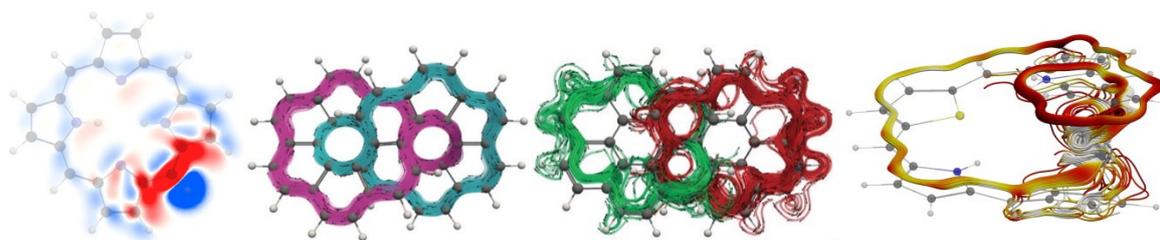


Current-densities, aromaticity and nuclear magnetic shieldings

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External magnetic fields induce current densities in the electron density of molecular systems. The current density is as fundamental as the electron density since magnetic properties can be calculated as a scalar product of the current density times the vector potential representing the studied magnetic property. Scalar functions containing information about spatial contributions to nuclear magnetic shielding constants can be calculated using the current density. Visualization or population-type analysis show the spatial origin of the nuclear magnetic shielding constants.[1,2] The approach has been used for understanding the ring-current contribution to magnetic shielding constants of ring-shaped organic molecules like, benzene, cyclobutadiene, and porphyrins.[1,2] Calculations of current densities and ring-current strengths are a powerful and generally accepted tool for assessing the degree of molecular aromaticity of complex ring-shaped molecules. We have studied the aromatic character of figure-eight shaped molecules by calculating the ring-current pathways and their strengths. Calculations on [12]infinifene showed that it sustains two independent ring currents and can be considered to be cylindrical aromatic as the B₂₀ ring. The dication of [12]infinifene sustains paratropic through-space ring currents.[3] Calculations on other figure-eight shaped molecules yielded basic principles for the current-density flux in such molecules. Molecular aromaticity is often based on Hückel's aromaticity rule that $(4n+2)$ π electrons lead to aromaticity and antiaromatic rings have $(4n)$ π electrons. This holds for planar rings, whereas for triplet states the opposite rules hold. However, the aromaticity rule for closed and open-shell molecules can indeed be unified. We showed that one should not count the number of electrons but rather consider the number of orbitals in the conjugation pathway. Molecules with even number of orbitals in the conjugation pathway are antiaromatic, whereas aromatic molecules have odd number of orbitals in the conjugation pathway.[4]



From left to right: Spatial magnetic shielding contribution to the ¹H NMR magnetic shielding of the meso hydrogen of free-base porphyrin; The diatropic ring currents in [12]infinifene; The paratropic ring currents in the [12]infinifene dication; The diatropic ring current in H₂-ferrocene-thiaporphyrin.

References:

- [1] R. Kumar Jinger, H. Fliegl, R. Bast, M. Dimitrova, S. Lehtola, D. Sundholm, *J. Phys. Chem. A* **125** (2021) 1778.
- [2] H. Fliegl, M. Dimitrova, R. J. F. Berger, D. Sundholm, *Chemistry* **3** (2021) 1005.
- [3] M. Orozco-Ic, R. R. Valiev, D. Sundholm, *Phys. Chem. Chem. Phys.* **24** (2022) 6404.
- [4] R. R. Valiev, T. Kurtén, L. I. Valiulina, S. Yu. Ketkov, V. N. Cherepanov, M. Dimitrova, D. Sundholm, *Phys. Chem. Chem. Phys.* **24** (2022) 1666.

On the molecular magnetic response to quantify aromaticity: The role of orbital contributions

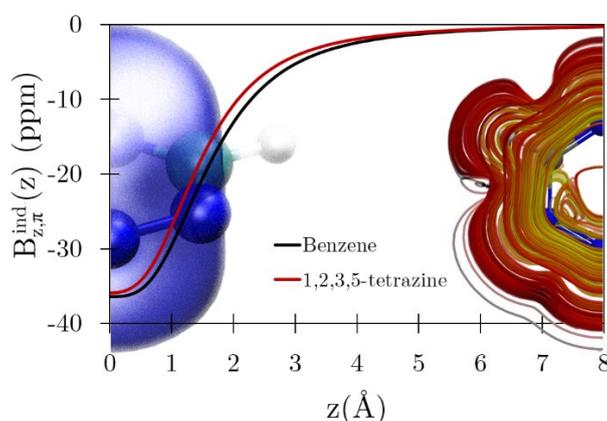
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At present, quantification of aromaticity in terms of the molecular magnetic response is commonly performed by calculating some quantity related to the induced current density or the induced magnetic field.^{1,2} In particular, the analysis of current densities allows visualization of current pathways and the current flux quantification (called the ring-current strength). Similarly, the induced magnetic field allows visualize the direction of the field to determine the shielding and deshielding regions. The size and shape of the so-called shielding (and deshielding) cones give rise to a quantification of the degree of aromaticity. These induced fields can be dissected into their orbital contributions. This makes it possible to determine which block of orbitals contributes to aromaticity, which is helpful for systems with multiple aromaticity as molecular clusters.

In this work, we analyze the molecular magnetic response in small and large planar and non-planar molecules, considering the corresponding warnings when using magnetic criteria. The role of the molecular geometry, curvature, and the orbital contributions to the magnetic response are investigated.³⁻⁸ The analysis focuses on the computation and visualization of induced magnetic fields and the magnetically induced current densities and their relationship to each other.



- [1] D. Sundholm, H. Fliegl and R. J. F. Berger, *WIREs: Comput. Mol. Sci.*, **2016**, 6, 639–678
- [2] R. Islas, T. Heine and G. Merino, *Acc. Chem. Res.*, **2012**, 45, 215–228.
- [3] M. Orozco-Ic, M. Dimitrova, J. Barroso, D. Sundholm and G. Merino, *J. Phys. Chem. A*, **2021**, 125, 5753–5764.
- [4] M. Orozco-Ic, J. Barroso, N. D. Charistos, A. Muñoz-Castro and G. Merino, *Chem.-Eur. J.*, **2020**, 26, 326–330.
- [5] M. Orozco-Ic, C. A. Celaya and D. Sundholm, *RSC Adv.*, **2020**, 10, 18124–18130.
- [6] Mesías Orozco-Ic, G. Merino. *Chemistry*, **2021**, 3, 1381–1391.
- [7] Mesías Orozco-Ic, N. D. Charistos, A. Muñoz-Castro, R. Islas, D. Sundholm, G. Merino. *Phys. Chem. Chem. Phys.*, **2022**, 24, 12158-12166.
- [8] Mesías Orozco-Ic, R. R. Valiev, D. Sundholm. *Phys. Chem. Chem. Phys.* **2022**, 24, 6404-6409.

