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Topology of the electronic current density in molecules

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This paper presents the first complete topological description of the electronic-probability current-density field in molecules under an external homogeneous magnetic field. The analysis is general, applying both to the many-electron current density and to its one electron (orbital) components. The singular lines of the vector field form a stagnation graph which is the skeleton of the qualitative theory presented here. This graph may be disconnected, with one connected part playing a leading role in the description. Other secondary connected parts are encased into topologically spherical separatrices defined by two isolated singular points. This is one of the types of separatrices which are introduced here. The other one is defined by saddle singular lines and encases the axial vortices which are associated with the vortex stagnation lines. The vertices of the stagnation graph are critical points of the current-density field, points where the stagnation lines may branch out according to an index theorem that is proved here. The basic units in this qualitative description of the current field are axial or toroidal vortices. Each vortex is a whirlpool of electronic-charge probability flowing around a vortex stagnation line and encased into a closed separatrix. Vortices may exist inside other vortices but separatrices cannot cross one another. Saddle stagnation lines belong to the boundary of four or more axial vortices.

I. MOTIVATION

The flux of probability density in N-electron molecules is of primary importance in determining many properties, namely, the molecular magnetic properties. The concepts developed in this paper concern an isolated molecule under the effect of an external, homogeneous, constant magnetic field. Its application to the case where no magnetic field is present is immediate and will be referred to; more complicated fields will not be considered here, but extensions are possible. The arguments evolved throughout the paper are of a topological nature, the mathematical formalization being avoided whenever possible.

Hirschfelder[1] discussed the axial and toroidal vortices which are associated with the nodal lines of one-electron state functions. For N-electron molecules, the analysis may be made on the $3N$-dimensional configuration space,[2] or the natural orbital components may be studied in ordinary space.[1(b)] However, these orbital components are not constrained to satisfy the continuity equation,[3] which makes the interpretation of the orbital current-density plots very difficult. The present author has proposed that the exchange currents[3] should be considered to form a complete orbital current that satisfies the continuity equation but leaves the orbital contribution to most properties unchanged.[4,5] The topological analysis made in this paper applies to any smooth, nondivergent vector field in three space. It may be used both for the N-electron currents and for the complete orbital current components. Extension of the theory to comprehend fields with a nonzero divergence (like the standard orbital current density) introduces certain complications, including new topological elements.[5] This will not be attempted in the present paper.

The basic elements for the topological analysis of a vector field are associated with its singular points, i.e., the points where it vanishes. The most interesting results of differential topology[6,7] apply to fields with isolated singularities only. In the present case, singular lines exist and play a role of foremost importance; accordingly, they will be given very special attention in the present study. The nodal lines considered by Hirschfelder[1(b)] have associated a vortex circulation. The singular lines of the N-electron current or the complete orbital current are not necessarily associated with nodal regions of the probability charge density. The present author[5] has shown that these singular lines (or stagnation lines, as they may also be called) have associated one of two regimes of circulation, either vortical or saddle-like (normal). Transitions between the two regimes may occur at certain critical points. There may be some control parameter leading to the change of regime at what is formally a catastrophe.[8] At a critical point, stagnation lines may branch out, a process ruled by theorem B proved in Sec. III. The set of all singular lines forms the stagnation graph of the system, a sort of skeleton defining the topology of the vector field. Another concept introduced in this paper is that of separatrix, a closed surface filled with asymptotic lines (i.e., lines of current originating and terminating at singular points) separating the domains of the different vortices which make up the current field.

In Sec. II, below, are discussed the types of isolated singularities allowed, and the concept of spherical separatrix associated with them is introduced. Line singularities are discussed in Sec. III, particularly their interconnections at the critical points. In Sec. IV, the structure of the stagnation graph is established, and its implications for the vector field are discussed. Two examples are considered in Sec. V for the application of the new concepts developed in the earlier sections. One is a model vector field given analytically whose topological structure is deduced and discussed; the other refers to the current density which is induced in the cyclopropenyl cation by an external magnetic field perpendicular to the molecular plane. Finally, in Sec. VI, the major conclusions of this work are summed up and some of its physical implications discussed.

II. ISOLATED SINGULARITIES AND THE SEPARATRIX

Consider an isolated molecule under an external, homogeneous, constant magnetic field. The N-electron probability current density[3] $\vec{j}$ is conserved:

$$\vec{\nabla}\cdot\vec{j}=0\ . \tag{1}$$

The same is true for the orbital components of the current density when natural orbital complete currents[4] (exchange part included) are considered.

