Towards an Automated Qualitative and Quantitative Analyses of $\mathbf{J}^{\mathbf{B}}$

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Motivation

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Electron Density Analogy

- physically relevant electronic properties (energy, elektrostatic moments, ...) are uniquely determined and computable from ρ.
- functions of the magnetic response like $\mathcal{W}$, σ or χ are uniquely determined and computable from $\mathbf{J^B}$.

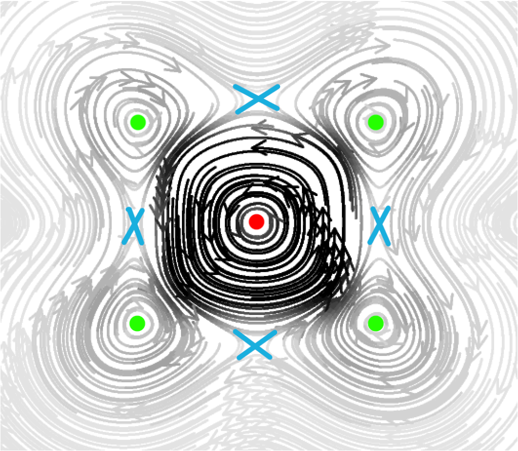
ρ can be characterized by Baders QT-AIM† methods in both a **qualitative** (=topological) and **quantitative** manner.

To date there is no such "theory" or method bundle to analyze $\mathbf{J^B}$ in a similar manner.

†) Bader, R. (1991). "A quantum theory of molecular structure and its applications". Chemical Reviews. 91 (5): 893–928.

State of Knowledge

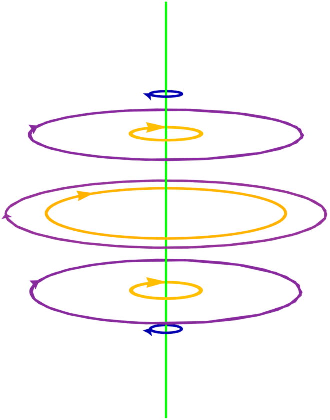
Stagnation Points (2D example)

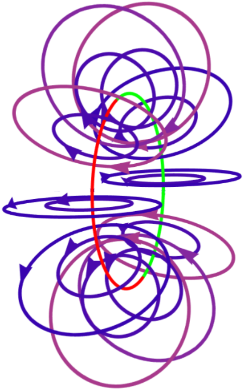


$$SP = \{\mathbf{r}_0 | \mathbf{J}^\mathbf{B}(\mathbf{r}_0) = 0\}$$

- diatropic ringcritical SP
- paratropic ringcritical SP
- × saddle point

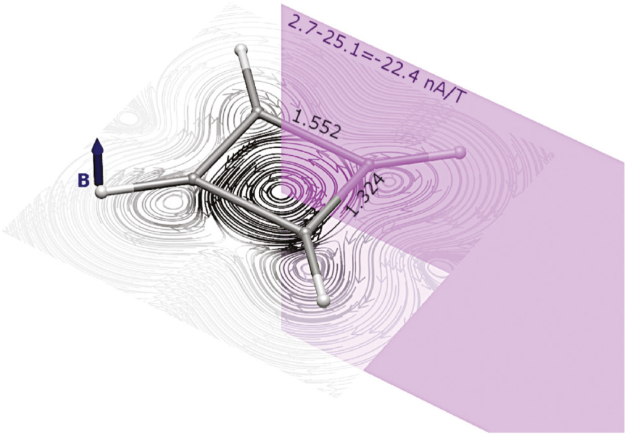
Stagnation Graph (SG)





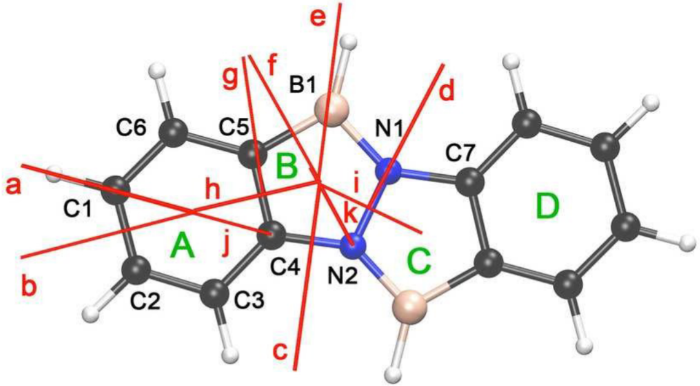
J. A. N. F. Gomes, Phys. Rev. A 28 (1984) 559; S. Pelloni, P. Lazzeretti, R. Zanasi, Theor. Chem. Acc. 123 (2011) 353.

