Topological elements of the magnetically induced orbital current densities

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A detailed topological analysis is given, both for the standard orbital current density and for the complete orbital current density. The concepts developed here provide a very useful instrument for the description of the vector field of the magnetically induced currents and should be very helpful for the understanding of the contributions that different regions of a molecule give to its magnetic properties. The ingredients for this topological analysis are (1) the symmetry properties of the electronic Hamiltonian in the presence of the magnetic field and (2) the nature of certain singular points. Two categories of singular points are considered: (i) Nodal vortices which have associated a circulation around a nodal line and may be of the axial or toroidal types as previously considered by Hirschfelder; (ii) Stagnation points where the current vanishes without the vanishing of the charge density. There is a considerable variety of stagnation points and, under certain conditions basically on the magnetic field, they may have associated a vortical circulation of currents in their immediate neighborhood. For the complete orbital current (defined as the sum of the standard orbital current and the orbital exchange current), the stagnation points may occur isolated or they may form stagnation lines. When the regime of the circulation around this line changes between vortical and normal, a new type of stagnation point, the transition point, is found.

I. INTRODUCTION

Maps of the probability current density induced in a ground state molecule by an external magnetic field have been used in the past to describe the way in which the electronic charge reacts to the external field. Some time ago, Lipscomb and co-workers[1] reported *ab initio* results for diatomics and, very recently, Lazzeretti and Zanasi[2-4] started reporting the results for larger molecules which are obtained with a newly developed set of *ab initio* programs. The maps obtained are rather complex and some sort of topological analysis is needed for the understanding of the three-dimensional vector field from its two-dimensional projection maps, and this will also be helpful for the extraction of quantitative information out of them. Riess[5] analyzed the nodal structure of the N-particle state function to discuss the probability current density. Hirschfelder[6] discussed what he called the axial and toroidal vortices formed by the current. The axial vortices have angular momentum and will thus interact with external homogeneous fields. In the absence of external magnetic fields, this angular momentum is quantized, provided the state function is an eigenfunction of $\hat{L}_z$. The current density was also found to vanish at points where the charge probability density is nonzero but these stagnation points (as they were called[6(a)]) attracted less attention. Bader and coworkers[7] made a topological analysis of the molecular charge distribution by looking at the orthogonal trajectories (Collard and Hall[8]), especially at the singular points of the charge density (points where ρ and $\nabla\rho$ vanish).

The purpose of this paper is to discuss the topological elements which may appear in the vector field of the orbital current densities induced in a molecule by an external, constant, homogeneous magnetic field. This is done by (i) looking at the symmetry of the electronic Hamiltonian for the molecule under an external magnetic field and (ii) considering the behavior of the current density (vector) field at the neighborhood of certain singular points. These are the points where the current density associated with each contributing natural orbital vanishes and are called nodal vortex points (V) or stagnation points (S), depending on whether the charge probability density is zero at their location or not. A complete classification of the types of singular points is presented. One rather inconvenient feature of the orbital currents usually defined is their nonconservation which makes the interpretation of the maps still harder and sometimes misleading. To avoid this problem, the orbital currents analyzed here are the complete orbital current densities which include the exchange currents.[9,10]

In Sec. II below, the general formalism of the magnetically induced current density is reviewed. A Cartesian second rank tensor is defined by the spacial differentiation of the (standard or complete) orbital current density. This tensor is instrumental to the topological analysis made in subsequent sections. In Sec. III, the technique of topological analysis is applied to the standard orbital current density. The regime of flow near the stagnation points is found to depend on the magnitude of the applied field. The analysis of the complete current density in Sec. IV starts with a discussion of the symmetry of the exchange currents and their behavior near points of high symmetry. Critical points of two categories are found to exist in general; nodal vortices and stagnation points, and these may occur isolated or may form lines. Finally, in Sec. V, the major topological properties of the orbital currents are summarized and the particular case of homonuclear diatomics is discussed in some detail as an example of the application of the theory developed earlier.

II. GENERAL FORMALISM

Consider a N-electron molecule under the effect of an external homogeneous, constant magnetic field. Within the Born–Oppenheimer approximation, the many electron state function (spin is disregarded throughout)

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

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is driven by an electrostatic Hamiltonian of the form

$$H=\frac{1}{2m_e}\sum_{\mu=1}^{N}\left(\frac{\hbar}{i}\nabla+e\mathbf{A}\right)^2 + \frac{e^2}{8\pi\epsilon_0}\sum_{\mu,\nu}\frac{1}{|\mathbf{r}_\mu-\mathbf{r}_\nu|}-\frac{e^2}{4\pi\epsilon_0}\sum_{\mu,\alpha}\frac{Z_\alpha}{|\mathbf{r}_\mu-\mathbf{r}_\alpha|}\ , \tag{2}$$

where **A** is the vector potential associated with the external field and $(Z_\alpha e)$ is the charge of nucleus α. If an orbital approximation is used for state function (1), it is well known that the charge probability current density may be written in terms of orbital components. For an orbital $\Psi_k(\mathbf{r})$, the standard current density[9,10] is

$$\mathbf{j}_k(\mathbf{r})=-\frac{e}{m_e}\,\mathrm{Re}\left[\Psi_k^*\left(\frac{\hbar}{i}\nabla+e\mathbf{A}\right)\Psi_k\right]. \tag{3}$$

