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Topological theory of the electronic currents in benzene†

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The author has very recently developed a qualitative theory of the magnetic currents based on a topological analysis of the current density vector field which leads to its description in terms of vortices encased by separatrices. This paper reports on its application to a proper definition of localized and delocalized currents.

The electronic current densities induced in molecules by external magnetic fields are at present calculated with very good accuracy, especially for small molecules, and the results are usually presented in the form of maps in carefully chosen planes. Both the representation and the extraction of useful information out of these maps is very hard, not least because the current density field is an $R^3 \rightarrow R^3$ function. The present author has reported [1–3] very recently on a qualitative theory that greatly simplifies the global description of the vector field. This theory is based on a topological analysis of the field. The most interesting features of the vector field are associated with its singularities (the points where the current density vanishes) which may be classified in a way resembling that of Collard and Hall [4]. The discussion will be restricted to divergenceless currents, a property that the total current, $\mathbf{j}(\mathbf{r})$, possesses. Orbital currents, $\mathbf{j}_k(\mathbf{r})$, however, are not generally divergenceless. An exchange current [5], $\mathbf{j}_k^{\text{exch}}(\mathbf{r})$, may be defined in terms of the non-local part $\hat{N}$ of the potential in the hamiltonian for orbital Ψ_k using the source function

$$S_k(\mathbf{r}) = (-2e/\hbar)\ \mathrm{Im}\ (\Psi_k \hat{N} \Psi_k). \tag{1}$$

The exchange current is then calculated

$$\mathbf{j}_k^{\text{exch}}(\mathbf{r}) = \nabla V_k(\mathbf{r}), \tag{2}$$

where the potential $V_k(\mathbf{r})$ is given by

$$V_k(\mathbf{r}) = \frac{1}{4\pi} \int d^3\,\mathbf{r}'\ \frac{S_k(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}. \tag{3}$$

A complete orbital current, $\mathbf{j}_k^{\text{c}}(\mathbf{r})$, may be defined

$$\mathbf{j}_k^{\text{c}} = \mathbf{j}_k + \mathbf{j}_k^{\text{exch}} \tag{4}$$

that is divergenceless,

$$\nabla \cdot \mathbf{j}_k^{\text{c}} = 0. \tag{5}$$

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It is to this field $\mathbf{j}_k^c$ or to the total (many-electron) current $\mathbf{j}$ that the theory applies in the form presented here. The extension to include the standard orbital current $\mathbf{j}_k$ could be made by considering some new topological elements.

Near a singular point the vector field may be described by the **D**-tensor

$$\mathbf{D} = \nabla \mathbf{j} \tag{6}$$

calculated at the singular point. The nature of the eigenvalues of this traceless tensor allows a classification of the singularities of the field :

(*a*) *Isolated singularities* when the **D**-tensor has three non-zero eigenvalues. Two of the eigenvalues must have the same sign (for its real parts, in the complex case) and the associated eigenvectors define a plane tangent to the separatrix at the singular point. Separatrices are surfaces filled by asymptotic lines, that is, by lines of current which originate and terminate at singular points. The third eigenvector defines an isolated asymptotic line without special interest.

(*b*) *Stagnation lines* are formed by singular points where the **D**-tensor has only two non-zero eigenvalues. The eigenvector associated with the zero eigenvalue is a tangent to the stagnation line. Two kinds of flow near the stagnation line may exist, depending on whether the two eigenvectors are real or not.

(*b*) (i) *Saddle lines* are the stagnation lines formed by points where the **D**-tensor has two real eigenvalues.

(ii) *Vortical lines* are the stagnation lines formed by points where the **D**-tensor has complex eigenvalues.

The set of all stagnation lines of the current density in a molecule forms the so-called *stagnation graph*, which may be disconnected.

(*c*) *Critical points* are the singular points with three zero eigenvalues. These are two points of the stagnation lines where a change of régime of flow may occur ; this will be associated with a branching of the stagnation line, converting the critical point into a vertex of the stagnation graph.

The major kinds of flow near singularities are sketched in figure 1.

Two kinds of separatrices are found. Isolated singularities generate topologically spherical separatrices ; these must satisfy the Poincaré-Hopf theorem [6, 7] implying that each separatrix has two isolated singular points, a source and a sink of asymptotic lines. Separatrices of a second kind are generated by saddle lines ; their shape may be described as that of a double cone having one or more saddle lines as geratrices and the two vertices coinciding with critical points.

The stagnation graph obeys the following two fundamental rules. (1) There is one and only one stagnation line extending to infinity, a vortical line which, at large distances from the molecule, becomes parallel to the magnetic field. (2) At the critical points the branchings that may occur conserve the total index of the stagnation lines. The topological index of a stagnation line is defined in a way similar to that used for singularities of planar fields [6, 7], $+1$ for vortical lines and -1 for the simplest saddle lines of the type sketched in figure 1 (*b*) (i).