Points where the field is nonzero are called regular. Those points where it vanishes are the singular points of the field, and the most interesting features of the vector field happen in their neighborhood. In this section I shall consider isolated singularities only.

The vector field near a singular point may be described by the $\underline{D}$ tensor,

$$\underline{D}=\nabla\vec{j}\ , \tag{2}$$

which is traceless for Eq. (1) to be satisfied. The singularities may be classified[9] according to the nature of the eigenvalues of $\underline{D}$. The rank of a singularity is the number of its nonzero eigenvalues; the signature is defined as the difference between the number of eigenvalues with a positive real part and the number of those with a negative real part. In this (rank, signature) classification, the isolated singular points must be of types $(3,\pm1)$. Singularities of type (2,0) form stagnation lines, which are considered in the next section; on these lines, certain critical points may occur which are in fact (0,0) singularities.

Consider the asymptotic lines of current, lines starting and finishing at singular points. For each isolated singularity, whatever its type may be, the asymptotic lines fill a surface with a single asymptotic line perpendicular to it at the singular point (Fig. 1). The plane, defined by the two eigenvectors associated with eigenvalues of the same sign for their real parts, (1) and (2), is locally tangent to what I define as the separatrix. The smoothness and lack of divergence of the vector field guarantee that the separatrix defined locally at the singular point is a closed boundaryless surface. Through any of its regular points passes an asymptotic current line which starts at a source and finishes at a sink singular point. The separatrix must satisfy the Poincaré-Hopf index theorem.[6,7] As all the singularities considered on the surface (Fig. 1) have index $+1$, this theorem establishes that its number equals the Euler characteristic of the surface. Now, the only compact, oriented, boundaryless two-many-fold with a positive Euler characteristic is the (topological) sphere. This proves the following.

Theorem A. All the separatrices associated with isolated singularities are topological spheres.

This is a simple but very important result since it guarantees that all individual pieces that compose the vector field are surrounded by topological spheres. Of course such spheres may exist inside one another but without intersecting or touching. Two types of separatrices associated with isolated singularities may exist, depending on whether the eigenvalues are real or complex. These are shown in Fig. 2 in stereographic projection.

III. LINE SINGULARITIES AND CRITICAL POINTS

It was pointed out in Sec. II that singular points of type (2,0) form stagnation lines. In fact, these are basically planar singular points with translation

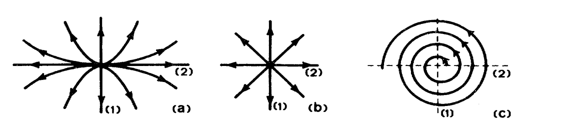

FIG. 1. Asymptotic lines near an isolated $(3,+1)$ singularity. The single asymptotic line outside the plane of the drawing converges into the singular point along axis (3). Case (a): $\lambda_1>\lambda_2>0$; case (b): $\lambda_1=\lambda_2$ are complex, $\lambda_1=\lambda_2^*$, $\mathrm{Re}(\lambda_1)>0$. The third eigenvalue is $\lambda_3=-\mathrm{Re}(\lambda_1+\lambda_2)$.

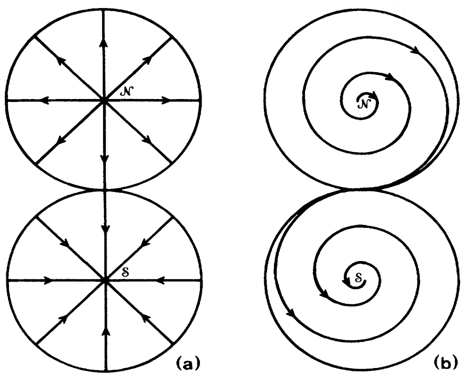

FIG. 2. Two types of separatrices associated with isolated singularities. Both are topological spheres shown here in stereographic projection with the source on the north pole and the sink on the south pole. When the eigenvalues of the $\underline{D}$ tensor are complex, the spiral case (b) occurs.

symmetry (locally) along the direction associated with the zero eigenvalue. The regime of circulation near the singularity depends on whether the eigenvalues are real or imaginary as displayed in Fig. 3.