When the Ψ_k are natural orbitals,[11] the total many electron current is given by

$$\mathbf{j}(\mathbf{r})=\sum_k n_k\mathbf{j}_k(\mathbf{r})\ , \tag{4}$$

where n_k is the occupation number of orbital Ψ_k; the corresponding expression for the charge probability density is

$$\rho(\mathbf{r})=\sum_k n_k\rho_k(\mathbf{r})\ , \tag{5}$$

with

$$\rho_k(\mathbf{r})=-e\Psi_k^*\Psi_k\ . \tag{6}$$

While the many electron current **j** satisfies the continuity equation and is therefore divergenceless,

$$\nabla\cdot\mathbf{j}=0\ , \tag{7}$$

the same is not true in general for the orbital components defined in the standard form [Eq. (3)]. A source function $S_k(\mathbf{r})$ may then be defined,

$$S_k=\nabla\cdot\mathbf{j}_k\ . \tag{8}$$

To compensate this lack of conservation, Atkins and Gomes[9] introduced an orbital exchange current $\mathbf{j}_k^{\mathrm{exch}}$ such that

$$\nabla\cdot\mathbf{j}_k^{\mathrm{exch}}=-S_k\ . \tag{9}$$

The complete orbital current $\mathbf{j}_k^c$,

$$\mathbf{j}_k^c=\mathbf{j}_k+\mathbf{j}_k^{\mathrm{exch}} \tag{10}$$

is divergenceless. The source function may be calculated[10] in terms of the nonlocal potential $\hat{N}$ in the Hamiltonian associated with orbital Ψ_k,

$$S_k=-\frac{2e}{\hbar}\,\mathrm{Im}(\Psi_k^*\hat{N}\Psi_k)\ , \tag{11}$$

and a scalar potential V_k may be obtained from this source function (by analogy with electrostatics)

$$V_k(\mathbf{r})=\frac{1}{4\pi}\int d^3r'\,\frac{S_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ . \tag{12}$$

Introducing

$$\mathbf{j}_k^{\mathrm{exch}}=\nabla V_k\ , \tag{13}$$

the defining equation [Eq. (9)] is automatically satisfied because of the well-known relation $\nabla^2(1/r)=-4\pi\delta(r)$. It has been shown[10] that this exchange current does not contribute to important classes of orbital properties, but it may induce electromagnetic transitions.[12]

A. Singularities of the current density

The topological analysis below depends on the behavior of the current field near the points where it vanishes, the singularities of the vector field. This is achieved by considering the Taylor series expansion

$$\mathbf{j}_k^c(\mathbf{r})=(\mathbf{r}-\mathbf{r}_0)\cdot(\nabla\mathbf{j}_k^c)_{\mathbf{r}_0}+\tfrac{1}{2}(\mathbf{r}-\mathbf{r}_0)(\mathbf{r}-\mathbf{r}_0):(\nabla\nabla\mathbf{j}_k^c)_{\mathbf{r}_0}+\cdots\ . \tag{14}$$

Of particular importance is the first term which depends on the second rank Cartesian tensor $(\nabla\mathbf{j}_k^c)$ which may be separated into its components of weights zero, one, and two,[13]

$$(\nabla\mathbf{j}_k^c)_{\mathbf{r}_0}\equiv\mathbf{D}=\mathbf{D}^{(0)}+\mathbf{D}^{(1)}+\mathbf{D}^{(2)}\ . \tag{15}$$

The zero-weight part $\mathbf{D}^{(0)}$ contains the trace

$$\mathbf{D}^{(0)}=(\nabla\cdot\mathbf{j}_k^c)_{\mathbf{r}_0}\mathbf{I}\ , \tag{16}$$

where **I** denotes the unit second-rank tensor. $\mathbf{D}^{(1)}$ is the antisymmetric part and is related to the curl of the current $\mathbf{j}_k^c$,

$$\mathbf{D}^{(1)}=\frac{1}{2}\begin{bmatrix}0 & c_3 & -c_2\\ -c_3 & 0 & c_1\\ c_2 & -c_1 & 0\end{bmatrix}\ , \tag{17}$$

with

$$(c_1,c_2,c_3)=\mathbf{c}=(\nabla\times\mathbf{j}_k^c)_{\mathbf{r}_0}\ . \tag{18}$$

The irreducible weight-two part $\mathbf{D}^{(2)}$ is the symmetric traceless part of the Cartesian tensor, which may be written

$$\mathbf{D}^{(2)}=\tfrac{1}{2}(\mathbf{D}+\mathbf{D}^t)-\mathbf{D}^{(0)}\ , \tag{19}$$

where $\mathbf{D}^t$ denotes the transposed of **D**.