As a consequence of these rules, the stagnation graph may have one or more connected parts. Each of these parts is constituted by a vortical line (open for

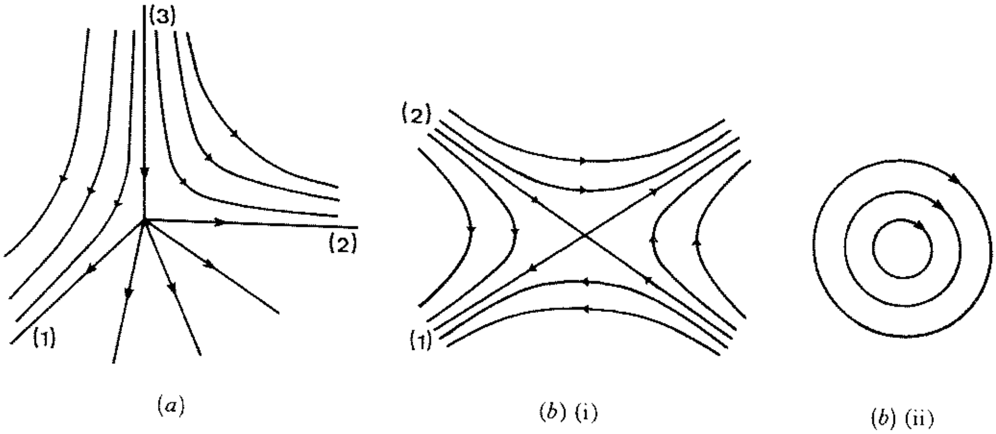

Figure 1. Major régimes of flow near singularities. (*a*) The isolated singularity has associated two positive eigenvalues that define the asymptotic plane (1)–(2) locally tangent to a spherical separatrix. (*b*) (i) At the saddle line meet four semi-planes defined by directions (1) and (2) which define the separatrices. (ii) The vortical line goes through the core of the flow shown here in cross section.

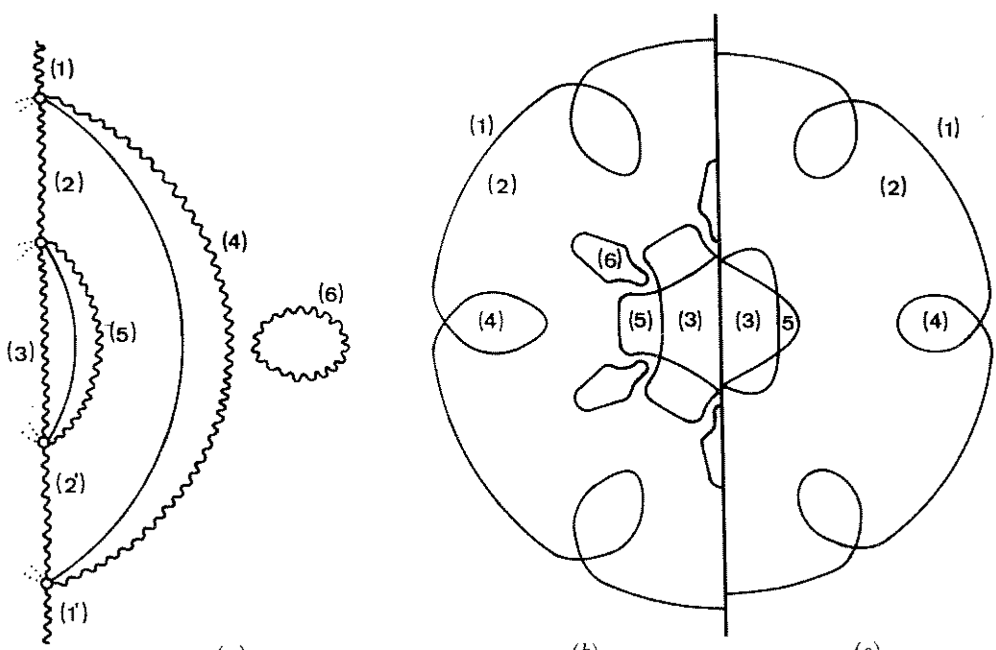

Figure 2. Topological description of the current density induced in the benzene molecule by a magnetic field perpendicular to the molecular plane. The stagnation graph (a $\pi/3$ sector is displayed in (*a*)) has four critical points at more than 0·7 a_0 out of the molecular plane. Sections of the separatrices at the molecular plane (*b*) and 0·7 a_0 out of that plane (*c*) are also shown. Spherical separatrices exist around each carbon atom, encasing a toroidal vortex each. (Based on calculations reported by Lazzeretti *et al.* [21, 22].)

the leading part and closed for all the other connected parts) and the stagnation lines and vortical lines into which it branches at the critical points satisfying the total index rule above.

This qualitative theory of the electronic current density in molecules leads to the description of the currents in terms of axial or toroidal vortices encased by well defined separatrices. This sheds new light on the concept of localization of molecular properties, especially for the interpretation of magnetic properties in terms of the current density. The rôle of delocalized currents in the properties of cyclic, conjugated hydrocarbons is an unresolved problem [1, 8–22].

In figure 2 is shown the stagnation graph of benzene and the sections of the separatrices by two planes, the molecular plane and another one $0{\cdot}7\ a_0$ above or below it, based on the results of very recent calculations by Lazzeretti and co-workers [21, 22]. The non-equivalent vortices are numbered (1) to (6) to show the correspondence between the stagnation graph and the maps of the current density. The toroidal vortex (6) is entirely contained between levels $\pm 0{\cdot}7\ a_0$. Vortex (3) and the six equivalent vortices (4) are the only paramagnetic ones. Vortices (1), (2) and (3) may be associated with a ring current now defined in a rigorous way. All the other vortices correspond to well localized circulations. It should be observed how well this interpretation fits with the discussion of the concepts of localized and delocalized currents that the present author reported [16], based on model wavefunctions.

I greatly benefited from discussion with Dr. Paolo Lazzeretti and Dr. Riccardo Zanasi of the University of Modena (Italy) of some of their recent calculations on benzene which are cited here. I am indebted to them for making available preprints of their work.

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