists, this being due, particularly, to the π electrons. A rigorous definition of delocalized current is proposed. This is achieved by considering the current contribution from each natural orbital, which is conserved (divergenceless, in a stationary problem) when the exchange currents are included. It is argued that these conserved orbital currents should be preferred for the analysis of the induced current density. The delocalized current now defined may be related to the ring current introduced in the context of semiempirical theories. The results of this paper appear to give substance to the conventional ring current ideas, a conclusion which is at variance with the most recent interpretations of the new *ab initio* calculations.

I. INTRODUCTION

In the hydrodynamic formulation of quantum mechanics¹⁻⁵ the fundamental quantities describing the system are the probability density $\rho(\mathbf{r}, t)$ and a velocity field or the probability current density $\mathbf{j}(\mathbf{r}, t)$. If an external magnetic field is applied, it couples directly with the velocity³ (or the current density) which makes the hydrodynamic formulation attractive for dealing with magnetic problems. However, difficulties, both practical and conceptual,^{6,7} have made the hydrodynamic formulation of very limited use. Nevertheless, properties of the quantum system may be expressed as functionals of $\rho(\mathbf{r}, t)$ and $\mathbf{j}(\mathbf{r}, t)$ and these fields may provide a very interesting description of the system. Quantities of this type were called subobservables by Hirschfelder.⁸ In this paper, I shall discuss the probability current density induced in the ground state of a molecule by an external homogeneous, constant, magnetic field. The most commonly measured observables related to it are the magnetic susceptibility and the NMR chemical shifts. Mono- and polycyclic conjugated hydrocarbons form a class of molecules for which the discussion in the literature has been very extensive. Benzene is considered here as the paradigm for this class.

The central problem addressed here is that of the delocalized currents induced in mono- or polycyclic conjugated hydrocarbons by a magnetic field perpendicular to the molecular plane. The peculiar properties of molecules of this class (observed as magnetic susceptibility exaltations discussed in the context of Pascal-type systems of increments^{9,10} or the unusual chemical shifts of the benzenoid protons) have traditionally been explained in terms of the so-called magnetic ring currents.¹¹⁻¹⁴ The concept of ring current was originally introduced¹¹⁻¹³ in a classical context as the resultant of the Larmor precession that π electrons (in benzene, say) would undergo under the external magnetic field. With the work of Pople¹⁵ and McWeeny,¹⁶ the ring-current model (RCM) became firmly established in the field of ¹H-NMR chemical shifts. The situation was upset by a strongly worded argument by Musher¹⁷ dooming the ring current as an unnecessary hypothesis and favoring localized models but counterarguments were put forward by several authors.^{18,19} Also, the numeri-

cally fitted "localized π bond" model proposed by Blustein²⁰ cannot be said to present strong evidence to counter the physical reality of the ring currents.

On a different footing are the *ab initio* results now being published by Lazzeretti and co-workers.²¹⁻²³ These are the best calculations so far performed on benzene and were interpreted²³ in a way that endorses the final departure from any ring-current ideas. This great step forward in the quality of the calculations available asks for a fresh approach to the definition of a ring current. In the standard^{15,16} theories, the ring current RC in benzene is never actually calculated; only ratios of the RC in a ring of another molecule to that in benzene are used to compute magnetic susceptibilities or chemical shifts. In Sec. II, below, the general formalism of the magnetically induced probability current densities is summarized; the constraints introduced by the symmetry magnetic point group are discussed and some relevant predictions from semiempirical theories are reviewed. In Sec. III, an analysis of *ab initio* current density results is presented, in such a way as to show whether delocalized currents exist. This is done both for benzene and for the cyclopropenyl cation. Separate plots of σ - and π -electron currents are prepared to test the conventional ideas about localization vs delocalization. The problem of defining an orbital component of the probability current density is discussed in Sec. IV. Such a definition satisfying a conservation condition is achieved by the introduction of the exchange currents and a thorough discussion of the effects on the calculated properties is given. In Sec. V, a rigorous definition of delocalized current is introduced. This is first defined for each natural orbital as a conserved component of the previously defined orbital current density. The aggregate delocalized current of the many-electron system includes all the current lines actually running around the ring and may substitute the traditional ring-current concept in the context of rigorous state functions.