Expressions for the divergence and the curl of orbital current are obtained now for later use. The orbital Ψ_k is, in general, a complex function which may be separated into its real and imaginary parts $\Psi_k=\Psi_k^r+i\Psi_k^i$. The standard current [Eq. (3)] takes the form

$$\mathbf{j}_k=-\frac{e\hbar}{m_e}(\Psi_k^r\nabla\Psi_k^i-\Psi_k^i\nabla\Psi_k^r)-\frac{e^2}{m_e}\mathbf{A}[(\Psi_k^r)^2+(\Psi_k^i)^2]\ . \tag{20}$$

The divergence and curl are calculated directly

$$\nabla\cdot\mathbf{j}_k=-\frac{e\hbar}{m_e}(\Psi_k^r\nabla^2\Psi_k^i-\Psi_k^i\nabla^2\Psi_k^r)-\frac{e^2}{m_e}\mathbf{A}\cdot\nabla[(\Psi_k^r)^2+(\Psi_k^i)^2]\ , \tag{21}$$

$$\nabla\times\mathbf{j}_k=-2\frac{e\hbar}{m_e}\nabla\Psi_k^r\times\nabla\Psi_k^i+\frac{e^2}{m_e}\mathbf{A}\times\nabla[(\Psi_k^r)^2+(\Psi_k^i)^2] -\frac{e^2}{m_e}\mathbf{B}[(\Psi_k^r)^2+(\Psi_k^i)^2]\ . \tag{22}$$

Alternatively, the orbital function may be written in polar form

$$\Psi_k=\sqrt{\rho_k/(-e)}\,\exp\left(\frac{i}{\hbar}\phi_k\right)\ , \tag{23}$$

where ρ_k is the charge probability density [Eq. (6)] and ϕ_k a phase function well defined outside the nodes of ρ_k.

The standard current density [Eq. (3)] takes the form

$$\mathbf{j}_k = \frac{1}{m_e}\rho_k(\nabla\phi_k + e\,\mathbf{A}) \,. \tag{24}$$

and its divergence and curl are

$$\nabla\cdot\mathbf{j}_k = \frac{1}{m_e}\,\rho_k\nabla^2\phi_k + \frac{1}{m_e}\nabla\rho_k\cdot(\nabla\phi_k + e\mathbf{A}) \,, \tag{25}$$

$$\nabla\times\mathbf{j}_k = \frac{e}{m_e}\,\rho_k\mathbf{B} + \frac{1}{m_e}\,\nabla\rho_k\times(\nabla\phi_k + e\,\mathbf{A}) \,. \tag{26}$$

For the exchange part, the definition [Eq. (13)] implies that it is irrotational and its divergence is simply given by Eq. (9).

III. TOPOLOGY OF THE STANDARD CURRENT

Some basic topological features of the standard orbital current density $\mathbf{j}_k$ were considered by Hirschfelder and co-workers,[6] [especially in Ref. 6(f)]. However, the specific consequence of its nonconservation [Eq. (8)] on the nature of the vortices and on the different types of stagnation points were not discussed. One consequence of this nonconservation is that lines of currents cannot be drawn, as these lines are not closed and the sources S_k extend continuously over space. Of course, plots may be prepared showing the direction of the current density at each point, but these must be interpreted with care and should not be confused with plots of lines of currents.

A. The nodal vortices

One category of singular points for the topological analysis of the standard current $\mathbf{j}_k$ are the nodes of the charge density ρ_k, where the standard current does necessarily vanish [Eq. (20)]. The vanishing of the charge density implies two conditions, one on the real part and the other on the imaginary part of the orbital functions Ψ_k. This results in nodal regions that are normally lines which may be closed upon themselves or may extend to the limits of configuration space. The current whirlpools associated with these nodal lines are toroidal vortices, in the first case, and axial vortices, in the second.

A velocity field $\mathbf{v}_k$ may be defined outside the nodes of ρ_k,

$$\mathbf{v}_k = \frac{1}{\rho_k}\,\mathbf{j}_k \,. \tag{27}$$

The circulation of this velocity around a circuit may be calculated using Eq. (24)

$$\oint d\mathbf{r}\cdot\mathbf{v}_k = n2\pi\frac{\hbar}{m_e} + \frac{e}{m_e}\Phi_B, \quad n=0,\ \pm1,\ \pm2,\ \ldots, \tag{28}$$

where Φ_B is the flux of the magnetic field across the circuit and n is zero if the circuit does not surround a nodal line.