Finite element calculations in strong magnetic fields

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Abstract

Modeling electronic structure in strong magnetic fields is difficult due to the significant deformations that occur in the electronic orbitals. However, these deformations can be captured with fully numerical calculations which have been possible for diatomic molecules at zero field for a long time [1]. Traditionally, the few programs that exist for this purpose are difficult to use, have a limited set of features, and often do not converge [1].

We implemented a modern finite element program, HelfEM, which is able to produce exact solutions for atoms [2] and diatomic molecules [3] at the Hartree-Fock or density functional level of theory. We have shown that in most cases, the program produces micro-eV accuracy total energies with minimal user intervention, facilitating the modeling of materials in extreme environments.

Applications of HelfEM for studying molecules in magnetic fields reaching 10 B₀ show that truncation errors with typical Gaussian gauge including orbital basis sets may exceed 1000 kcal/mol [4].

- [1] S. Lehtola, *Int. J. Quantum Chem.* 119, e25968 (2019). doi:10.1002/qua.25968
- [2] S. Lehtola, *Int. J. Quantum Chem.* 119, e25945 (2019). doi:10.1002/qua.25945
- [3] S. Lehtola, *Int. J. Quantum Chem.* 119, e25944 (2019). doi:10.1002/qua.25944
- [4] S. Lehtola, M. Dimitrova, and D. Sundholm, *Mol. Phys.* 118, e1597989 (2020). doi:10.1080/00268976.2019.1597989

Analyzing Magnetically Induced Currents in Molecular Systems Using Current-Density-Functional Theory

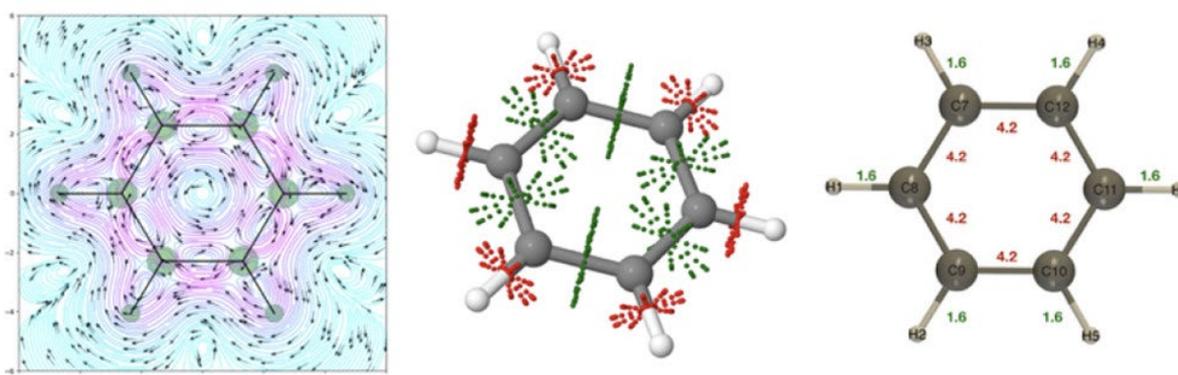
Tom J. P. Irons^a, Lucy Spence^a, Grégoire David^a, Benjamin T. Speake^a, Trygve Helgaker^b, and **Andrew M. Teale**^{a,b}

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Current-density functional theory has become a practical tool for performing calculations on molecular systems in the presence of arbitrary strength magnetic fields [1-3]. A natural by-product of such calculations is access to the physical induced magnetic current. Analysis of these currents is well established in the weak field regime using response theory with London atomic orbitals via programs such as GIMIC [4,5]. In this presentation we extend the applicability of these approaches to systems under arbitrary strength magnetic fields.

A suite of tools for the analysis of magnetically induced currents is introduced [6,7]. These are applicable to both the weak-field regime (0–100 Tesla), well described by linear response perturbation theory, and to the strong-field regime (up to 235000 Tesla), which is inaccessible to such methods. A disc-based quadrature scheme is proposed for the analysis of magnetically induced current susceptibilities, providing quadrature that is consistently defined between different molecular systems and applicable to both planar 2D and general 3D molecular systems in a black-box manner. The applicability of the approach is demonstrated for a range of planar ring systems, the ground and excited states of the benzene molecule, and the ring, bowl, and cage isomers of the C₂₀ molecule in the presence of a weak magnetic field. In the presence of a strong magnetic field, the para- to diamagnetic transition of the BH molecule is studied, demonstrating that magnetically induced currents present a visual interpretation of this phenomenon.



- [1]. G. Vignale and M. Rasolt, *Phys. Rev. Lett.* 1987, **59**, 2360–2363
- [2]. E. I. Tellgren, S. Kvaal, E. Sagvolden, U. Ekström, A. M. Teale, T. Helgaker *Physical Review A*, 2012, **86**, 062506.
- [3]. S. Kvaal, A. Laestadius, E. Tellgren, and T. Helgaker, *J. Phys. Chem. Lett.* 2021, **12**, 1421–1425
- [4]. J. Juselius, D. Sundholm, J. Gauss, *J. Chem. Phys.* 2004, **121**, 3952–3963
- [5]. GIMIC: gauge-including magnetically induced currents, <https://github.com/qmcurrents/gimic>
- [6]. T. J. P. Irons, L. Spence, G. David, B. T. Speake, T. Helgaker, and A. M. Teale *J. Phys. Chem. A* 2020, **124**, 1321–1333
- [7]. QUEST, a rapid development platform for QUantum Electronic Structure Techniques; <https://quest.codes>.

Extending Semi-Empirical Approaches for Molecular Systems in Strong Magnetic Fields

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Abstract

Due to their low computational cost, semi-empirical methods can be used as a pre-processor method for more computationally expensive methods for the exploration of molecular structures, conformations and dynamics. Alternatively, they may also be employed directly for the study of large systems that are out of reach of present state-of-the-art quantum chemical methods.

We present our developments to extend the popular extended tight-binding (xTB) semi-empirical methods [1-3] to calculations that include interactions with magnetic fields in a non-perturbative manner [4], allowing us to take the advantages of a semi-empirical method to the strong field regime. By carefully adding the appropriate correction terms to the xTB Hamiltonian we obtain relative energies and geometries that qualitatively reproduce Hartree-Fock (HF) and Density-Functional theory (DFT) results under a strong magnetic field.

With the general idea validated for relative energies and molecular structures, we examine how to apply our model to the calculation of current densities, magnetizabilities, NMR shielding constants and other properties. Qualitative agreement between xTB and HF/DFT is obtained for current densities and magnetizabilities. However, the calculation of NMR shielding constants is more challenging, which may be due to the valence electron treatment and the particular choice of the basis functions used in the xTB model, possible strategies for overcoming these limitations will be discussed.