The saddle line shown in Fig. 3(a) has a D_{2h} local symmetry. The index associated with it is -1, while the vortex line has an index $+1$. Saddle lines with higher D_{nh} local symmetry may exist, their points being in fact (0,0) singularities. Their analysis needs derivatives higher than the first used in defining the $\underline{D}$ tensor. Following a technique parallel to that used in Ref. 5 for the exchange current, it is easily shown that the index associated with a D_{nh} saddle line is $(1-n)$.

There are no asymptotic lines of current associated with a vortex line. On the contrary, for the saddle line, four asymptotic directions exist in the plane of Fig. 3(a), which extend in space to form two surfaces which touch at the saddle line, where they

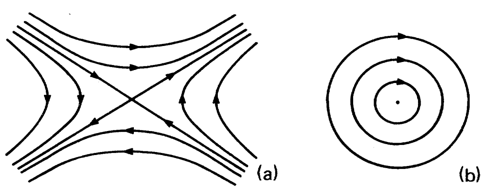

FIG. 3. Regime of circulation near a stagnation line. Stagnation lines are dense one manifolds of (2,0) singular points. Real eigenvalues correspond to a normal regime (a) near what shall be called a saddle line; imaginary eigenvalues are associated with the vortex regime (b) around what shall be called a vortex line. The transition between the two regimes may occur at critical points which are (0,0) singularities and is ruled by theorem B in the text.

bend back. These surfaces are separatrices of a new kind. Having one (or more) saddle lines, this suggests that they are cylindrical; it will become clear further down that they are typically pea-pod shaped with one or more ribs (the saddle lines) running all the way from vertex to vertex (where the critical or transition points are located). Examples are given in Sec. V.

I shall now consider the properties of critical points to show their role as branching points of the stagnation lines. The final result is condensed into the statement of theorem B; it is convenient to consider first the particular case of the branching of a vortex stagnation line.

Lemma B1. A vortex line may branch out at one of its critical points into N new stagnation lines with conservation of the index sum,

$$i_0 = +1 = \sum_{k=1}^{N} i_k \; . \qquad (3)$$

This statement is misleadingly elementary. The discussion of the proof in some detail will help to understand its implications. A first implication of the wording of the lemma is that the stagnation lines are to be considered as directed, i.e., that inspection of the $(N+1)$ lines coalescing at the critical point allows the identification of the matrix vortex line, the one with an index $i_0 = +1$ that branches out into a set of N lines. The stagnation graph discussed in the next section is thus a directed graph. The proof of lemma B1 may be given with the following argument. It is possible to construct a topological sphere around the critical point and locally orthogonal to all the stagnation lines that meet there, such that the current is everywhere tangent to it. The Poincaré-Hopf theorem[6,7] may be applied to this surface with an Euler characteristic $\chi = 2$. Since the matrix vortex line has an index $+1$, the sum of the indices of all other lines (indices of the singularities on the sphere) must equal $+1$ as prescribed by (3). The simplest case of this class of branchings is sketched in Figs. 4(a) and 4(b). The general law of branchings at critical points may be considered now.

Theorem B. The branchings of stagnation lines that may occur at critical points do conserve the sum of the indices associated with the lines.

This is a generalization of lemma B1 to include the branching of a saddle stagnation line and other more complex cases. A simple proof of this theorem is obtained by starting with the branching of a vortex line as in Fig. 4 and enlarging the sphere to enclose new critical points. This is possible be-

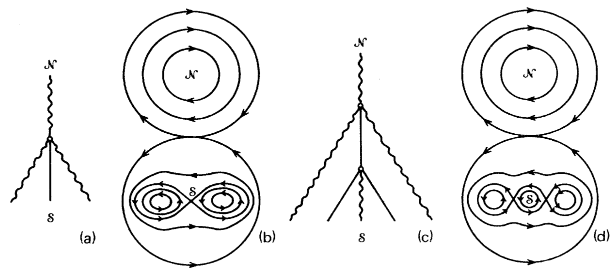

FIG. 4. Branching of a vortex stagnation line at a critical point. The northbound vortex line (waving) branches out into two new vortex lines and a saddle line (straight). In (b) is represented the stereographic projection of the field on a sphere around the critical point. In (c) a further branching of the saddle line is considered. Enlarging the sphere to enclose both critical points leads to a field on its surface which is represented in (d) in stereographic projection.

cause of the fact shown in Sec. IV that any connected part of the stagnation graph has a vortex line. As a new critical point is enclosed into the topological sphere, the sum of the indices of the lines crossing the surface must be unchanged as its Euler characteristic is invariant. This proves theorem B.