The behavior of $\mathbf{j}_k$ near the nodal line may be studied using the **D** tensor [Eq. (15)]; in particular, the integer n in Eq. (28) is related to it in the important case of symmetry determined nodes. The **D** tensor at a nodal point may be calculated using Eq. (20) for the current. It is antisymmetric and completely described by the vector $\mathbf{c}$ [Eq. (18)],

$$\mathbf{c} = -2\,\frac{e\hbar}{m_e}\,(\nabla\Psi_k^r\times\nabla\Psi_k^i)_V \,, \tag{29}$$

which is directed along the nodal line at the vortex node (V) considered. To first order in the displacement from the node, the current [Eq. (14)] is of the form

$$\mathbf{j}_k(R) = -\frac{e\hbar}{m_e}\,\left|(\nabla\Psi_k^r\times\nabla\Psi_k^i)_V\right| R\hat{u}_\theta \,, \tag{30}$$

where R is the cylindrical radius and $\hat{u}_R$, $\hat{u}_\theta$ are the radial and angular (cylindrical) unit vectors. The charge density at a distance R from the nodal line is given (to first order) by

$$\rho_k(R) = R^2\{[\hat{u}_R\cdot(\nabla\Psi^r)_V]^2 + [\hat{u}_R\cdot(\nabla\Psi^i)_V]^2\} \,. \tag{31}$$

The simplest case is that of D_{2h} local symmetry, when the real and imaginary nodal surfaces intersect at right angles and $|\nabla\Psi_k^r| = |\nabla\Psi_k^i|$. Direct calculation of the circulation integral [Eq. (28)] leads to the zero-order (in R) term $2\pi\hbar/m_e$, showing that $n=+1$. (The sign depends on the choice of the sense of circulation.) The argument may be generalized to higher order symmetries D_{nh} by considering that symmetry functions behave near the node like $R^n\exp(in\theta)$, with which is associated a circulation number n (see Sec. IV).

B. The stagnation points

The current density may vanish at points other than the nodes of the charge density. Equation (24) implies that the following condition is satisfied at these stagnation points (S):

$$\nabla\phi_k + e\,\mathbf{A} = 0 \,. \tag{32}$$

The **D** tensor has in general components of weights zero, one, and two

$$\mathbf{D}^{(0)} = \frac{1}{m_e}\,\rho_k(\nabla^2\phi_k)_S\,\mathbf{I} \,, \tag{33}$$

$$\mathbf{D}^{(1)}:\mathbf{c} = \frac{e}{m_e}\,\rho_k\mathbf{B} \,, \tag{34}$$

$$\mathbf{D}^{(2)} = \frac{1}{m_e}\,\rho_k[(\nabla\nabla\phi_k)_S - (\nabla^2\phi_k)_S\mathbf{I}] \,. \tag{35}$$

The general analysis of this **D** tensor for the behavior of the currents near the S point is difficult. If there were no magnetic field present, the problem would be reduced to that of a potential ϕ_k that is conveniently studied by the method of the orthogonal trajectories. Assume that $\alpha_1 > \alpha_2 > \alpha_3$ are the real eigenvalues of the Hessian matrix $(\mathbf{D}^{(0)} + \mathbf{D}^{(2)})$. The stagnation point is classified by a pair of numbers (rank, signature), the rank being the number of nonzero eigenvalues and the signature the excess of positive over negative eigenvalues. The trace of **D** gives the value of the source function

$$S_k = \alpha_1 + \alpha_2 + \alpha_3 \,. \tag{36}$$

A similar analysis was applied by Bader *et al.*[7(b)] to the charge density using the Hessian $\nabla\nabla\rho_k$.

I shall consider now the effect of the antisymmetric part $\mathbf{D}^{(1)}$. If it occurred alone, it would produce a cylindrical circulation around the stagnation point with the axis along $\mathbf{c}$. This current is of the form $[(e/m)\rho_k\mathbf{A}]$,

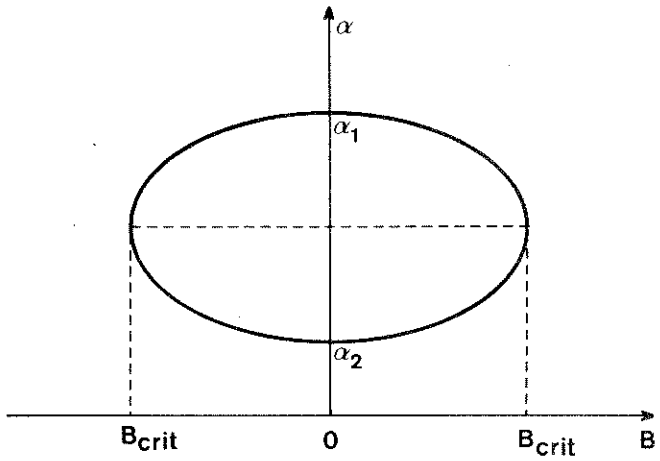

FIG. 1. Effect of a perpendicular magnetic field on the eigenvalues of the **D** tensor. These are real for small fields $|e\rho_k B/m_e| \leq (\alpha_1 - \alpha_2)$.

with the origin of the vector potential at the stagnation point. The general analysis is not very illuminating. The detailed study of a very particular case will do better to clarify the joint effects of the symmetric and antisymmetric parts. Assume that the **D** tensor is expressed in the local frame that diagonalizes the symmetric part and that, in this reference frame, the vector **c** has just one component c_3

$$\mathbf{D} = \begin{bmatrix} \alpha_1 & c/2 & 0 \\ -c/2 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{bmatrix} . \tag{37}$$