References

1. C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher, S. Grimme, *WIREs Comput. Mol. Sci.* **2020**, 11, e01493.
2. S. Grimme, C. Bannwarth, P. Shushkov, *J. Chem. Theory Comput.* **2017**, 13, 1989.
3. C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput.* **2019**, 15, 1652.
4. Chi Cheng et. al. manuscript in preparation.

Towards Predicting the Direction of Flow of Topological Ring-Currents and Bond-Currents in Conjugated π -Ring Systems

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Abstract

Ask anyone working in the field to predict the direction of current flow of Benzene in an applied magnetic field and they are likely to say something like Diamagnetic, Diatropic, Anticlockwise or Aromatic. By convention they might say the opposite but if you then ask that person to predict the direction of flow in Cyclo-octatriene they would most likely say the opposite namely Paramagnetic, Paratropic, Clockwise or Antiaromatic. If pushed for an explanation, they will say that the former molecule has $4n+2$ π electrons whilst the latter has $4n$ π electrons. Whilst these statements are true, they are not sufficient to predict the direction of flow in molecules with multiple rings¹, charged species² or molecules in an excited state³. The goal of our work is to try to produce a simple set of rules or procedures that can be followed to be able to make a reliable prediction. This project is still very much work in progress. The presenter plans to discuss a few preliminary hypotheses and is keen to hear other delegates attending this workshop for their ideas, suggestions, and observations in this field.

To calculate ring currents the authors use a simple topological method based on the ideas of Hückel, London, Pople and McWeeny⁴. This simple topological method is not claimed accurately to calculate ring currents compared to more elaborate quantum mechanical techniques, but it has been shown to be a remarkably accurate tool for predicting qualitatively, and in some cases quantitatively, the magnitude as well as the direction of current flow, when compared to more sophisticated techniques⁵.

1. Topological ring-currents and bond-currents in the altan-[r,s]-coronenes. TK Dickens, RB Mallion – *Chem. Commun.* (2015) 51, 1819-1822 (DOI: [10.1039/c4cc07322c](https://doi.org/10.1039/c4cc07322c)).
2. Topological ring currents and bond currents in some neutral and anionic altans and iterated altans of corannulene and coronene. TK Dickens, RB Mallion – *J. Phys. Chem. A* (2018) 122, 7666-2627 (DOI: [10.1021/acs.jpca.8b06862](https://doi.org/10.1021/acs.jpca.8b06862)).
7. Substituent effect on triplet state aromaticity of enzene. M. Baranac-Stojanović, *J. Org. Chem.* (2020), 85, 4289-4297. (DOI: [10.1021/acs.joc.9b03472](https://doi.org/10.1021/acs.joc.9b03472))
4. Topological ring-currents in conjugated systems. TK Dickens, RB Mallion – *MATCH Commun. Math. Comput. Chem.* (2016) 76, 297-356.
5. Some comments on topological approaches to the π -electron currents in conjugated systems. TK Dickens, JANF Gomes, RB Mallion – *J Chem. Theory Comput.* (2011) 7, 3661-3674 (DOI: [10.1021/ct2002539](https://doi.org/10.1021/ct2002539)).

Topological Ring-Currents and Bond-Currents in Neutral and Dianionic

Altans and Iterated *Altans* of Benzene, Naphthalene, and Azulene

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IN previous studies, the Hückel–London–Pople–McWeeny (HLPM) method^{1–3} was used to calculate the ‘topological’ ring-currents and bond-currents that are associated with the mono-*altans*,⁴ and the doubly and triply iterated *altans*, of corannulene and coronene and their respective dianions.⁵ This gave rise to some intriguing patterns in these currents,⁵ which were partially rationalised by a detailed examination of the lone non-bonding orbitals that each of these structures possesses. In the present work,⁶ the same HLPM approach is used to investigate whether analogous changes in bond-current patterns are observed when going from the neutral species to the dianions of the *altans* and iterated *altans* derived from some other, simpler, ‘parents’ having molecular graphs with a nullity of zero. The *altans* and iterated *altans* of three of the simplest parents are studied: the neutral species (*altan*)ⁿ-benzene, (*altan*)ⁿ-naphthalene, and (*altan*)ⁿ-azulene, with $n = 1, 2, \text{ and } 3$, together with their corresponding dianions. Analogous bond-current patterns are indeed revealed, some of which are likewise accounted for by a detailed consideration of the nonbonding orbitals. It is hoped that further rationalisation of these observations might be forthcoming by discussion in the present Workshop.

References

- (1) T. K. DICKENS & R. B. MALLION. Topological ring-currents in conjugated systems. *MATCH Commun. Math. Comput. Chem.* **2016**, *76*, 297–356.
- (2) R. B. MALLION. Topological ring-currents in condensed benzenoid hydrocarbons. *Croat. Chem. Acta* **2008**, *81*, 227–246.
- (3) A. T. BALABAN, T. K. DICKENS, I. GUTMAN & R. B. MALLION. Ring currents and the PCP rule. *Croat. Chem. Acta* **2010**, *83*, 209–215.
- (4) R. ZANASI, P. DELLA PORTA & G. MONACO. The intriguing class of *altan*-molecules. *J. Phys. Org. Chem.* **2016**, *29*, 793–798.
- (5) T. K. DICKENS & R. B. MALLION. Topological ring-currents and bond-currents in some neutral and anionic *altans* and iterated *altans* of corannulene and coronene. *J. Phys. Chem. A* **2018**, *122*, 7666–7678.
- (6) T. K. DICKENS & R. B. MALLION. Topological ring-currents and bond-currents in some neutral and dianionic *altans* and iterated *altans* of benzene, naphthalene and azulene. *J. Phys. Chem. A* **2021**, *125*, 10485–10499.

Topological Analysis of Magnetically Induced Current Densities In Strong Magnetic Fields Using Stagnation Graphs

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In the strong-field regime, magnetic interactions become comparable in significance to Coulomb interactions; as a result, the changes in electronic structure and nature of chemical bonding in such conditions can differ significantly from the familiar zero-field picture¹. The magnetically induced current density can be a rich source of chemical information², the topology of which reflects the chemical structure of the molecule and its interaction with an applied magnetic field³. Analysis of the magnetically induced current density therefore offers significant opportunities for interpreting and rationalising the exotic nature of chemical bonding in strong magnetic fields.

The magnetically induced current is a relatively complicated vector field, and as such, tools for its analysis and interpretation of its main features in a simple manner are highly desirable. It has previously been found that a topological approach to analysis of the magnetically induced current density, in particular through the location and classification of stagnation points - at which the current density has zero magnitude, can distill the main features of the complicated current vector field into a much simpler form⁴.

In this work⁵, an implementation capable of producing these stagnation graphs in arbitrarily strong magnetic fields, using current-density-functional theory is presented. This enables the study of changes in the topology of the current vector field with changes in the strength and orientation of the applied magnetic field.