II. THE MAGNETIC CURRENT DENSITY

The general expression of the (charge) probability current density in a many-electron system described by the state function

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (1)$$

is²⁴

$$\mathbf{j}(\mathbf{r}) = \sum_{\nu=1}^N \int d^3 r_1 d^3 r_2 \dots d^3 r_N \delta(\mathbf{r}_\nu - \mathbf{r}) \times [(ie\hbar/2m_e)(\Psi^* \nabla_\nu \Psi - \Psi \nabla_\nu \Psi^*) - (e^2/m_e)\mathbf{A}(\mathbf{r}_\nu)\Psi^* \Psi] \quad (2)$$

Spin coordinates are not displayed, in order to simplify the notation and because they would cause no new features to arise.

When the state function [Eq. (1)] has the structure of a single determinant of orthonormal spin-orbitals $\psi_k(\mathbf{r})$,

$$\Psi = |\psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N)|, \quad (3)$$

the probability current density may be calculated by

$$\mathbf{j}(\mathbf{r}) = \sum_{k=1}^N [(ie\hbar/2m_e)(\psi_k^* \nabla \psi_k - \psi_k \nabla \psi_k^*) - (e^2/m_e)\mathbf{A}(\mathbf{r}) \psi_k^* \psi_k] = \sum_{k=1}^N \mathbf{j}_k(\mathbf{r}), \quad (4)$$

where I introduce the orbital property $\mathbf{j}_k(\mathbf{r})$ defined as the summand in brackets. An expression formally similar to this one is still obtained for a general multideterminant state function, if natural orbitals (NO)²⁵ are used. The (charge) probability density $\rho(\mathbf{r})$ associated with a multideterminant state function takes the general form

$$\rho(\mathbf{r}) = -e \sum_{k,i=1}^K \phi_k^*(\mathbf{r}) P_{ki} \phi_i(\mathbf{r}), \quad (5)$$

where K is the number ($K \geq N$) of orbitals ϕ_k used and the matrix P_{ki} may be chosen Hermitian. By a standard diagonalization procedure, one finds the NOs $\psi_k(\mathbf{r})$ (eigenvectors), and their occupations n_k (eigenvalues $0 \leq n_k \leq 1$). The probability density takes the diagonal form

$$\rho(\mathbf{r}) = -e \sum_{k=1}^K n_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}). \quad (6)$$

The probability current density written in terms of the NOs takes a form comparable to Eq. (4),

$$\mathbf{j}(\mathbf{r}) = \sum_{k=1}^K n_k \mathbf{j}_k(\mathbf{r}). \quad (7)$$

The vector field $\mathbf{j}(\mathbf{r})$ defined by Eq. (2) has the properties of a quantum mechanical observable; its associated operator can be written²⁶

$$\hat{\mathbf{j}}(\mathbf{r}) = \sum_{\nu=1}^N \{(ie\hbar/2m_e)[\nabla_\nu \delta(\mathbf{r} - \mathbf{r}_\nu) + \delta(\mathbf{r} - \mathbf{r}_\nu) \nabla_\nu] - (e^2/m_e)\mathbf{A}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_\nu)\}. \quad (8)$$

Quantities like $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ are of the type that Hirschfelder⁸ calls subobservables. Their properties are completely classical and they may be incorporated freely in a classical way of thinking. For example, the energy of interaction of an electronic system with an external magnetic field is given by the classical formula²⁴

$$-\frac{1}{2} \int d^3 r \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}). \quad (9)$$

The peculiarities of the quantum mechanical behavior

are present in the equations of motion of the subobservables.⁸ For the probability current density, the equations of the hydrodynamic formulation of quantum mechanics¹⁻⁷ contain a potential term which has no classical equivalent

$$V_q = -(\hbar^2/2m_e) \rho^{-1/2} \nabla^2 \rho^{1/2}. \quad (10)$$

For stationary problems, the continuity equation guarantees²⁴ that the probability current density field be divergenceless,

$$\nabla \cdot \mathbf{j} = 0. \quad (11)$$

The same cannot be said, in general, for each component \mathbf{j}_k , due to what Atkins and Gomes²⁴ called exchange currents; these are originated by nonlocal potentials in the one-particle Hamiltonians, as discussed in Sec. IV below.