(These conditions are fulfilled, at least at points on an axis of symmetry of the molecule, if that axis is paralle to the external magnetic field.) The eigenvalues of the matrix [Eq. (37)] are α_3 and

$$\tfrac{1}{2}(\alpha_1 + \alpha_2 \pm \sqrt{(\alpha_1 - \alpha_2)^2 - c^2}) .$$

Let us consider the plane defined by the eigenvectors associated with eigenvalues α_1 and α_2 of the Hessian matrix ($\mathbf{D}^{(0)}$ and $\mathbf{D}^{(2)}$). The dependence on the field is represented in Fig. 1. The eigenvalues remain real when the following condition is satisfied:

$$\frac{e}{m_e}\rho_k|\mathbf{B}| \leq (\alpha_1 - \alpha_2) . \tag{38}$$

The magnetic field is a control parameter and the equality sign in Eq. (38) corresponds to a fold catastrophe.[14] For higher magnetic fields, Eqs. (38) is not satisfied and the eigenvalues become complex. This corresponds to a change of regime of circulation of currents near the stagnation point. This effect of the external field is visualized in Figs. 2 and 3, where the cases $\alpha_1 > \alpha_2 > 0$ (Fig. 2) and $\alpha_1 > 0 > \alpha_2$, $(\alpha_1 + \alpha_2) > 0$ (Fig. 3) are considered. It should be stressed that the quantity $[(e/m_e)\rho_k|\mathbf{B}|]$ in Eq. (38) is the curl of the current density $\mathbf{j}_k$ at the stagnation point [Eq. (26)]. The arrowed lines in Figs. 2 and 3 cannot be interpreted as lines of current; all they give is the direction of the vector $\mathbf{j}_k$ at each point in the neighborhood of the stagnation point. One important feature to notice is the resemblance of the high field (vortical) regime to the pattern of currents in a plane perpendicular to a nodal line; and, of course, in a degenerate or near degenerate case ($\alpha_1 \approx \alpha_2$) this is the only regime observed for any size of the external magnetic field. This similarity might lead to incorrect assignments in maps of magnetic currents.

IV. TOPOLOGY OF THE COMPLETE ORBITAL CURRENT

The complete orbital current is a divergenceless vector field formed by the addition of the exchange current to the standard orbital current [Eq. (10)]. With the exchange part defined by Eq. (13), while most orbital properties are not changed[10] the topology of the complete orbital current may be markedly different from that of the standard one. In this section, I shall consider first the properties of the exchange current and then analyze the topology of the complete current.

A. The source function

The source function S_k is given by Eq. (11), where the nonlocal potential $\hat{N}$ is a consequence of two body interactions. S_k is therefore a homogeneous quadratic form in the orbitals Ψ_i and also in their complex conjugates Ψ_i^*. If the orbitals are assumed to be symmetry adapted functions of the molecular point group (field not considered), the source function S_k transforms like the rotation R_z (z along the external magnetic field). A more rigorous symmetry treatment which requires the consideration of time inversion and space-time point groups is given elsewhere.[15] The potential V_k [Eq. (12)] is gener-

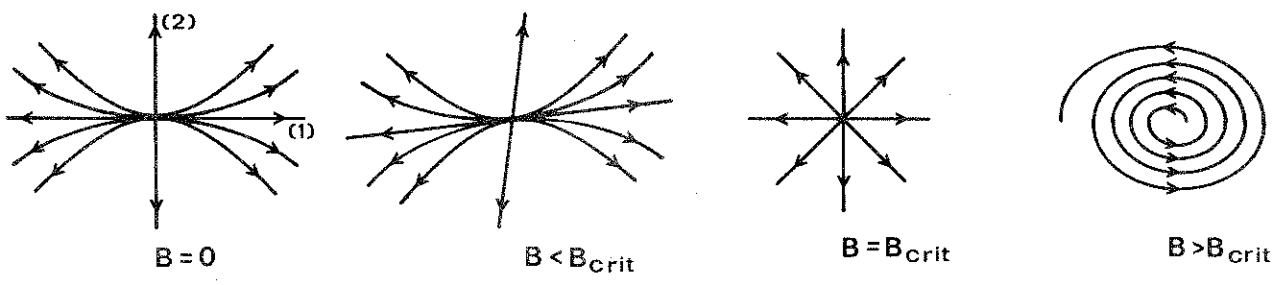

FIG. 2. Effect of an increasing magnetic field on the standard orbital current ciculating near a stagnation point ($\alpha_1 > \alpha_2 > 0$). At the critical value $B_{crit} = (\alpha_1 - \alpha_2)m_e/e\rho_k$ there is a change from the normal to the vortical regime.