Common Integration Methods

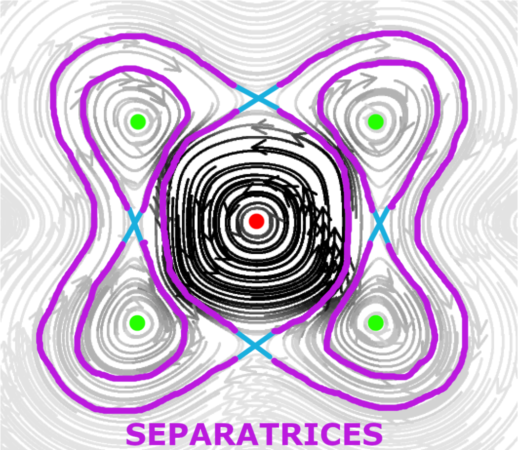


J. Jusélius, D. Sundholm, J. Gauss, J. Chem. Phys. 121, 3952.

Example from the literature

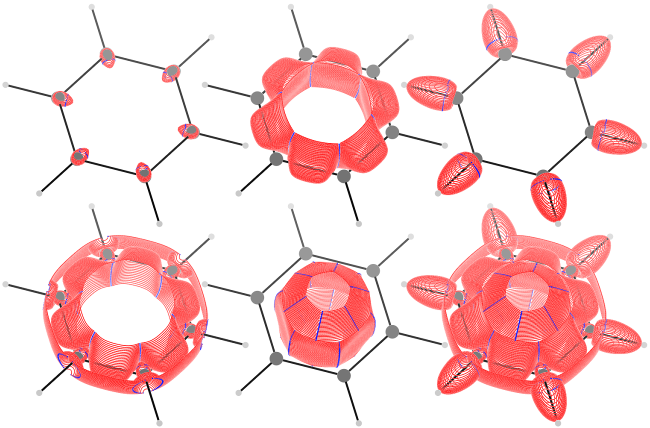


Separatrix Surfaces / Current Density Domains / Vortices



G. Monaco, R. Zanasi, J. Phys. Chem. A 123, 8 (2019) 1558.

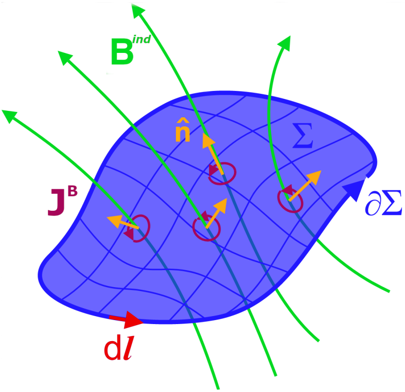
Separatrix Surfaces



G. Monaco, R. Zanasi, J. Phys. Chem. A 123, 8 (2019) 1558.

New Results

'Ampére-Maxwell-Integration' – Theorie



$$\mathbf{B}^{ind} = -\begin{pmatrix} NICS_{xz} \\ NICS_{yz} \\ NICS_{zz} \end{pmatrix}$$

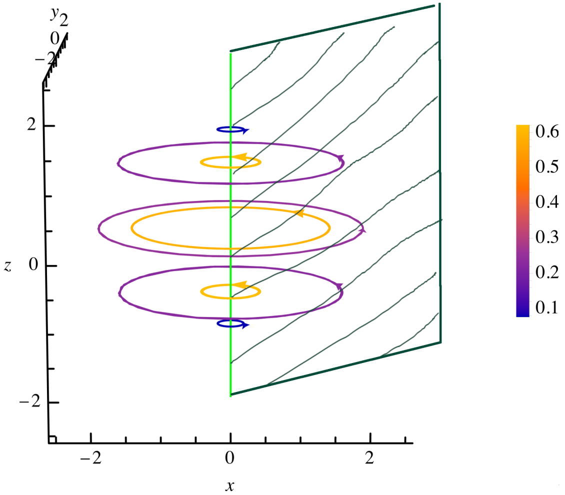
$$\mathbf{J}^{\mathbf{B}} = \mu_0^{-1} \nabla \times \mathbf{B}^{ind} \qquad \text{(D-AM)}$$