The conservation condition (11) implies that the lines of current close on themselves. The system benzene molecule plus external field has a single plane of symmetry, that containing the nuclei. No line of current may cross this plane. The other planes of symmetry of the molecular point group are parallel to the external magnetic field; when the magnetic field is brought into consideration, these remain planes of symmetry only if accompanied by time inversion. The new group is isomorphic of D_{6h} , with elements $E, 2C_6, 2C_3, C_2, 3(C_2')T, 3(C_2'')T, i, 2S_6, 2S_6, \sigma_h, 3(\sigma_d)T, 3(\sigma_v)T$, where T is the time inversion operator. This is the magnetic point group²⁷ $6/mmm$ (in the international notation, or $m \cdot 6:m$ in Shubnikov's notation). No further symmetry restrictions are imposed upon the probability current density field. This vector field must be described over a sector of $\pi/12$ and to one side of the molecular plane; no line of current may cross this plane and, when crossing planes ($\sigma_d T$) or ($\sigma_v T$), they will run perpendicularly to them.

The analysis of the nodal topology along the lines proposed by Hirschfelder and co-workers^{8,28} and also discussed by Bader and co-workers,²⁹ provides a method of description of the current density field. Nodal lines of the state function, either infinite or closed upon themselves, have associated certain patterns of currents which Hirschfelder^{28(t)} called axial vortices and toroidal vortices, respectively. This is useful in describing the magnetic behavior of the molecule (and will be used in Sec. IV); however, it has no predictive value at present. In benzene, with the magnetic field perpendicular to the molecular plane, the main axis of symmetry will coincide with a nodal line of several molecular orbitals. The associated axial vortices describe a part of the total current density which may have a nonzero flux across a semi-infinite plane extending away from the C_6 axis. Other vortices will be considered as representing local circulations of charge. A major difficulty of the description outlined here should be pointed out immediately. The total current density \mathbf{j} is separated into its NO parts \mathbf{j}_k and these are divided into its component vortices. However, the components \mathbf{j}_k are not constrained by a conservation condition as \mathbf{j} is. So, the currents associated above with the main axial vortices are not necessarily conserved; particularly, the cur-

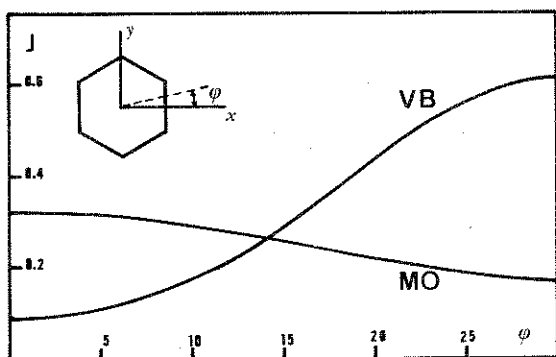


FIG. 1. Current density flux across sectioning planes at angles ϕ for two types of π electron semiempirical state functions (in a. u.).

rent flux across the semi-infinite ring-sectioning planes is not necessarily the same for all of them. A way of overcoming this unpleasant feature is presented in Sec. IV.

Measurable properties of molecules depend upon the current density in a variety of functional ways. Two typical functionals are those associated with the magnetic susceptibility and the NMR chemical shift of a particular nucleus. These are also the most important properties in this connection. The magnetic susceptibility χ is given³⁰ by

$$\chi = (N_{Av} \mu_0 / B^2) \int d^3r \mathbf{j}^{(1)}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}), \quad (12)$$

where N_{Av} is Avogadro's number and $\mathbf{j}^{(1)}(\mathbf{r})$ is the current density first order in the field B . The chemical shift $\sigma(\mathbf{r}_0)$ for a nucleus at position \mathbf{r}_0 is calculated from the secondary field given by the Biot-Savart law

$$\sigma(\mathbf{r}_0) = \frac{\mu_0}{4\pi} \int d^3r \hat{\mathbf{z}} \cdot \mathbf{j}^{(1)}(\mathbf{r}) \wedge \frac{(\mathbf{r}_0 - \mathbf{r})}{|\mathbf{r}_0 - \mathbf{r}|^3}, \quad (13)$$