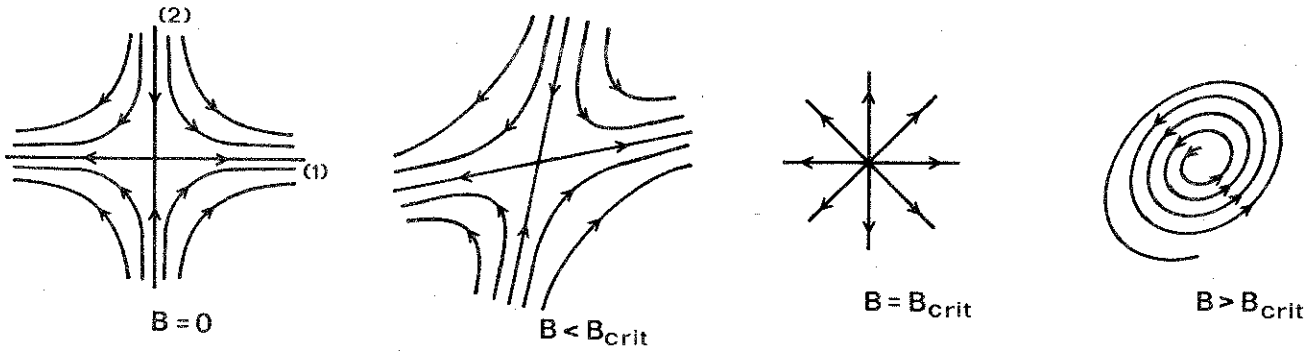

FIG. 3. Effect of an increasing magnetic field on the standard orbital current circulating near a stagnation point ($\alpha_1 > 0 > \alpha_2$, $\alpha_1 + \alpha_2 > 0$). At the critical value $B_{crit} = (\alpha_1 - \alpha_2) m_e / e\rho_k$ there is a change from normal to vortical regime.

ally a smooth function extending all over the molecule and its gradient gives the exchange current according to Eq. (13). The symmetry of $\mathbf{j}_k^{exch}$ may be directly obtained from that of S_k. The **D** tensor associated with $\mathbf{j}_k^{exch}$ at any point of space is symmetric and its trace is $(-S_k)$. It is useful to study its symmetry determined stagnation points as they may coincide with those of $\mathbf{j}_k$, thus being also stagnation points of the complete current. Particularly interesting are points along the principal axis of a D_{nh} point group molecule, but the theory below will apply equally to any situation where that is just the local symmetry.

Let the scalar potential V_k [Eq. (12)] be expanded in spherical tensors around the stagnation point

$$V_k(\mathbf{r}_0 + \mathbf{r}) = \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} D_{plm}\, r^{l+p}\, Y_l^m , \tag{39}$$

where $\mathbf{r}_0$ is the position of the stagnation point considered, r is the spherical radius, and Y_l^m is a spherical harmonic (a function of the angular coordinates). The D_{nh} symmetry imposes certain constraints:

If n even: l even; $m = \pm n,\ \pm 2n,\ \pm 3n,\ \ldots$,

If n odd: either l even; $m = \pm 2n;\ \pm 4n,\ \ldots$,

or l odd; $m = \pm n,\ \pm 3n,\ \ldots$. (40)

In the plane perpendicular to the C_n axis (the xy plane), the spherical tensors $r^l Y_l^m$ reduce to the polynomials listed in Table I; for each value of n, the leading (lowest $l + p$) expansion polynomial is shown. Also listed in Table I are the gradients of the potential terms $d^{(n)}(x,y)$—the exchange current contributions—and the directions of their orthogonal trajectories. These results may be summarized by saying that a D_{nh} stagnation point of the exchange currents may be analyzed by the method of the orthogonal trajectories with a nth degree potential, leading to the determination of $2n$ orthogonal trajectories; of these, n converge to the center and alternate with those which diverge. The trace of $\nabla \mathbf{j}^{exch}$ vanishes in any of these cases.

B. The complete orbital current

The complete orbital current density is considered now. The associated **D** tensor given by Eq. (15) is traceless by Eqs. (8)–(10) and therefore, maps of the lines of current may be drawn to describe the direction and intensity of the current field. The antisymmetric part $\mathbf{D}^{(1)}$ is defined by vector **c** [Eq. (18)], which is of the form [Eq. (26)]

$$\mathbf{c} = \frac{e}{m_e}\rho_k \mathbf{B} + \frac{1}{\rho_k}\nabla\rho_k \times \mathbf{j}_k .$$

The symmetric part has the general form

$$\mathbf{D}^{(2)} = \frac{1}{2m_e}[\nabla\rho_k(\nabla\phi_k + e\mathbf{A}) + (\nabla\phi_k + e\mathbf{A})\nabla\rho_k] + \frac{1}{m_e}\rho_k \nabla\nabla\phi_k + \nabla\nabla V_k$$

The complete current density $\mathbf{j}_k^c$ may vanish at two cate-

TABLE I. Leading expansion polynomials [for Eq. (39)] and the corresponding expansion functions for the exchange current density for points at the principal axis of a system of D_{nh} symmetry. (r the spherical radius and θ the longitudinal angle).