Kelvin-Stokes theorem ⇒ "integral Form" of the AM

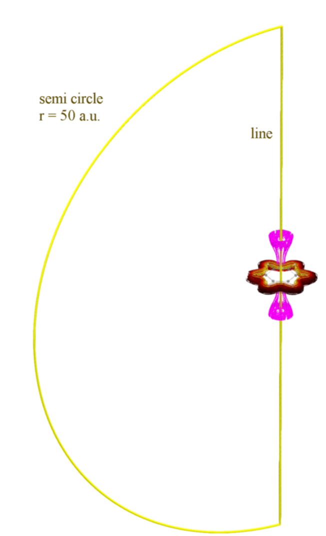
$$\iint_{\Sigma} \mathbf{J}^{\mathbf{B}} \cdot \mathrm{d}\hat{\mathbf{n}} = \mu_0^{-1} \oint_{\partial\Sigma} \mathbf{B}^{ind} \cdot \mathrm{d}\mathbf{l} \quad \text{(I-AM)}$$

Berger, Dimitrova, Nasibullin, Valiev, Sundholm PCCP 24 (2022) 624.

'Ampére-Maxwell-Integration' – Example



'Ampére-Maxwell-Integration' – Application Benzene



height	path integral for path		
	semi circle	line	semicircle ∪ line
50	0.01821	11.20840	11.22661
100	0.00457	11.23570	11.24027
200	0.00107	11.24250	11.24357
400	-0.00000	11.24420	11.24420

Table 2 Numerical convergence of total current integral in benzene depending on the integration path height (given in atomic units) on the z axis. Current flux (susceptibility) values are given in nA/T. The support points of the numerical path integrals for height of 50 a.u. is shown in

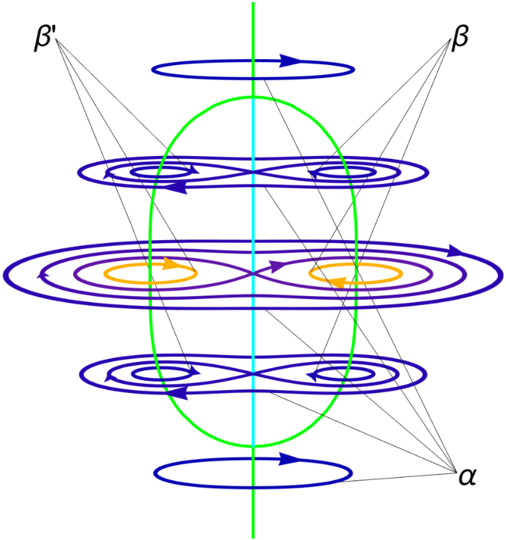
$$\Phi \approx \mu_0^{-1} \sum_{k=-n}^{n} \mathrm{NICS}_{zz}(k)$$

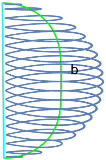
$$\mu_0^{-1} = 0.042110$$

C_6H_6, $n = 100 \Rightarrow 11.21$ vs 11.24 nA/T[a]

[a] Berger, Dimitrova PCCP (2022) 24 23089.