where $\hat{\mathbf{z}}$ is the unit vector along the direction of the external field and σ is in fact the ZZ component of the corresponding tensor. It is clear that a single number cannot convey enough information about the field $\mathbf{j}(\mathbf{r})$ to allow reasonable estimates of properties like χ and σ . However, the traditional ring-current theories do assume that the RC carries the more distinctive features of the current distribution over a ring. Although this is avoided in traditional theories, the explicit calculation of the current associated with the semiempirical π -electron functions used will help to elucidate the role that nonlocal circulations play. This will also be used for comparison with the *ab initio* results in Sec. III. The π -electron current density flux across semi-infinite planes away from the C_6 axis was calculated for the semiempirical functions obtained in an SCF-MO formalism³⁰ and in a VB-type calculation²⁴ where the five covalent plus the 12 orthopolar structures were considered. This is shown in Fig. 1, where the reference frame is also displayed. A more detailed description is given by the plot (Fig. 2) of the radial distribution of the current density flux

$$- \int_{-\infty}^{+\infty} dz j_y(x, y=0, z) \quad (14)$$

calculated for the SCF-MO and the VB-type semiempirical π electron state function.

III. ANALYSIS OF THE *AB INITIO* CURRENT DENSITY CALCULATIONS

The detailed discussion in Sec. II about the magnetically induced currents in a ring molecule like benzene led to the conclusion that the symmetry of the problem (molecule plus field) does not forbid a circulation of charge around the ring. This delocalized current could be measured by the flux of the probability current density $\mathbf{j}(\mathbf{r})$ across a semi-infinite plane S secting the ring and having as edge the main axis of symmetry of the molecule

$$J = \int_S d^2r \hat{\mathbf{n}} \cdot \mathbf{j}(\mathbf{r}). \quad (15)$$

The unit vector $\hat{\mathbf{n}}$, perpendicular to the plane S , is taken to be in the direction corresponding to the diamagnetic circulation (opposing the external magnetic field). For exact state functions, the charge conservation condition (11) guarantees that the current J defined by Eq. (15) is independent of the plane S used; if this were not the case, there would be a source (or sink) of charge in the sector limited by the two planes. For approximate functions, J may depend on the sectioning plane used, as displayed in Fig. 1 for the traditional semiempirical π electron state functions.

A correct evaluation of the importance of the delocalized current depends on the availability of good calculations which have not been available for cyclic conjugated hydrocarbons of the type discussed here. Lazzeretti and Zanasi²¹⁻²³ have now started the publication of results using an *ab initio* system of programs that they developed. A basis set of (11s 7p; 5s/6s 5p; 3s) contracted Gaussian orbitals is used for each (C; H) pair of atoms and a coupled Hartree-Fock perturbation procedure is applied to account for the effect of the external magnetic field. In this section, I analyze some of their results to clarify certain points about the size and distribution of the delocalized currents.

From the maps of the current density given by Lazzeretti and co-workers for benzene,^{22,23} I extract the results referring to a plane bisecting a bond and these are plotted in Figs. 3 and 4. The probability current density $\mathbf{j}(\mathbf{r})$ of the 42 electron benzene molecule is plotted in Fig. 3 vs the axial coordinate both in the plane

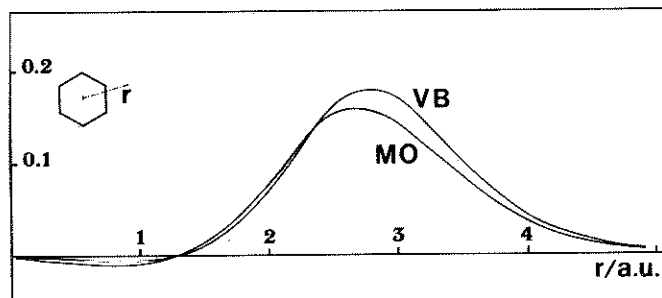


FIG. 2. Radial distribution of the π electron current density flux [Eq. (14)] over the sectioning plane at $\phi = 15^\circ$ (in a. u.).