Applications to CH₄, C₂H₂ & C₂H₄ are presented, in each case considering the molecular geometries optimised in the presence of the magnetic field. The stagnation graphs reveal subtle changes to this vector field where the symmetry of the molecule remains constant. However, when the electronic state and symmetry of the corresponding equilibrium geometry changes with increasing field strength, the changes to the stagnation graph are extensive.

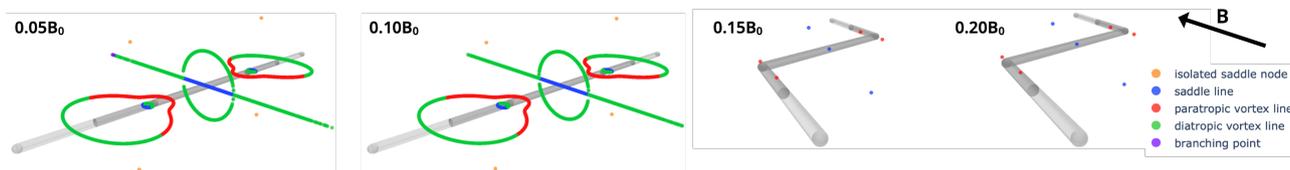


Figure 1. Stagnation graphs of C₂H₂ at increasing magnetic field strengths, at its ground-state & equilibrium geometry.

References

- 1 K. K. Lange, E. I. Tellgren, M. R. Hoffmann, T. Helgaker, *Science* **2012**, 337, 327.
- 2 D. Sundholm, H. Fliegl, R. J. Berger, *WIREs Comput. Mol. Sci.* **2016**, 6, 639–678.
- 3 T. A. Keith, R. F. W. Bader, *J. Chem. Phys.* **1993**, 99, 3669–3682.
- 4 S. Pelloni, P. Lazzeretti, *Int. J. Quantum Chem.* **2010**, 111, 356–367.
- 5 T. J. P. Irons, A. Garner, A. M. Teale, *Chemistry* **2021**, 3, 916-934.

Current(s) News from Salzburg

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Abstract

Part 1 Instead of integrating the current density (CD, $\mathbf{J}^B(x, y, z)$) over a surface to obtain current flux strengths Φ , one can integrate the induced magnetic field \mathbf{B}^{ind} , better known as NICS,¹ around the boundary of the surface to obtain Φ after multiplication with the inverse of the vacuum permeability ($1/\mu_0$).² These line integrals are especially meaningful and useful in subdomains of zero-current density, which contain the so called stagnation graph (SG) and also all numerically infinitely distant points from the center of charge. In the simplest case of a sufficiently symmetric (for example cyclic) and small molecule the total ring current can be roughly approximated by

$$\Phi \approx -\mu_0^{-1} \sum_{i=-n}^n \text{NICS}_{zz}(i),$$

where n stands for a sufficiently large positive integer in units of bohr radius a_0 (e.g. 100). Whenever \mathbf{J}^B can be partitioned uniquely into subdomains of non intersecting or non-overlapping current, so called vortices, the flux of these vortices, can be obtained from line integrals of $\mu_0^{-1} \mathbf{B}^{ind} \cdot ds$ along closed loops of stagnation lines, which always exist in such a case.³

Part 2 The CD can be decomposed into dia- and paramagnetic contributions. The decomposition is a functional of the gauge choice of the centre of the origin of the magnetic vector potential. An often used vector field extension of this gauge choice is called “continuous transformation of the origin of the current density” (CTOCD). We introduce a general CTOCD scheme that aims to annihilate the divergence of the diamagnetic (thus also the paramagnetic) contribution alone and call it CTOCD-D(ivergence-free)C(omponents).^{4,5} The well established CTOCD-DZ scheme is a special case thereof.

Another interesting special case of CTOCD-DC can be seen in the well-known toroidal-poloidal decomposition of divergence-free vector fields.⁶ This decomposition is mathematically unique as it yields two unique scalar fields (ψ and ϕ , see box). We assign one to the diamagnetic and the other one to the paramagnetic part. Then the CD can be topologically analyzed component-wise. It is to be expected that both the toroidal and the poloidal part will show a much simpler topology than the total CD, with mostly connected SGs, for each component.⁷

$$\mathbf{J}^B(x, y, z) = \underbrace{\nabla \times (\mathbf{B}^{ext} \psi(x, y, z))}_{\text{toroidal} = \text{dia}} + \underbrace{\nabla \times \nabla \times (\mathbf{B}^{ext} \phi(x, y, z))}_{\text{poloidal} = \text{para}} \quad \text{component}$$

¹PvR Schleyer, C Maerker, A Dransfeld, H Jiao, NJRvE Hommes, JACS 118 (1996) 6317.

²RJF Berger, M Dimitrova, RT Nasibullin, RR Valiev, PCCP 24 (2022) 624.

³RJF Berger, M Dimitrova, ChemrXiv (2022) preprint.

⁴RJF Berger, G Monaco, R Zanasi, JCP 152(2020) 194101.

⁵D Sundholm, M Dimitrova, RJF Berger, ChemCommun 57 (2021) 12362.

⁶BJ Schmitt, Wv Wahl, Lecture Notes in Mathematics 1530 (1992) Springer: Berlin, Heidelberg.

⁷Unpublished results.

Ring-current mapping for benzenoids: combinatorics, comparisons, consensus and contradictions

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Abstract

Conjugated-circuit (CC) models, though not without their limitations, offer a conceptually simple framework for estimation and rationalisation of ring currents in benzenoids and related species. The methods based on molecular-orbital (MO) theory that we have used for some years also have strong claims to explanatory power. Extensive comparisons of CC with MO ab initio ipsocentric, pseudo- π , Huckel_London calculations will be described here, and some further research questions will be suggested.

- [1] W. Myrvold, PWF, J. Clarke: Partitioning Hückel-London Currents into Cycle Contributions. *Chemistry* 3 (2021) 1138-1156.
- [2] PWF, W. Myrvold, C.M. Gibson, J. Clarke, W.H. Bird: Ring-Current Maps for Benzenoids. *J Phys Chem A*, 124 (2020) 4517-4533.
- [3] PWF, W. Myrvold, D. Jenkinson, W. H. Bird: Perimeter ring currents in benzenoids from Pauling bond orders, *PCCP*, 18 (2016) 11764-11776.

Non-bonding orbitals in altans and iterated altans

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Abstract

Altanisation originated in the chemical literature as a formal device for constructing generalised coronenes. The altan of chemical graph G , denoted $a(G, H)$, depends on the attachment set H (the natural choice is the set of h CH positions on the perimeter of a polycyclic hydrocarbon).

The nullity of a graph is the number of NBOs in Hückel theory. The NBOs play a key role in the ring currents of altans. It is proved that:

- (1) for any attachment set with odd h , nullities of altan and parent are equal;
- (2) for any attachment set with even h , the nullity of the altan exceeds that of the parent by 0, 1 or 2;
- (3) k -th altans of a given parent all have the same nullity as the first altan.