Current Density Domains in the SG - 1

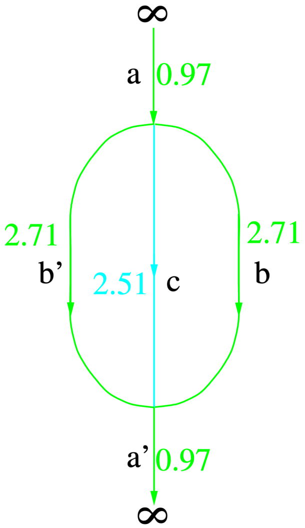




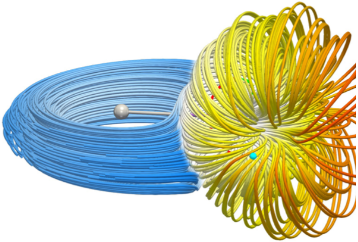
Current Density Domains in the SG - 2

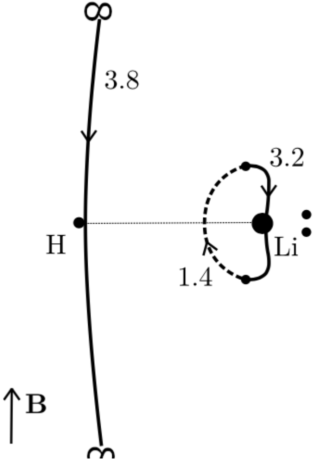
- Boundaries of surfaces through which the total current of a current vortex domain flows can be constructed from segments of the stagnation graph.
- Each current vortex is represented in the stagnation graph in this way. (conjecture)
- Note: The motif of nested vortices is quite common.

The Oriented Flux-Weighted Stagnation Graph



The Oriented Flux-Weighted Stagnation Graph: LiH



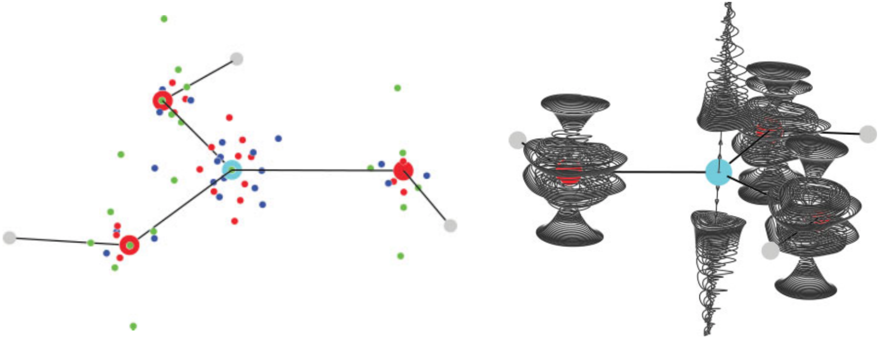


Berger, Dimitrova PCCP 2022, 24, 23089.

Mission completed — isn't it?

Problem (and Approach to Solutions)

$B(OH)_3$



Pelloni, Lazzeretti IJQC 111 (2011) 356.

The Ugly = The Good + The Bad

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"Magnetic Decomposition" of $\mathbf{J}^{\mathbf{B}}$ with $\mathbf{B} = (0, 0, 1)^T$

$$\mathbf{J}^{\mathbf{B}} = \mu_0^{-1} \nabla \times \mathbf{B}^{ind} \tag{AM}$$

$$= \mu_0^{-1} \nabla \times \left(\begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix} + \begin{pmatrix} B_x \\ B_y \\ 0 \end{pmatrix} \right)$$

$$= \underbrace{\mu_0^{-1} \begin{pmatrix} \partial_y B_z \\ -\partial_x B_z \\ 0 \end{pmatrix}}_{:=\mathbf{J}_\perp} + \underbrace{\mu_0^{-1} \begin{pmatrix} -\partial_z B_y \\ \partial_z B_x \\ \partial_x B_y - \partial_y B_x \end{pmatrix}}_{:=\mathbf{J}_{||}} \tag{MZ}$$

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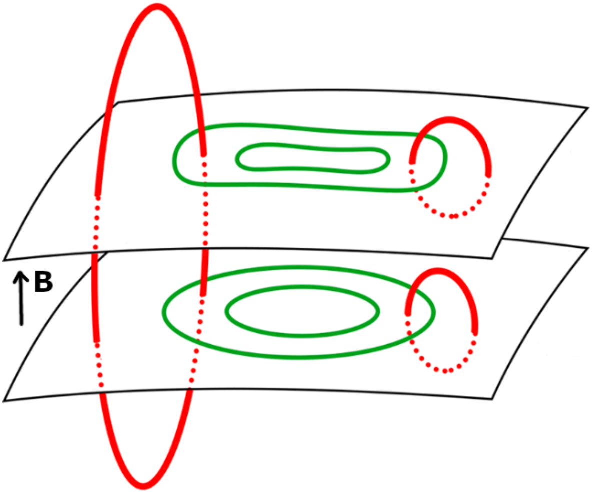
MD Graphically