In the particular case of the branching of a saddle line into a number of new stagnation lines, theorem B implies that the sum of the indices of the new lines equals -1. In a general case where M lines merge at a critical point and then branch out into N new stagnation lines, theorem B may be put in the form of Eq. (4),

$$\sum_{k=1}^{M} i_k = \sum_{l=1}^{N} i_l \; . \tag{4}$$

This may occur due to the high (local) symmetry of the particular molecule being studied. In such complex cases the directionality of the stagnation lines becomes very important and great care must be exercised to avoid inconsistencies.

IV. THE STAGNATION GRAPH AND THE VORTEX CIRCULATIONS

The stagnation graph of the electronic current density in a molecule under an external magnetic field is the set of all stagnation lines. The vertices of the graph are the critical points of the vector field where stagnation lines (the edges of the graph) merge. The stagnation graph is in general disconnected, each of the connected subgraphs being made up of a vortex line with ramifications at critical points obeying theorem B above. The first result I prove concerns the nature of these subgraphs.

Proposition C. The stagnation graph of a molecule under an external magnetic field is composed of a number of connected subgraphs. One of these, the primary stagnation subgraph, is constituted by an open vortex line along the external field; other connected subgraphs may exist, the secondary stagnation subgraphs, constituted by closed vortex lines. Any of the above-mentioned vortex lines may branch into saddle lines and new vortex lines at vertices of the graph which coincide with the critical points of the vector field.

This long statement about the structure of the stagnation graph follows immediately from two facts. First, there are no restrictions on the number of connected subgraphs and, second, only one of these subgraphs may be open, its vortex line extending to infinity. This I shall prove presently. Consider the molecule at the center of a sphere with a radius large compared with the molecular dimensions. The effect of the external magnetic field on the (minute) electronic charge located on the sphere is equivalent to its rigid rotation. The current field on the sphere is regular everywhere except for two vortex centers [Fig. 3(b)] on the opposite poles (obviously, satisfying Poincaré-Hopf theorem). The singularities of the sphere at the poles are at the intersection with the vortex line as it extends to infinity, northward and southward. This shows that one (and only one) such open vortical line exists. This line may branch out in the region closer to the molecule, originating the primary, connected, stagnation subgraph. Other stagnation lines not connected to the primary subgraph may exist, but they cannot extend to infinity. As boundary points do not exist, they must form closed cycles. Having established the basic structure of the stagnation graph, I discuss now its implications for the current density vector field.

Proposition D. Given the stagnation graph of a smooth vector field, this has the following elements.

(1) Associated with each finite vortex line, there is a vortex which is encased into a pea-pod shaped separatrix having one or more saddle lines as ribs. These separatrices may exist one inside another and, as vortex and saddle lines may terminate at different critical points (at one end), a fusion between two separatrices may occur.

(2) Associated with both the northbound and the southbound infinite vortex lines, there is a vortex which completely surrounds the molecule.

(3) Associated with a closed (vortex) loop, there is a toroidal circulation which is encased by a topologically spherical separatrix with two isolated singular points on its surface.

In the language of algebraic topology,[10,11] the portions of space limited by the separatrices are associated with conjugacy classes of the fundamental group, and the current loops in them are freely homotopic.

The contents and justification of proposition D above is best understood through an example such as the one created in Figs. 5 and 6. As one moves south, the vortex circulation (A) breaks up at critical point (1) into two encased new vortices separated by the saddle line as shown in section (B). When the critical point (2) is reached, the right-hand side internal vortex originates two new vortices again separated by a saddle line. To understand the changes between sections (C) and (D) in Fig. 6, it is better to restart the analysis from the south pole. Events at (4) are identical to those at (1). Next, at (3), the saddle line breaks up to originate a new vortex in between two saddle lines that define its separatrix. Now, between (C) and (D) there is no change in the stagnation graph, and therefore no discontinuity exists. Considering the schematical drawings in Fig. 6, (D) may be obtained from (C) by making the right-hand side (rhs) lobe of the external separatrix to contract, squeezing the current lines between the two. This process of fusion of separatrices is essential in the interpretation of the flows associated with many stagnation graphs. The rhs vortex in (B) which is originated at (1) has as its southern limit the region of fusion of separatrices.