n	$d^{(n)}(r,\theta)$	$d^{(n)}(x,y)$	$\nabla d^{(n)}(x,y) = \frac{\partial}{\partial x} d^{(n)}(x,y);\ \frac{\partial}{\partial y} d^{(n)}(x,y)$	Orthogonal trajectories (angle θ in degrees)
2	$r^2 \sin 2\theta$	$2xy$	$2y;\ 2x$	45; 135
3	$r^3 \sin 3\theta$	$3x^2y - y^3$	$6xy;\ 3(x^2 - y^2)$	0; 60; 120; 180
4	$r^4 \sin 4\theta$	$4x^3y - 4xy^3$	$4(3x^2y - y^3);\ 4(x^3 - 3xy^2)$	22.5; 67.5; 112.5; 157.5
5	$r^4 \sin 5\theta$	$5x^4y - 10x^2y^3 + y^5$	$20(x^3y - xy^3);\ 5(x^4 - 6x^2y^2 + y^4)$	18; 54; 90; 126; 162
6	$r^6 \sin 6\theta$	$6x^5y - 20x^3y^3 + 6xy^5$	$6(5x^4y - 10x^2y^3 + y^5);\ 6(x^5 - 10x^3y^2 + 5xy^4)$	15; 45; 75; 105; 135; 165

gories of singular points: (a) nodal vortices (V), where $\mathbf{j}_k^c = 0$ and $\rho_k = 0$; (b) stagnation points (S), where $\mathbf{j}_k^c = 0$ but $\rho_k \neq 0$. Nodal vortices of the complete current are far less common than those of the standard current $\mathbf{j}_k$. In fact, most of the nodal vortices (the toroidal and some axial) are displaced from their location (for the standard current) by the additive exchange current. This mechanism originates stagnation points of rank two, unexpected for the components $\mathbf{j}_k$ or $\mathbf{j}_k^{\text{exch}}$; these points may constitute infinite lines or closed loops. A nodal vortex of the complete current may still exist when the exchange current vanishes at the nodal line. This occurs when the magnetic field is parallel to an axis of symmetry of the molecule, which is a node of ρ_k. This nodal vortex has the same properties as discussed in Sec. III for the standard current; in particular, its circulation number n in Eq. (28) is the degree of rotational symmetry of the orbital. An argument similar to that leading to Table I above, suggests that an orbital with a C_n axis of (maximum) symmetry behaves near the axis like $r^n \exp(\pm\, n\theta)$; direct calculation of Eq. (28) with this function leads to a value $\pm n$ for the circulation number.

Stagnation points may be classified according to rank and signature (as in Sec. III). The traceless condition restricts the possible types to $(3, \pm 1)$, $(2, 0)$, and $(0, 0)$. If $\alpha_1 \geq \alpha_2 \geq \alpha_3$, $\alpha_1 + \alpha_2 + \alpha_3 = 0$, are the three real eigenvalues of $\mathbf{D}^{(2)}$, the matrix $\mathbf{D}$ may be written in the local frame of reference defined by the eigenvectors in the form

$$\mathbf{D} = \begin{bmatrix} \alpha_1 & c_3 & -c_2 \\ -c_3 & \alpha_2 & c_1 \\ c_2 & -c_1 & \alpha_3 \end{bmatrix} . \tag{41}$$

This nonsymmetric matrix has real eigenvalues when

$$(\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1 + |\mathbf{c}|^2)^3 + \tfrac{27}{4}(\alpha_1\alpha_2\alpha_3 + \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_2 c_3^2)^2 \leq 0 . \tag{42}$$

When the equal sign holds in Eq. (42), there is at least two degenerate eigenvalues. If Eq. (42) is not satisfied, two of the eigenvalues are complex and a vortical regime sets in.

Assuming the exchange current $\mathbf{j}_k^{\text{exch}}$ to be a small and smooth function in the region where $\mathbf{j}_k$ has a nodal vortex, its effect upon addition to form $\mathbf{j}_k^c$ is likely to be that of displacing the nodal vortex, converting it into a stagnation line. This displacement $\mathbf{r}$ is given approximately by the solution of the equation

$$\mathbf{j}_k^{\text{exch}} + \mathbf{c} \times \mathbf{r} \approx 0 , \tag{43}$$

the distance from the nodal line being of the order $|\mathbf{j}_k^{\text{exch}}|/|\mathbf{c}|$. For stagnation points on the displaced nodal line, one of the eigenvalues is zero and the other two may be either (i) real symmetric or (ii) pure imaginary conjugate. The conditions to be satisfied by $\mathbf{D}$ [Eq. (41)] in each of these cases are as follows:

(i) Normal regime. (Eigenvalues: $0, \pm\lambda$)

$$\begin{cases} \alpha_1\alpha_2\alpha_3 + \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_3 c_3^2 = 0 , \\ \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1 + |\mathbf{c}|^2 = -\lambda^2 < 0 . \end{cases} \tag{44}$$

(ii) Vortical regime. (Eigenvalues: $0, \pm i\lambda$)

$$\begin{cases} \alpha_1\alpha_2\alpha_3 + \alpha_1 c_1^2 + \alpha_2 c_2^2 + \alpha_3 c_3^2 = 0 , \\ \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1 + |\mathbf{c}|^2 = \lambda^2 > 0 . \end{cases} \tag{45}$$

These are effectively type $(2, 0)$ stagnation points and the change over from regime (i) — (ii) is made through a type $(0, 0)$ point. The stagnation lines may be open and infinite or closed, forming a loop. In any case, they are made of stagnation points of type $(2, 0)$, possibly with a discrete number of points of type $(0, 0)$, where a change of regime may occur. Stagnation points may also occur isolated, and these are of types $(3, \pm 1)$ with a normal or a vortical regime, depending on whether Eq. (42) is satisfied or not.