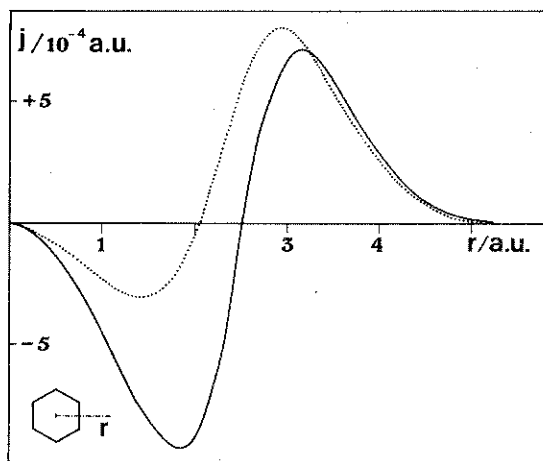


FIG. 3. Current density vs radial coordinate for the 42-electron benzene molecule (in a. u.) in the plane and (dotted line) 0.75 a. u. above or below the molecular plane.

and 0.75 bohr above (or below) that plane. There is a diamagnetic circulation in the outer region which is largely canceled (apparently) by the paramagnetic circulation seen in the inner core. This paramagnetic circulation appears to decrease quickly with distance from the plane of the molecule. The difference between the pattern of currents in and out of the plane suggests that this may be due to the different behavior of σ and π electrons. The molecular plane is a node for the π -electron orbitals and therefore the current density in the plane is purely of σ origin. In Fig. 4, are plotted the σ - and π -electron components of the current density 0.75 bohr out of the plane. (It should be recalled that these two components are not separately conserved; there are σ - π exchange currents.) The π component appears to be diamagnetic everywhere, while the σ component qualitatively reproduces the same pattern as in the molecular plane.

Another system calculated by Lazzeretti and Zanasi²¹ using the same method was the cyclopropenyl cation. The basis set used was a contracted Gaussian (11s 7p 2d;

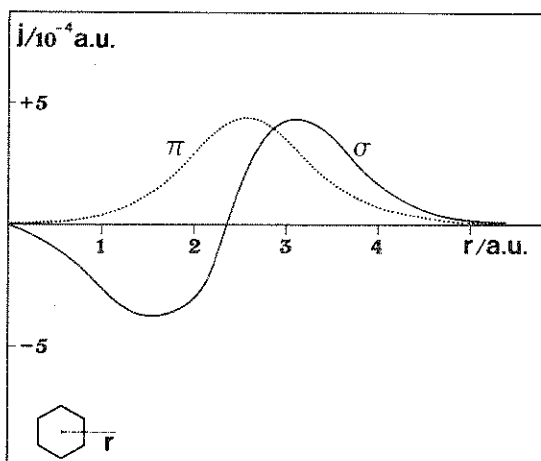


FIG. 4. σ and π components of the current density 0.75 a. u. above the benzene molecular plane vs the radial coordinate.

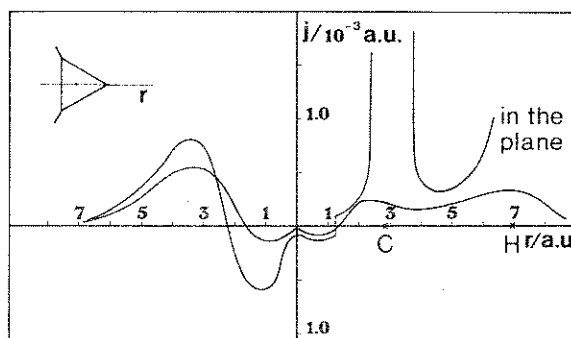


FIG. 5. Current density vs radial coordinate for the 20-electron cyclopropenyl cation (in a. u.) in the plane and 0.8 a. u. above or below the molecular plane.

5s 1p/6s 5p_x 5p_y 7p_z 1d; 3s 1p). The current density in certain regions of the plane of symmetry containing the C_3 axis is plotted in Fig. 5 vs the radial coordinate. As in the case of benzene, a diamagnetic circulation is seen in the outer regions which appears to be partially canceled by a paramagnetic circulation in the inner core. The plot to the right-hand side is more complicated, especially that referring to points in the molecular plane, for the carbon and hydrogen nuclei lie along this line. Near the nucleus the state functions change rapidly and the current density may be very intense; furthermore, it is likely that the state functions suffer large errors in these regions.