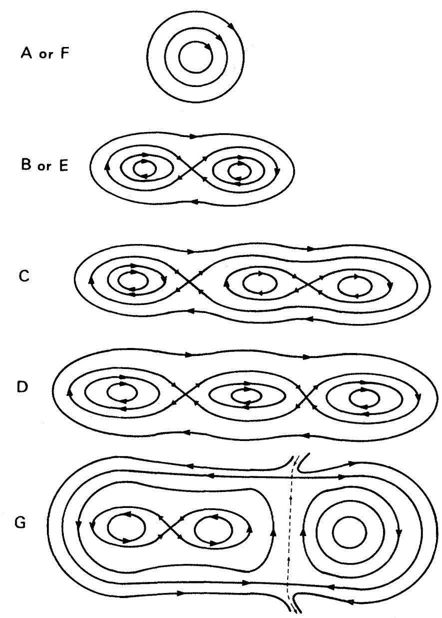

FIG. 6. Patterns of circulation (sketched) in certain sections of the molecule with the stagnation graph in Fig. 5. Between (C) and (D), there is no change in the stagnation graph; however, the internal separatrix with vertex at critical point (2) fuses with the separatrix that has its vertex at (3). The process of fusion is continuous and therefore it is not associated with any singular feature. (G) represents the section of the toroidal circulation in a region where one of the arms is branched. The dashed line is the isolated asymptotic that crosses the spherical separatrix at the isolated singularities.

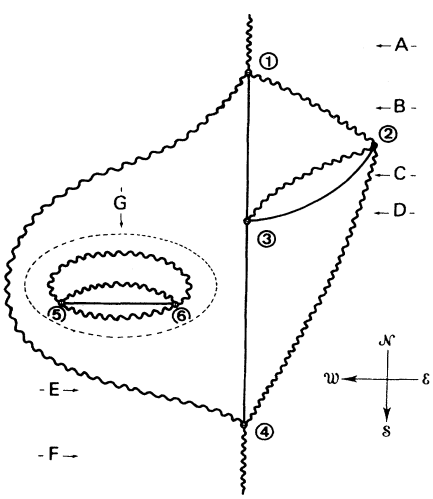

FIG. 5. Stagnation graph of a molecule. This made-up example comprehends the primary subgraph and one secondary subgraph. The direction of the branching at the singularities is indicated by the equator drawn in each little sphere; this may be associated to a north to south direction in the primary subgraph and a clockwise (or east to west) direction in the secondary one. The dashed line surrounding the whole secondary subgraph represents schematically the separatrix which is a topological sphere with two singular points, a source and a sink. The current flow that is associated with this stagnation graph in certain regions [dividing planes (A)—(G)] is sketched in Fig. 6.

One secondary subgraph is considered in Fig. 5. The gross features of the circulations associated with it are those of a toroidal vortex encased in a spherical separatrix. It was shown in Sec. II that all such separatrices associated with isolated singularities are in fact topological spheres with two singular points, a source and a sink. The isolated asymptotic line, dashed in (G) of Fig. 6, which is locally orthogonal to the separatrix will follow the neighboring lines of current without any special role.

V. EXAMPLES

In this section I shall discuss first a model example with a stagnation graph of certain complexity to clarify the process of branching of the lines and help the visualization of the three-dimensional vector field. The second example is based on the very recent calculations of Lazzeretti and Zanasi[12] on the 20-electron system $C_3H_3{}^+$.

A. Model vector field

Consider the vector field defined by equations

$$j_x = y^3 + y(z^2 - z - 2) ,$$
$$j_y = -x^3 - x(z^2 + z - 2) , \quad (5)$$
$$j_z = 0 .$$

The stagnation graph associated with this vector field is sketched in Fig. 7. As the current is everywhere parallel to the xy plane, it is convenient to study the map of currents in a plane at constant z.