V. CONCLUSIONS

The main goal of this paper is to give the basis for a topological analysis of the complete orbital current, and this will be of primary importance to gain some understanding of the molecular properties from the maps of the current density. The complete orbital current is preferred to the standard orbital currents [Eq. (3)] due to the difficulties arising from the nonconservation of this vector field. This is achieved through the consideration of the exchange current [Eq. (13)] which is a simple longitudinal vector field related to the source function [Eq. (9)]. The topology of the complete orbital current depends on certain singular points where it vanishes. These are of two kinds, depending on whether (a) the charge density also vanishes—nodal vortices—or (b) not—stagnation points. The nodal vortices are associated with the nodal lines of the orbital state function and these may be infinite (axial vortices) or may form closed loops (toroidal vortices). These nodal vortices have a nonzero circulation number [Eq. (28)] and the properties discussed by Hirschfelder.[6(d)] Nodal vortices of the complete current are less frequent than those of the standard current due to the contribution of the exchange current. Some of the nodal lines, however, are symmetry determined in such a way that the exchange current also vanishes at their location. Other nodal vortices of the standard current are moved away from the nodal line by the exchange part of the current originating stagnation lines. The general theory of stagnation points given in Sec. IV shows that they may be classified according to (rank, signature) into three major types:

(i) Isolated stagnation points $(3, \pm 1)$. The regime of flow near these points depends on whether condition (42) is satisfied or not. If it is with the less than sign, the regime is normal with three well-defined eigendirections. If Eq. (42) is not satisfied, there is a vortical regime of flow in the neighborhood of the critical point.

(ii) Stagnation lines $(2, 0)$. These may be open extending to the limits of configuration space or closed forming loops. They are expected to result from the displacement of the nodal vortices of the standard current. The regime near the line depends on which of the conditions, (44) or (45), is satisfied. The transition between the normal and the vortical regimes is made at points (iii).

(iii) Transition points $(0, 0)$. These are the points of the stagnation lines where a transition of regime occurs.

TABLE II. Molecular orbitals of a homopolar diatomic molecule in presence of a magnetic field (to first order) perpendicular to the interatomic axis. In the last column is indicated the type of critical point at the center of the molecule.

Real part		Imaginary part		Type of critical point at the origin
MO ($D_{\infty h}$)	Symmetry (D_{2h})	Symmetry (D_{2h})	MO($D_{\infty h}$)	
σ_g	A_g	B_{1g}	$\pi_g(x)$	S
σ_u	B_{2u}	B_{3u}	$\pi_u(x)$	V
$\pi_u(z)$	B_{1u}	A_u	...	...
$\pi_u(x)$	B_{3u}	B_{2u}	σ_u	V
$\pi_g(z)$	B_{3g}	B_{2g}	...	...
$\pi_g(x)$	B_{1g}	A_g	σ_g	S

A. Example: Homopolar diatomics

As an example of application, I shall consider the case of homopolar diatomic molecules with the magnetic field (z axis) perpendicular to the internuclear (y) axis.

The molecular states are classified in relation to the $D_{\infty h}$ molecular point group. The magnetic field reduces the symmetry to D_{2h}[16] (in fact, a space-time point group[15] isomorphic to D_{2h}). In Table II are listed the symmetries of the molecular orbitals in the conventional notation followed by their symmetry in relation to the group D_{2h} and the states which are mixed in by the magnetic field to first order. These are, in fact, the symmetries of the imaginary parts of each molecular orbital. Consider the cases of molecules N_2 and F_2, with electronic configurations[17]

$N_2 : KK\, 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4$ (lowest unoccupied MOs : $1\pi_g$; $3\sigma_u$),

$F_2 : KK\, 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4$ (lowest unoccupied MO : $3\sigma_u$) .

Major contributors to the first-order current density may be expected to involve the transitions $3\sigma_g - 1\pi_g(x)$ and $1\pi_u(x) - 3\sigma_u$ in N_2 and just the second one in F_2. This allows the prediction that there may be an axial vortex in fluorine while, in nitrogen, the superposition of an axial vortex, with a stagnation point at the origin is expected. Lipscomb *et al.*[1(c),(d)] reported results for the (standard) current density in these systems which fit well with these predictions. In nitrogen,[1(c)], the center of the molecule resembles a stagnation point of the type shown in Fig. 3 ($B < B_{crit}$). In fluorine,[1(d)] the center resembles closely a vortical circulation in agreement with the prediction above. When the gauge origin is taken at one of the fluorine nuclei, the position of the vortex is displaced[1(d)] but this must be due to errors inherent in all calculations of this type.

If the exchanged parts were computed to form the complete orbital currents, the nature of the critical point at the origin and its axial vortex (when it exists) are not a affected. Elsewhere, the topology of the current field might change noticeably, as discussed in the previous section.

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