It should be stressed that the current density vector has a direction that cannot be predicted, in general. Above, I choose only points lying in planes of symmetry of the molecular point group so that it can be easily predicted to be perpendicular to the plane (if the plane is parallel with the magnetic field) or parallel with it (if the plane is perpendicular to the field).

These results appear to suggest a behavior which qualitatively corresponds to the traditional intuitive ideas of chemists— π electrons behaving in a delocalized way and so giving a consistently diamagnetic circulation. σ electrons, on the other hand, give a much more complex pattern of currents that are however essentially characterized by a diamagnetic circulation in the outer region and a paramagnetic circulation in the inner core; this is characteristic of a localized model in the sense of that earlier proposed by the present author.¹⁹

IV. THE CONSERVED ORBITAL CURRENT DENSITY

In the analysis made in Secs. II and III of the N -electron probability current density j induced in a cyclic conjugated hydrocarbon by a magnetic field perpendicular to its molecular plane, I drew attention to cylindrical circulations [$j(r) \propto \hat{z} \wedge r$] or to the flux of j across secting planes [Eq. (15)]. These are the sort of circulations that traditional RCMs suggest to be significant for magnetic susceptibilities or chemical shifts. The breakdown of j into orbital components j_a was attempted in Sec. II and is frequently used,^{23,32} but these suffer from the unpleasant feature of not being forced to satisfy a conservation condition of the form of Eq. (11). I now look into this problem and propose an orbital cur-

rent density which is conserved but leaves important orbital properties unchanged.

Assume the orbitals ψ_k to be eigenfunctions of a Hamiltonian of the form

$$\hat{H} = \hat{T} + \hat{V} + \hat{N}, \quad (16)$$

where the kinetic energy part \hat{T} is of the general form

$$\hat{T} = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla + e \mathbf{A} \right)^2, \quad (17)$$

\hat{V} is a local potential and \hat{N} a nonlocal potential.

Adams³¹ derived Hamiltonians with this structure for the multiconfiguration SCF orbitals and also for the NOs. The quantity introduced by Eq. (4) or (7), which may be written

$$\mathbf{j}_k = \frac{-e}{m} \operatorname{Re} \left[\psi_k^* \left(\frac{\hbar}{i} \nabla + e \mathbf{A} \right) \psi_k \right] \quad (18)$$

is an effective (orbital) probability current density in the sense discussed by Atkins and Gomes.²⁴ It is not conserved, in general, and a source function $S_k(r)$ may be defined by

$$S_k(\mathbf{r}) = \nabla \cdot \mathbf{j}_k(\mathbf{r}). \quad (19)$$

This nonconservation is a consequence of the nonlocal part of the potential \hat{N} in the Hamiltonian. In fact, the direct evaluation of $S_k(\mathbf{r})$ by Eqs. (19) and (18), with the assumption that ψ_k is an eigenfunction of the Hamiltonian (16), leads, after some manipulation, to the simple result

$$S_k(\mathbf{r}) = (-2e/\hbar) \operatorname{Im}(\psi_k^* \hat{N} \psi_k). \quad (20)$$

In a single configuration SCF Hartree-Fock theory, the nonlocal potential is represented by the standard exchange term²⁴ and the source function (20) takes the form

$$S_k(\mathbf{r}) = \frac{-2e}{\hbar} \operatorname{Im} \left[-\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{l \neq k} \psi_k^*(\mathbf{r}) \psi_l(\mathbf{r}) \int d^3r' \psi_l^*(\mathbf{r}') \times \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{r}') \right], \quad (21)$$

where the summation in l includes all the occupied orbitals. This is an expression first derived by Hirschfelder.⁸ More generally, Adams³¹ derived the Hamiltonians for the NOs of multiconfiguration state functions; Eq. (20) may then be used to determine the source function associated with each NO of the state function.