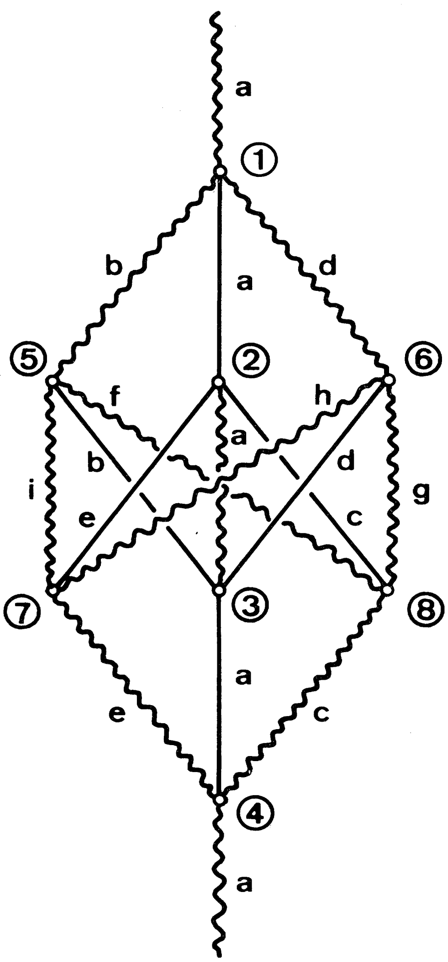

FIG. 7. Stagnation graph of vector field (5). This is a three-dimensional graph: the edges represent vortex (waving) or saddle (nonwaving) stagnation lines; the vertices represent the critical points. The location of these elements in configuration space is better understood through the general map in Fig. 8.

The most complex maps occur for $z \in]-1, +1[$ and this is the case shown in Fig. 8. Singularities may occur at points (a)—(h) with coordinates

(a) $(x=0; y=0)$. Stagnation line in $z \in]-\infty, +\infty[$ with critical points (1)—(4) at $z=+2$, $+1$, -1, and -2 and the regimes shown in Fig. 7;

(b) and (d) $[x=0; y=\pm(-z^2+z+2)^{1/2}]$. Stagnation lines in $z \in]-1; +2[$ with critical points (1)-(5)-(3) and (1)-(6)-(3) and the regimes shown in Fig. 7;

(c) and (e) $[x=\pm(-z^2-z+2)^{1/2}; y=0]$. Stagnation lines in $z \in]-2; +1[$ with critical points (2)-(8)-(4) and (2)-(7)-(4) and the regimes shown;

(f), (g), (h), and (i) $[x=\pm(-z^2-z+2)^{1/2}; y=\pm(-z^2+z+2)^{1/2}]$. Stagnation lines in $z \in [1, +1]$ with critical points (5)-(8), (6)-(8), (6)-(7), and (5)-(7) and the regimes shown.

It is worth analyzing in some greater detail the elemental vortices that integrate the vector field and to identify certain fusions of separatrices. An external, unbound vortex exists associated with vortical line (a) north of critical point (1) and south of critical point (4). At critical point (1) two new vortices are originated encased into the separatrices with the stagnation line (a) between (1) and (2). At $z=+1$, three critical points occur, (2), (5), and (6) originating five new vortices (Fig. 9). Meanwhile, the vortices originated at (1) die off at the fusion of separatrices that occurs at $z=0$. The pattern of currents

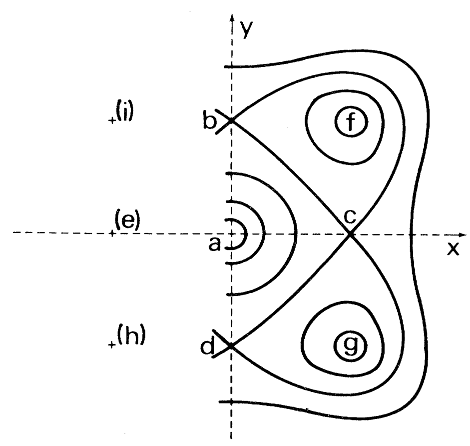

FIG. 8. Map of the current density field (5) for $z=0$. Points (a)—(i) are the singularities of the map, i.e., the intersections of the stagnation lines with the plane $z=0$. The nine singularities exist for $z \in]-1, +1[$, but the square symmetric arrangement is characteristic of $z=0$. For example, at $z=+1$ (f) and (i) coincide with (b), corresponding to critical point (5); (g) and (h) coincide with (d), corresponding to critical point (6); and (c) and (e) coincide with (a) for critical point (2).