Altans of benzenoids have nullity at least 1. The possibility of excess nullity 2 had not been noticed before, but for benzenoids it occurs first for a parent structure with just 5 hexagons

This is joint work with Patrick W. Fowler.

References:

Bašić, N. and Fowler, P. W. (2022) On the nullity of altans and iterated altans.

MATCH Commun. Math. Comput. Chem. 88, 705-745. DOI:10.46793/match.88-3.705B Bašić, N. and Fowler, P. W. (2022) A curious family of convex benzenoids and their altans. Discrete Math. Lett. 9, 111–117. DOI:10.47443/dml.2021.s218

What can we learn about the magnetically-induced current density from selected derived scalar fields? The Topological Data Analysis approach.

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We present the Topological Data Analysis (TDA) approach to study selected scalar fields derived from the magnetically-induced current density (MICD) tensor field.^(a) In this talk, we mainly focus on scalar functions that describe vortex structures in MICD, which are essential for discussing localized and delocalized currents and the concept of molecular aromaticity. We demonstrate the ability of various scalar functions to capture different types of vortices (axial, toroidal). We also quantify the extracted vortices using the notion of topological persistence - one of TDA's key concepts. In TDA,^(b) the persistence value of a topological feature is associated with its lifespan and often interpreted as its importance. Considering the well-founded mathematical background of TDA and the robustness of its methods, we argue that such parameters are viable candidates for quantifiers of MICD.

In this presentation, we hope to encourage the audience to test TDA techniques. For this purpose, we also present a qcten library^(c) that allows using the TTK software^(d) interactively and reproducing the demonstrated analyses.^(e)

Finally, we discuss the issues related to deriving simple functions (e.g., scalar fields) from more complex vector or tensor fields - which criteria should such a simple descriptor have? What are the pros and cons of such an approach? What can guide us towards unsupervised analyses on large molecular sets?

^(a) M. Olejniczak, J. Tierny, *in prep.*

^(b) C. Heine, *et al.*, Comput. Graph. Forum 2016, 35, 643

^(c) Available at <https://github.com/gosiao/qcten>

^(d) J. Tierny, *et al.*, IEEE Trans. Vis. Comput. Graph. (Proc of IEEE Vis) 2017, 24, 832; TTK website: <https://topology-tool-kit.github.io/>

^(e) Available at <https://github.com/gosiao/tda-micd>

Topological analysis of electronic properties defined on arbitrary DFT grids

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Abstract

A robust algorithm is presented that is capable of identifying topological properties of a function defined on an arbitrary grid (in particular, real-space DFT grids). This algorithm is capable of identifying maxima and minima (both local and spatially-extended), basins of attraction and critical paths (paths connecting maxima or minima through saddle points) of the function in $O(n \log(n))$ time (where n is the number of DFT grid points). Applications to the investigation of electronic properties in atoms and molecules are investigated, including Bader charge and bond analysis, analysis of electronic shell structure from the topology of the Laplacian of the electron density and the construction of stagnation graphs of the electronic current density. The dependence of these properties on an applied magnetic field is investigated.

Aromaticity: topology vs geometry, energy vs *magnetism*

Remi Chauvin and all the authors of cited reports

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Abstract

Though perhaps non-unique,^[1] the concept of aromaticity is imposed by observed correlations between measurable features of two types, structural-energetic (stabilization of symmetric planar geometries from spectroscopic or crystallographic measurements) and magnetic (anisotropy from NMR or magnetic susceptibility measurements), themselves quantitatively analyzed from more abstract geometry-dependent theoretical features, either topological (resonance/stabilization energies with respect to putative acyclic references) or directional (induced dia-/para-tropic ring currents). The talk will consist in two parts aiming at delineating relationships between the two criteria. In the first part, the non-observable nature of aromaticity is attributed to its topological nature, i.e. the effect of a fictitious ring opening operation with vanishing geometrical perturbation. Therefore, quantification of "pure aromaticity" must not only rely on a topological treatment, such as the Hückel molecular orbital (HMO) method, but also on the design of a fictitious (non-molecular) acyclic reference. Within this context, long after Aihara's and Trinajstić-Gutman's mathematical definition of topological resonance energy (TRE),^[2] a chemical interpretation was proposed for unicyclic π systems:^[3] a Möbius-twisting head-to-tail ring opening-ring closing metathesis cyclo-dimerization, corresponding to a twisting duplexation of the molecular graph.^[4] The reaction was also envisaged at the DFT level for the benzene molecule under "real" catalytic conditions.^[5] Generalization to polycyclic systems will be considered, while avoiding calculation of the large twisted molecular duplexes by hyper-complex weighting of the monomeric graphs. The bicyclic case will be illustrated by the naphthalene and azulene isomers and their ring *carbo*-mers.^[6] Results for azulene and *carbo*-azulene suggest the relevance of the notion of "zwitterionic aromaticity", and in the whole series, total and partial TRE values were found to correlate not only with the Hückel rule and other energetic aromaticity indices (FLU, MCI), but also with magnetic aromaticity indicators (NICS, AICD). In a second part, an heuristic model of a cyclic π MO system as a single turn of electric coil is proposed: by formal application of the virial theorem and interpretation of aromatic resonance energies, an "intrinsic ring current" (IRC) is defined.^[7] This definition is different from the Haddon's formula of the London's reduced ring current (RC) of [N]annulenes in terms of the Dewar resonance energy ($RC = 3 S RE/\pi^2$, $RE = E - 4 N/\pi$) in the presence of an external magnetic field.^[5] Using IRC, the "intrinsic magnetic energy" (IME) of a cyclic π -system is defined by analogy with macroscopic coil, $ME = 1/2 L I^2$, where L is the self-inductance of the coil, a geometrical parameter. IME thus appears as a unifying magnetic aromaticity index combining energetic and geometrical factors: over a complete set of annulene derivatives and their ring *carbo*-mers, a remarkable correlation NICS(0) vs IME was indeed found to be more accurate than the correlation NICS(0) vs RE (e.g. for the Breslow resonance energy).

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- [1] a) A. R. Katritzky, P. Barczynski, G. Musumarra, D. Pisano, M. Szafran, *J. Am. Chem. Soc.* **1989**, *111*, 7; b) P. v. R. Schleyer, H. Jiao, *Pure & Appl. Chem.* **1996**, *68*, 209.
- [2] a) J. Aihara, *J. Am. Chem. Soc.* **1976**, *98*, 2750; b) I. Gutman, M. Milun, N. Trinajstić, *J. Am. Chem. Soc.* **1977**, *99*, 1692.
- [3] a) R. Chauvin, C. Lepetit, P. W. Fowler, J.-P. Malrieu, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5295; b) R. Chauvin, C. Lepetit, *Phys. Chem. Chem. Phys.* **2013**, *15*, 3855.
- 4) H. E. Simmons, R. E. Merrifield, *Chem. Phys. Lett.* **1979**, *62*, 235; b) *ibid* **1980**, *74*, 348. [5] A. Poater, M. C. D'Alterio, G. Talarico, R. Chauvin, *Eur. J. Org. Chem.* **2020**, 4743.
- [6] J. Poater, J. Heitkamper, A. Poater, V. Maraval, R. Chauvin, *Eur. J. Org. Chem.* **2021**, 6450.
- [7] R. C. Haddon, *J. Am. Chem. Soc.* **1979**, *101*, 1722.
- [7] R. Chauvin, *manuscript in preparation*.