This nonconservation of the effective orbital current $\mathbf{j}_k(r)$ led Hirschfelder^{23(c)} to refer to it as a component of a compressible, viscous and rotational many-component fluid. The result is a fairly intractable description of limited use for visualizing the distribution of currents over the molecule. A way of avoiding these difficulties was suggested by Atkins and Gomes²⁴ who introduced an exchange current $\mathbf{j}_k^{\text{exch}}(\mathbf{r})$ associated with the nonlocal potentials. The complete orbital current density $\mathbf{j}_k^c(\mathbf{r})$ is then the sum of two components,

$$\mathbf{j}_k^c(\mathbf{r}) = \mathbf{j}_k(\mathbf{r}) + \mathbf{j}_k^{\text{exch}}(\mathbf{r}), \quad (22)$$

where the effective part $\mathbf{j}_k(\mathbf{r})$ is given by Eq. (18). The complete current \mathbf{j}_k^c satisfies a conservation equation

$$\nabla \cdot \mathbf{j}_k^c = 0 \quad (23)$$

as the sources associated with \mathbf{j}_k [Eq. (19)] are compensated by equivalent sinks of $\mathbf{j}_k^{\text{exch}}$. This exchange current is such that

$$\nabla \cdot \mathbf{j}_k^{\text{exch}} = -S_k \quad (24)$$

and it may be calculated by

$$\mathbf{j}_k^{\text{exch}}(\mathbf{r}) = -\frac{1}{4\pi} \int d^3r' \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} S_k(\mathbf{r}'). \quad (25)$$

The global N -electron probability current density [Eq. (7)] is not altered by the exchange terms which must cancel out,²⁴

$$\mathbf{j} = \sum_k n_k \mathbf{j}_k^c. \quad (26)$$

Magnetic properties which are functionals of $\mathbf{j}(r)$ may be expressed additively over the orbitals, either through the effective currents \mathbf{j}_k [Eq. (18)] or through the complete \mathbf{j}_k^c given by Eqs. (22) and (25). Discussion of the orbital contributions and, particularly, the plots of orbital current components should preferably be based on \mathbf{j}_k^c which is divergenceless according to Eq. (23).

It is interesting to observe that not only is the global N -electron current insensible to the exchange currents [Eq. (26)], but so also are the orbital contributions to many properties unaffected by these extra terms when defined by Eq. (25). In fact, the orbital exchange current [Eq. (25)] may be written in this other form

$$\mathbf{j}_k^{\text{exch}}(\mathbf{r}) = \frac{1}{4\pi} \nabla \int d^3r' \frac{S_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (27)$$

i. e., as the gradient of a scalar function. Consider three classes of properties defined as functionals of the current density $P = P\{\mathbf{j}(\mathbf{r})\}$ of types

$$(a) \int d^3r g(\mathbf{r}) \mathbf{j}(\mathbf{r}), \quad (28)$$

$$(b) \int d^3r g(\mathbf{r}) \wedge \mathbf{j}(\mathbf{r}), \quad (29)$$

$$(c) \int d^3r g(\mathbf{r}) \cdot \mathbf{j}(\mathbf{r}), \quad (30)$$

where $g(\mathbf{g})$ is a scalar (vector) function of position \mathbf{r} . When the following conditions:

$$(a) \nabla g(\mathbf{r}) = 0, \quad (28')$$

$$(b) \nabla \wedge g(\mathbf{r}) = 0, \quad (29')$$

$$(c) \nabla \cdot g(\mathbf{r}) = 0 \quad (30')$$

are satisfied, the exchange part [Eq. (27)] of the orbital current density gives a vanishing contribution to the functional. Examples of special importance are the magnetic susceptibility [Eq. (12)] and the chemical shift [Eq. (13)]. These properties are defined by functionals (12, 13) of types (c) and (b), respectively, with multiplicative functions g of the form $\hat{z} \wedge (\mathbf{r} - \mathbf{r}_0)$ and $\nabla[1/(\mathbf{r} - \mathbf{r}_0)]$; conditions (30') and (29') are clearly satisfied. This means that, by introducing the exchange current $\mathbf{j}_k^{\text{exch}}$ one obtains a conserved orbital current \mathbf{j}_k^c without affecting the orbital contribution to any of these important properties.

The vortex structure^{28(f)} of the one-electron functions will be changed by the consideration of the exchange currents. However, nodal lines with positions defined by symmetry must be unaffected by these currents which obey the same symmetry constraints. This is the case, particularly, for the main axis of symmetry. It is a nodal line for several orbitals and, in terms of the j_k^c , the analysis of the current lines may proceed to identify those lines which encircle it. These are the currents wholly responsible for the flux J [Eq. (15)], the delocalized currents. The remainder of j_k^c has a different character which may justifiably be called "local."