$\mathbf{J}_\perp$

$\mathbf{J}_{||}$

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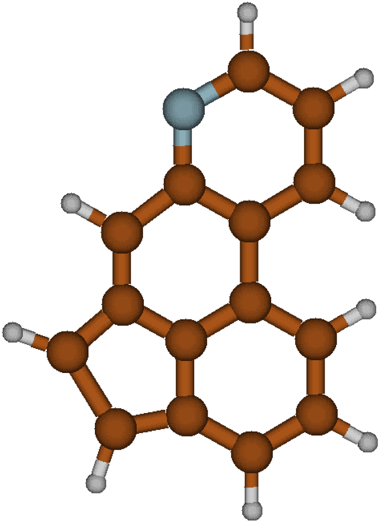
MD — Properties

$$\boxed{\underbrace{\mathbf{J}^{\mathbf{B}}}_{ugly} = \underbrace{\mathbf{J}_\perp}_{good} + \underbrace{\mathbf{J}_\parallel}_{bad}} \qquad \text{(MDJ)}$$

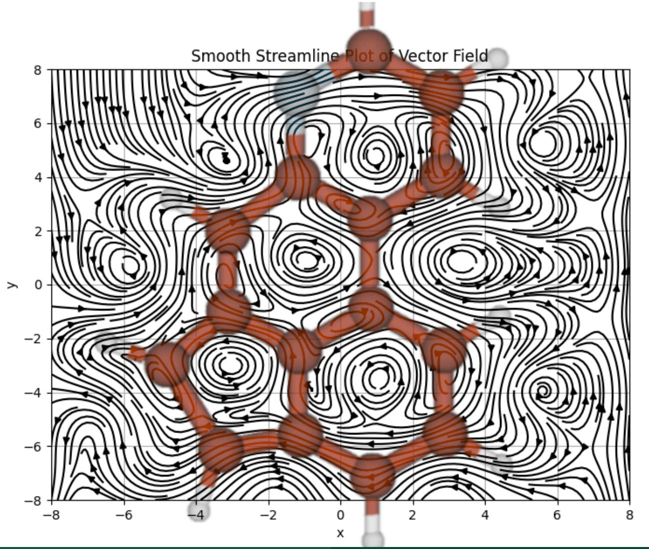
- $\mathbf{J}_\perp$ and $\mathbf{J}_\parallel$ are solenoidal.
- $\mathbf{J}_\parallel$ does not contribute to the magnetization energy.
- $\mathbf{J}_\parallel$ does not contribute to the magnetic susceptibility.
- $\mathbf{J}_\perp$ has nicely (branched) stagnation *lines*.
- alternatives exist (see James' poster).

unpublished results.

Example $\mathbf{J}$ vs $\mathbf{J}_\perp$ (via D-AM)