Symmetry of Magnetically Induced Currents

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Abstract. The calculation of magnetically induced current densities provides insight into how molecules respond to the application of external magnetic fields, thus offering a powerful tool to probe the electronic structures and magnetic properties of such systems.^{1,2} Much work has already been done to understand and classify the topology of magnetically induced current densities, from which qualitative information about the topology of molecular magnetic responses can be deduced.²⁻⁵

In this contribution, a complementary method to analyse the symmetry of magnetically induced current densities based on group and representation theories will be described. This enables a systematic quantification of the relationship between the symmetry of multiple electronic states and that of induced currents calculated from them in arbitrarily strong uniform magnetic fields.⁵ In particular, the implications of degeneracy and symmetry breaking in ground and excited wavefunctions on the symmetry of magnetically induced currents will be examined for a range of planar and non-planar systems. Consequently, the understanding from this symmetry-based investigation will complement existing topological methods in shedding light on the practical calculation and interpretation of molecular magnetic responses for systems with complex electronic structures.

References.

1. D. Sundholm, H. Fliegl, R. J. Berger, *WIREs Comput. Mol. Sci.* **6**, 639–678, DOI [10.1002/wcms.1270](https://doi.org/10.1002/wcms.1270) (2016).
2. D. Sundholm, M. Dimitrova, R. J. F. Berger, *Chem. Commun.* **57**, 12362–12378, DOI [10.1039/D1CC03350F](https://doi.org/10.1039/D1CC03350F) (2021).
3. T. A. Keith, R. F. Bader, *J. Chem. Phys.* **99**, 3669–3682, DOI [10.1063/1.466165](https://doi.org/10.1063/1.466165) (1993).
4. S. Pelloni, P. Lazzarotti, *Int. J. Quantum Chem.* **111**, 356–367, DOI [10.1002/qua.22658](https://doi.org/10.1002/qua.22658) (2011).
5. T. J. P. Irons, A. Garner, A. M. Teale, *Chemistry (MDPI)*. **3**, 916–934, DOI [10.3390/chemistry3030067](https://doi.org/10.3390/chemistry3030067) (2021).

Effect of Substitution on Triplet State (Anti)aromaticity of Benzene, Cyclopentadienyl Cation and Some Polycyclic Hydrocarbons

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(Anti)aromaticity rules in the first $\pi\pi^*$ triplet excited state are opposite to Hückel rules for the ground singlet state, as shown by Baird.¹ This means that benzene is antiaromatic and cyclopentadienyl cation is aromatic in triplet state. By employing theoretical calculations we showed that substitution of one hydrogen atom of benzene can be used to tune its triplet state antiaromaticity from highly antiaromatic to strongly aromatic.² Analysis of triplet state aromaticity using cyclopentadienyl cation as a model compound showed that it is more sensitive to substituent effect than singlet state aromaticity.³ Interestingly, when nitroso group is a substituent both benzene and cyclopentadienyl cation retain their ground state aromaticity and antiaromaticity, respectively.^{2,3} Literature data show that polycyclic aromatic hydrocarbons tend to localize spin density and triplet state antiaromaticity to certain subunit(s).^{4,5} We found that substitution of carbon atom(s) with one or two silicon atom(s) always localizes spin density to silacycle which becomes nonaromatic or weakly antiaromatic. This spin localization enables all-carbon subunits to recover their Hückel aromaticity. Depending on the type of all-carbon subunits and extent of their aromaticity the singlet-triplet energy gaps of polycyclic compounds can be fine-tuned.⁶

References

1. C. Baird, *J. Am. Chem. Soc.* **1972**, *94*, 4941.
2. M. Baranac-Stojanović, *J. Org. Chem.* **2020**, *85*, 4289.
3. Milovan Stojanović, Jovana Aleksić, M. Baranac-Stojanović, *Chemistry* **2021**, *3*, 765.
4. R. Papadakis, H. Li, J. Bergman, A. Lundstedt, K. Jorner, R. Ayub, S. Haldar, B. O. Jahn, A. Denisova, B. Zietz, R. Lindh, B. Sanyal, H. Grennberg, K. Leifer, H. Ottosson, *Nat. Commun.* **2016**, *7*, 12962.
5. G. Markert, E. Paenurk, R. Gershoni-Poranne, *Chem. Eur. J.* **2021**, *27*, 6923.
6. M. Baranac-Stojanović, Milovan Stojanović, Jovana Aleksić, *Chem. Asian J.* **2022**, *17*, e202101261.

(Anti)Aromaticity-enhanced reactivity of frustrated Lewis pairs

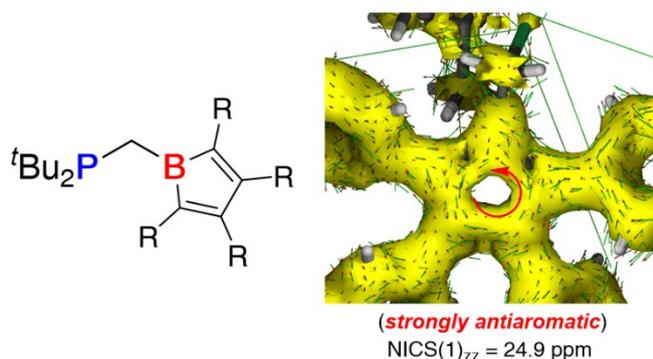
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Frustrated Lewis pairs (FLPs) are species typically composed of a pair of a sterically encumbered Lewis acid and Lewis base, which prevents the formation of a classical donor-acceptor bond between both centers. Due to this particular bonding situation, these compounds exhibit a unique reactivity as a result of the cooperative action of the FLP antagonists. Thus, FLPs have emerged as potential metal-free catalysts able to, among other processes, activate small molecules (H_2 , CO, CO_2 , SO_2 , N_2O , etc.).¹

In the last years, we have explored the factors controlling the cooperative action of the Lewis antagonists by means of state-of-the-art computational methods.^{2,3} In addition, we aimed at predicting new FLPs exhibiting enhanced reactivity towards the activation of small molecules. In this talk, we shall discuss our recent findings on how (anti)aromaticity can enhance the reactivity of geminal FLPs.^{4,5} Nuclear Independent Chemical Shift (NICS) values and the Anisotropy of the Induced Current Density (ACID) method have been key to understanding the role of (anti)aromaticity in the considered transformation mediated by FLPs (see Figure).