V. THE DELOCALIZED CURRENT

By delocalized current in a cyclic molecule, I mean that part of the probability current density $j(\mathbf{r})$ which represents a flow of electronic charge around the ring. Discussing a particular model of electrons, each localized in one sector of a ring, the present author¹⁹ showed how this could lead to lines of current running around the ring. The resultant pattern did however differ markedly from that predicted for the corresponding delocalized model. The difference is best seen in the current distribution across a plane secting the ring¹⁹: while the delocalized model carries a regular distribution of diamagnetic currents, in the localized model one gets diamagnetic currents in the external region and a paramagnetic circulation in the inner core. The net flow of current through any secting plane is zero as required in a truly local model. Conventional semi-empirical π -electron theories predict a pattern of currents shown in Figs. 1 and 2 which fits to a large degree the delocalized model just mentioned.

Ab initio theories give a current density distribution which is naturally far more complex.²³ However, if one looks at the distribution across a secting plane, certain features stand out which are easily understood. The radial distribution of current plotted in Fig. 3 shows a remarkable (qualitative) resemblance to Fig. 2. This suggests that the traditional views tested through crude π -electron calculations are likely to be substantially correct. A separate analysis of the π contribution plotted in Fig. 4 fits a delocalized description, being consistently diamagnetic in the entire range. The σ contribution is plotted in Fig. 3 (in the molecular plane) and in Fig. 4 (0.75 bohr out of the plane). It appears to be close to a localized description but a nonzero net flow of current is likely to result. It should be stressed again that there is no reason to preclude the flow of σ charge around the ring. Traditional chemical ideas about the localization of the σ bonds transferred into the domain of its magnetic properties led people to expect them to give purely local circulations. The results displayed here point towards a behavior which is not strictly local; however, when compared with the π component, it appears that the traditional perception is still remarkably good.

The analysis of the behavior of a many-electron system is much helped by one-electron (orbital) descriptions, to the extent that they apply. This is particularly a consequence of the simplicity of the nodal structure

of one-electron state functions, relative to the $3N$ -dimensional analysis.³³ One method frequently used for many-electron state functions is to separate the natural-orbital components, but with the sacrifice of the conservation condition. A solution of this difficulty is proposed in Sec. IV, consisting of the introduction of the exchange currents.²⁴ An orbital probability current density j_k^c is thus defined [Eq. (22)] which has the following properties:

- (1) It is conserved. For stationary problems this implies that it is divergenceless, with lines of current closing upon themselves. Maps of j_k^c are then very informative, the density of lines of current being directly related to its intensity.
- (2) The calculation of the orbital contribution to most properties may be made using j_k^c or the simpler j_k where the exchange part is excluded, as this gives no contribution in well-defined cases [Eqs. (28)–(30)].
- (3) The probability current density of the N -electron system is given by the summation of the j_k^c , weighted by the natural-orbital occupation numbers. The same type of composition applies to any property which is a linear functional of the probability current density.
- (4) A definition of the delocalized current may be formulated. For each orbital component j_k^c consider those lines of current which encircle the axis of the molecule. This shall be taken to be the orbital contribution to the delocalized current. Summing up over all natural orbital (with the respective occupations) one obtains the delocalized current of the N -electron molecule.

The concept of delocalized current which was just defined quantitatively is to be compared with the ring-current concept used in the context of unsophisticated theories. A few points should be stressed in relation to this:

- (1) The current density flux across a ring-secting plane as defined by Eq. (15) is wholly the result of the delocalized current just defined.
- (2) The overlap of the different orbital components of the delocalized current may result in some mutual cancellation. This is the same type of interorbital cancellation that may occur for the magnetic or any other properties.
- (3) For larger molecules, especially polycyclic hydrocarbons, a component of the type of the delocalized current just introduced should be expected to carry most of the effect of the overall structure of the molecule. The remaining local components should be mainly dependent on the properties of the atoms (or bonds) comprising the molecule. This is, however, an intuitive reasoning that awaits confirmation through further quantitative work.

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