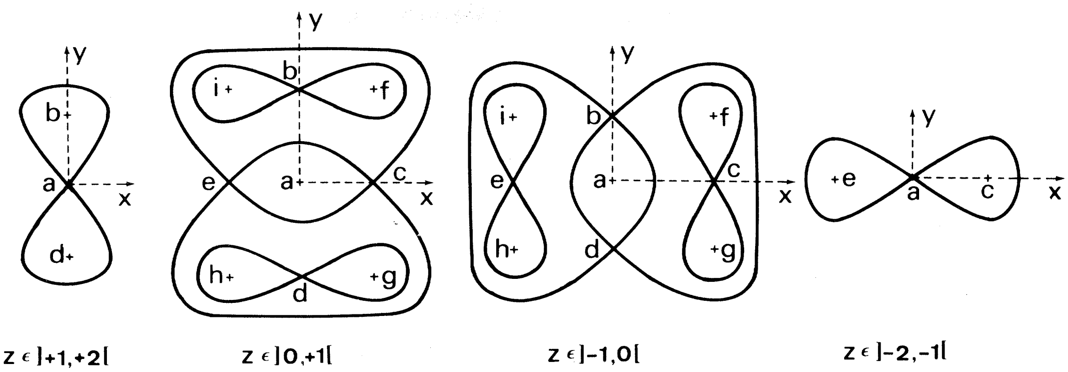

FIG. 9. Separatrices of current-density field at planes z=const. The transition between the pictures shown occurs with critical points at $z = +2, +1, -1$, and -2. At $z = 0$ occurs a fusion of separatrices which may be understood if the pattern in Fig. 8 is considered for the transition between those here for positive and negative z.

in planes at $z < 0$ is similar to those described but for a rotation of $\pi/4$. The vector field has a pseudoaxis of rotation of degree 4. This is an excellent example of the wealth of information provided by the stagnation graph assuming that the location of its elements in physical space is known.

B. The cyclopropenyl cation

The second example discussed is the one provided by the magnetically induced currents in the cyclopropenyl cation as calculated very recently by Lazzeretti and Zanasi.[12] Maps are calculated for the current density in the plane of the molecule and in planes 0.8 a.u. off it. In this case, the current-density vector is not constrained to the projection plane. The interpretation of the vector field is made very easy by the consideration of the stagnation graph in Fig. 10. Associated with the four vortex lines from (1) to (2), there are four vortices encased by double-conical separatrices touching one another at the three saddle lines. Further out, there are three toroidal vortices encased into spherical separatrices.

VI. CONCLUDING REMARKS

The global topological analysis of the current-density field in molecules which is introduced in this paper allows a clear identification of subdomains of the physical space associated with each vortex. The boundaries between these subdomains are the separatrices of the two types which are defined in Secs. II and IV. The first type of separatrix is a topological sphere which is associated with two isolated singular points. Encased into this sphere is a toroidal vortex, possibly with a number of axial vortices resulting from branchings of the main vortex line. The second type of separatrix is a tubelike closed surface better described, generally, as pea-pod shaped having one or more singular lines as ribs. This type of separatrix encases an axial vortex of the current-density field.

This presentation of the qualitative theory of the magnetic current density in molecules avoids the formal language of topology, using instead a language closer to the physical phenomenology. However, the topological concepts developed here may gain generality and perhaps clarity with the introduction of the formal apparatus of topology. Attempts in this direction have been made for some problems with important analogies to the one dealt with here; among them are the study of defects in ordered media,[10,11] the rotational dislocations in liquid crystals,[13] or the hydrodynamics of superfluids.[14] Aspects of plasma transport[15] and of mag-

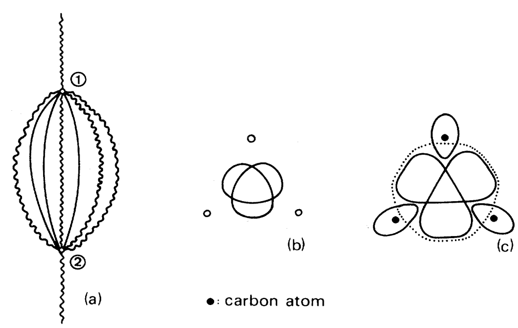

FIG. 10. Stagnation graph (a) and the separatrices in the molecular plane (c) and 0.8 a.u. above that plane (b) for the cyclopropenyl cation. The critical points (1) and (2) occur at a distance greater than 0.8 a.u. from the molecular plane; the three spherical separatrices [defined by two isolated singularities each, as seen in (c)] are entirely contained in between levels ±0.8 a.u. The dotted line represents an asymptotic line linking the six isolated singularities. [Based on data calculated by Lazzeretti and Zanasi (Ref. 12).]

netic turbulence[16] do also resemble the phenomenology studied here. Important work is in progress in these related fields which may be relevant to the description and properties of the electronic currents in molecules.