References

1. Selected reviews: (a) D. W. Stephan, G. Erker, *Angew. Chem., Int. Ed.* **2015**, *54*, 6400; (b) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306; (c) D. W. Stephan, *Chem* **2020**, *6*, 1520.
2. Selected examples: (a) D. Yepes, P. Jaque, I. Fernández, *Chem. Eur. J.* **2016**, *22*, 18801; (b) J. J. Cabrera-Trujillo, I. Fernández, *Chem. Eur. J.* **2018**, *24*, 17823; (c) J. J. Cabrera-Trujillo, I. Fernández, *Inorg. Chem.* **2019**, *58*, 7828; (d) J. J. Cabrera-Trujillo, I. Fernández, *Chem. Eur. J.* **2021**, *27*, 3823.
3. For a recent review, see: I. Fernández, *Chem. Commun.* **2022**, *58*, 4931.
4. J. J. Cabrera-Trujillo, I. Fernández, *Chem. Commun.* **2019**, *55*, 675.
5. J. J. Cabrera-Trujillo, I. Fernández, *Chem. Commun.* **2022**, *55*, 6801.

From NICS to Bond Currents

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The Nucleus Independent Chemical Shift (NICS) method is the most common computational approach for assessing the magnetic aromaticity of molecules. However, NICS values are just a proxy to the actual property of interest (i.e., the induced current density of aromatic rings). In fact, it has been shown that the three-dimensional current density cannot be uniquely reconstructed from a set of NICS values.¹ Relatedly, it is often claimed that NICS values cannot be used to infer information about induced current patterns, especially in complex polycyclic aromatic molecules.²

We show that by targeting bond currents instead of the three-dimensional current density and by making physically motivated assumptions, a unique conversion scheme from NICS values to bond-current graphs can be defined. Building on the previously observed accuracy of NICS values calculated from bond currents,³ we developed an efficient method for converting NICS values from GIAO-DFT calculations into bond-current graphs.⁴ The resulting bond currents are quantitatively in good agreement with bond currents obtained by integration of the current density from DFT calculations, and provide clear visualization of ring-current patterns even in complex polycyclic aromatic molecules.

(1) Van Damme, S.; Acke, G.; Havenith, R. W. A.; Bultinck, P. *Phys. Chem. Chem. Phys.* **2016**, *18*, 11746–11755.

(2) Fias, S.; Fowler, P. W.; Delgado, J. L.; Hahn, U.; Bultinck, P. *Chem. Eur. J.* **2008**, *14*, 3093–3099.

(3) Paenurk, E.; Feusi, S.; Gershoni-Poranne, R. *J. Chem. Phys.* **2021**, *154*, 024110.

(4) Paenurk, E.; Gershoni-Poranne, R. *Phys. Chem. Chem. Phys.* **2022**, *24*, 8631–8644.

Track and trace magnetic aromaticity by experiments and computations

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Abstract

The rich information contained in the magnetically induced current density can be compressed in different ways, leading to chemical shifts, magnetizabilities, bond and ring current strengths. While their connection via the Biot-Savart law would be straightforward for a single infinitely-thin loop of current, it is definitely less trivial for many circuits of finite size and irregular shape as should be considered for polycyclic molecules.

We will review past and recent results on the matter, spanning from small monocycles to plain and decorated nanorings, endowed with unusually strong magnetic responses.

(1) Landi et al. Chemistry 2021

(2) Landi et al. ChemPhysChem 2022

Modelling the aromaticity of azaboro-annulenes.

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Abstract:

Despite a long tradition of descriptions of borazine as an 'inorganic benzene', arising from satisfying an $4n+2$ π -electron count, borazine is non-aromatic under the magnetic (ring-current) criterion. Borazine, borazocine, and the larger neutral $(\text{BN})_n\text{H}_{2n}$ azaboro-annulene heterocycles in planar conformations, although π -isoelectronic with $[2n]$ annulenes, support only localized induced currents in perpendicular magnetic fields. Qualitative orbital analysis based on the ipso-centric approach to calculation of induced current density suggests that global induced currents could be produced through strategic changes to the π electron count. In *ab initio* calculations, azaboro-annulenes with rings of size [8]- and larger were indeed found to support global diatropic ring currents in both anionic and cationic forms with $(4N + 2) \pi$ electron counts. The planar conformation of the charged ring typically occupies a stationary point of higher order on the potential energy surface, rather than a minimum. However we found one candidate occupies a planar minimum, supports a diatropic ring current of strength comparable to that in benzene, and is predicted to participate in sandwich compounds; it is therefore a good candidate for an aromatised azaboro-annulene.

Disk aromaticity in singlet and triplet boron clusters. A current density point of view

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Abstract

The disk-like boron clusters are among the most captivating boron cluster forms. It has been proposed that molecular orbital distribution in these clusters can be predicted based on the simple particle-on-a-disk model. In this model, the molecular orbitals come by pairs except for $m = 0$ (no angular nodes). Within the CTOCD-DZ (continuous transformation of origin of current density method - diamagnetic zero) method the induced current density of the particle-on-a-disk-based model can be rationalized by applying simple symmetry- and energy-based selection rules on the virtual orbital transitions. The particle-on-a-disk model predicts that if the number of valence electrons is increased or reduced by two electrons, the disk-like boron clusters that are aromatic (sustain diatropic currents) in their ground states remain aromatic in their lowest-lying triplet states. In this study we employed the magnetically induced current densities to test the performance and limits of the particle-on-a-disk model in description of the electronic structure of the disk-like boron clusters. It was found that Hückel and Baird's rules can be successfully applied to predict aromatic character of the studied disk-like boron clusters in their lowest-lying singlet and triplet states, with the exception of triplet ${}^3B_{19}$.

Ring Currents and All-Metal Aromaticity in Bismuth Clusters

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Traditionally, ring currents and the concept of aromaticity are of great importance for organic compounds. In contrast, their occurrence in purely metallic systems is less widespread. Molecules comprising only metal atoms (M) show “aromatic features”, sustaining ring currents inside an external magnetic field along M–M connection axes (σ -aromaticity) or above and below the plane (π -aromaticity) of cyclic or cage-type molecules. However, the mobility that is inherent to electrons in all-metal compounds has not been exhausted in its dimensionality. Most systems consist of three- to five-membered planar monocycles with a σ - and/or π -type ring current. Herein, we show that larger bismuth clusters [1–5] such as $[\text{Th@Bi}_{12}]^{4-}$ or $[\text{U@Bi}_{12}]^{3-}$ also feature a strong ring current based on a non-localizable π -type molecular orbital [2, 4]. Moreover, regular $\{\text{Bi}_6\}$ prisms may exhibit a non-localizable molecular orbital of f-type symmetry and generate a strong ring current that leads to an unprecedented type of aromaticity [5].