Example $\mathbf{J}$ vs $\mathbf{J}_\perp$



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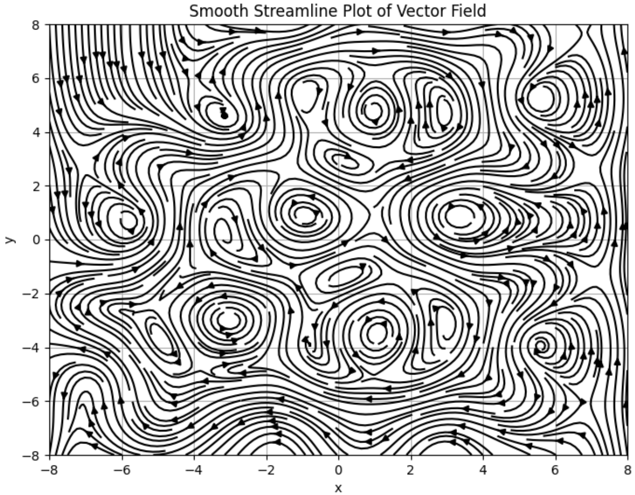
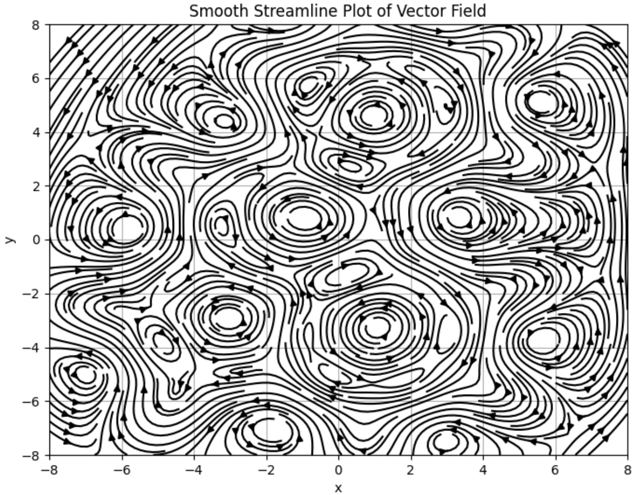
J (The Ugly)



$\mathbf{J}_\perp$ (The Good)



Summary

1

New method to compute $\mathbf{J}^\mathbf{B}$
e.g. TM, via chem. Shieldings, Relativity, divergence-free;

3

Oriented flux weighted stagnation graphs represent the QT-AIM analog of molecular graphs for the density

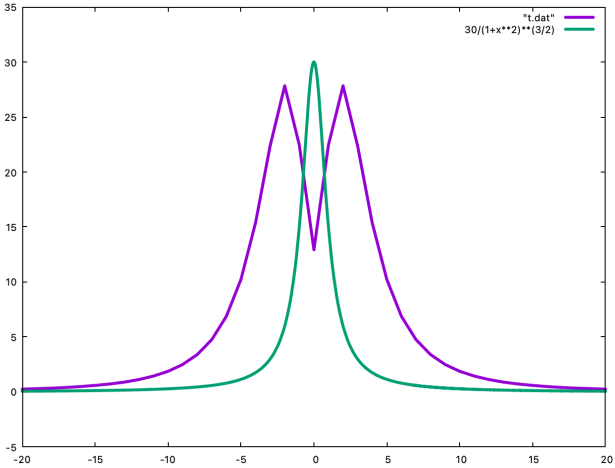
$$\mathbf{J}^\mathbf{B} = \mu_0^{-1} \nabla \times \mathbf{B}^{ind}$$

$$\iint_\Sigma \mathbf{J}^\mathbf{B} \cdot \mathrm{d}\hat{\mathbf{n}} = \mu_0^{-1} \oint_{\partial\Sigma} \mathbf{B}^{ind} \cdot \mathrm{d}\mathbf{l}$$

2

new more efficient method to compute flux integrals of $\mathbf{J}^\mathbf{B}$; very simple and fast for planar symmetric rings, but also rectangular boundaries for complex problems, no $\mathbf{J}^\mathbf{B}$ required. X2C, ...

A word on NICS



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- Prof. em. Dr. Riccardo Zanasi (UNISA)
- Dr. James Asher (SAS)
- ...

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Wann Stagnations*linien*?

- one e^- case, lines are expected[a]
- rough dimensional analysis (3 equations for 3 unknowns) suggests isolated points
- *Preimage theorem* (using the rank of the differential of the map) says isolated points
- J_z is purely "paratropic" $\Rightarrow$ lines for diamagnetic cases
- symmetry enforces sometimes local "diamagneticity" or at least $J_z = 0$

a) P.A.M. Dirac, Proc. R. Soc. Lond. A. 133 (1931) 60.

(Philosophical) Q&A

- Which flux (integrals) make sense?
- Are there "bond currents"?
- There are separable vortices (via separatrix surfaces).
- "Current domain" = "separate vortex"
- Closed loops in stagnation graphs! *(conjectural)*
- What if only separate stagnation *points*?
- Rigorouos answer — or ... (mind: Topology is unstable against small perturbations (bondpaths))