From the quantum chemical point of view, this qualitative theory may suggest new techniques to deal with classical problems such as that of the atoms in molecules and the distinction between local and nonlocal effects or properties. The proposal made by the present author[5] towards the introduction of an appropriate definition of delocalized current in cyclic conjugated hydrocarbons may be improved and generalized by considering the global analysis presented here.

A very important problem which is outside the scope of this paper is that of the relations between the topology of the electronic current density, which is discussed here, and the topology of the electronic charge density, which was approached by techniques related to those used here by Collard and Hall[9] and then extensively studied by Bader and co-workers.[17] Mezey[18] made a thorough topological study of the molecular energy hypersurface as a function of the nuclear coordinates. His analysis of the distribution of singular points (where the gradient of the potential vanishes and are also called critical points by some authors) leads to a rigorous topological definition of molecular structure and reaction mechanism. Research on functional dependence of the molecular properties on the charge density is currently very active,[19] especially in relation with the Hohenberg-Kohn theorem.[20]

ACKNOWLEDGMENT

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[1](a) D. F. Heller and J. O. Hirschfelder, J. Chem. Phys. 66, 1929 (1977); (b) J. O. Hirschfelder, *ibid* 67, 5477 (1977); (c) 68, 5151 (1978).

[2]J. Riess and H. Primas, Chem. Phys. Lett. 1, 545 (1968); J. Riess, Ann. Phys. (N.Y.) 57, 301 (1970); Phys. Rev. D 2, 647 (1970); Ann. Phys. (N.Y.) 67, 347 (1971); Helv. Phys. Acta 45, 1067 (1972); Phys. Rev. B 13, 3862 (1976).

[3]P. W. Atkins and J. A. N. F. Gomes, Mol. Phys. 32, 1063 (1976).

[4]J. A. N. F. Gomes, J. Chem. Phys. (in press).

[5]J. A. N. F. Gomes, J. Chem. Phys. (in press).

[6]V. Guillemin and A. Pollack, *Differential Topology* (Prentice-Hall, Englewood Cliffs, N. J. 1974).

[7]J. W. Milnor, *Topology from the Differentiable Point of View* (University of Virginia Press, Charlottesville, VA, 1965).

[8]R. Thom, *Structural Stability and Morphogenesis* (Benjamin, New York, 1975); T. Poston and I. N. Stewart, *Taylor Expansions and Catastrophes* (Pitman, London, 1976).

[9]K. Collard and G. G. Hall, Int. J. Quantum Chem. 12, 623 (1977).

[10]N. D. Mermin, Rev. Mod. Phys. 51, 591 (1979).

[11]V. Poénaru, in *Ill-Condensed Matter* edited by R. Balian *et al.* (North-Holland, Amsterdam, 1979), Course 4.

[12]P. Lazzeretti and R. Zanasi, Chem. Phys. Lett. 80, 533 (1981).

[13]M. Kléman, *Points. Lignes. Parois* (Les Éditions de Physique, Orsay, France, 1977).

[14]S. Putterman, Phys. Rep. 4, 67 (1972).

[15]H. Grad, Ann. Acad. Sci. (N.Y.) 357, 223 (1980).

[16]W. H. Matthaeus and D. Montgomery, Ann. Acad. Sci. (N.Y.) 357, 203, (1980).

[17]Two very recent comprehensive reviews of the subject are R. F. W. Bader, T. T. Nguyen-Dang, and Y. Tal, Rep. Prog. Phys. 44, 893 (1981); and R. F. W. Bader and T. T. Nguyen-Dang, Adv. Quantum Chem. 14, 63 (1981).

[18]P. G. Mezey, in *Computational Theoretical Chemistry,* edited by I. G. Csizmadia and R. Daudel (D. Reidel, Dordrecht, Holland, 1981); Theor. Chim. Acta 54, 95 (1980); 58, 309 (1981); 60, 97 (1981); Int. J. Quantum Chem. Biol. Symp. 8, 185 (1981); Int. J. Quantum Chem. Symp. 15, 279 (1981); Theor. Chim. Acta 60, 409 (1982).

[19]S. R. Gadre and R. K. Pathak, Phys. Rev. A 24, 2906 (1981); J. Riess and W. Münch, Theor. Chim. Acta 58, 295 (1981); L. J. Bartolotti, Phys. Rev. A 24, 1661 (1981).

[20]P. Hohenberg and W. Kohn, Phys. Rev. 136, 864 (1964).