Our general theoretical framework is based on the gauge-including magnetically induced current (GIMIC) method [6]. The ground-state and response density matrix needed for GIMIC are calculated with either an effective relativistic Hamiltonian using standard pseudopotentials [7] or relativistic all-electron exact two-component (X2C) theory [8]. Furthermore, the paramagnetic current density is used to generalize the kinetic energy density of meta-generalized gradient approximations and local hybrid functionals [9, 10]. This ensures that the iso-orbital constraint in density functional theory holds and leads to substantial improvements for NMR shielding constants and shifts [10].

- [1] A. R. Eulenstein, Y. J. Franzke, P. Bügel, W. Massa, F. Weigend, and S. Dehnen, *Nat. Commun.* 2020, **11**, 5122.
- [2] A. R. Eulenstein, Y. J. Franzke, N. Lichtenberger, R. J. Wilson, L. Deubner, F. Kraus, R. Clérac, F. Weigend, and S. Dehnen, *Nat. Chem.* 2021, **13**, 149.
- [3] N. Lichtenberger, R. J. Wilson, A. R. Eulenstein, W. Massa, R. Clérac, F. Weigend, and S. Dehnen, *J. Am. Chem. Soc.* 2016, **138**, 9033.
- [4] S. Gillhuber, Y. J. Franzke, and F. Weigend, *J. Phys. Chem. A* 2021, **125**, 9707.
- [5] B. Peerless, A. Schmidt, Y. J. Franzke, and S. Dehnen, *Nat. Chem.* 2022, revision submitted.
- [6] J. Jusélius, D. Sundholm, and J. Gauss, *J. Chem. Phys.* 2004, **121**, 3952.
- [7] K. Reiter, M. Kühn, and F. Weigend, *J. Chem. Phys.* 2017, **146**, 054102.
- [8] Y. J. Franzke and F. Weigend, *J. Chem. Theory Comput.* 2019, **19**, 2928.
- [9] C. Holzer, Y. J. Franzke, and M. Kehry, *J. Chem. Theory Comput.* 2021, **15**, 1028.
- [10] Y. J. Franzke and C. Holzer, *J. Chem. Phys.* 2022, **157**, 031102.

Persistent strong diatropic ring currents in aromatic *closo*- and *nido*-carboranes

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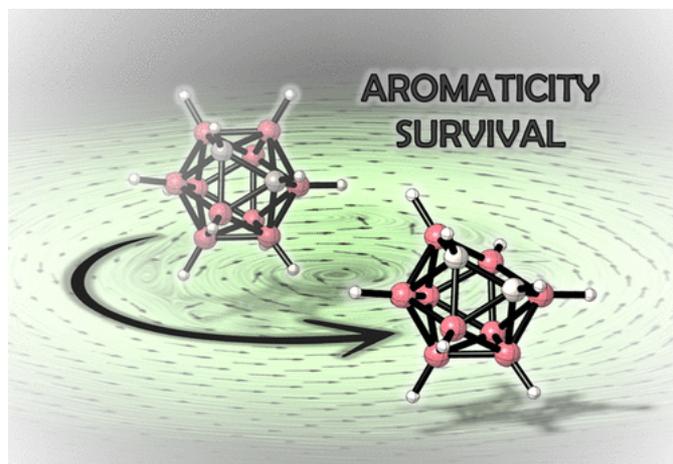
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o-C₂B₁₀H₁₂ isomerizes to *m*-C₂B₁₀H₁₂ upon heating at 400 °C. Deboronation in *o*-C₂B₁₀H₁₂ is a relatively easy process, whereas it is more difficult in *m*-C₂B₁₀H₁₂. These two experimental facts indicate that *m*-C₂B₁₀H₁₂ is thermodynamically more stable than *o*-C₂B₁₀H₁₂. On the other hand, it is widely accepted that *closo*-boranes and -carboranes are aromatic compounds. In this work, we relate the difficulty in the deboronation of the carboranes with their stability and aromaticity. We do this by combining lab work and DFT calculations. Computationally, our results show that the higher thermodynamic stability of *m*-C₂B₁₀H₁₂ is not related to aromaticity differences but to the location of the C atoms in the carborane structure. It is also demonstrated that the aromaticity observed in *closo*-boranes and -carboranes is also present in their *nido* counterparts, and consequently, we conclude that aromaticity in boron clusters survives radical structural changes. This observation is the first unique evidence that proves experimentally the existence of diatropic currents, and thence aromaticity, in clusters and is comparable to the existence of diatropic currents in planar aromatic compounds. This research accounts very well for the “paradigm for the electron requirements of clusters”, in which a *closo*-cluster that is aromatic upon addition of 2e⁻ becomes also an aromatic *nido*-species, and explains the informative schemes by Rudolph and Williams.¹⁻⁶



[1] J. Poater, C. Viñas, I. Bennour, S. Escayola, M. Solà, F. Teixidor, *J. Am. Chem. Soc.* 2020, 142, 9396.

[2] J. Poater, M. Solà, C. Viñas, F. Teixidor, *Chem. Eur. J.* 2016, 22, 7437.

[3] J. Poater, M. Solà, C. Viñas, F. Teixidor, *Angew. Chem. Int. Ed.* 2014, 53, 12191.

[4] J. Poater, M. Solà, C. Viñas, F. Teixidor, *Chem. Eur. J.* 2013, 19, 4169.

[5] J. Poater, M. Solà, C. Viñas, F. Teixidor, *Angew. Chem. Int. Ed.* 2022, e202200672.

[6] J. Poater, M. Solà, C. Viñas, F. Teixidor, *Nat. Comm.* 2022, 23, 3844.

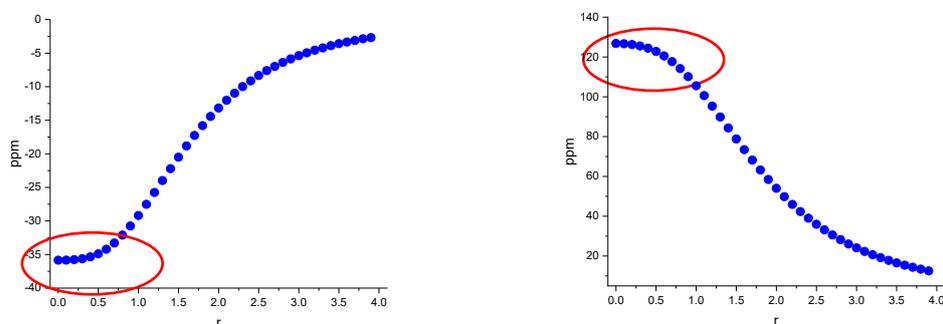
Why all versions of NICS(0) should not be used.

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Abstract

All the versions of NICS-scan (including the most relevant for aromaticity purposes, the $\text{NICS}_{\pi,zz}$) show a change of slope when getting close to the molecular plane. This behavior cannot be



CMO- $\text{NICS}_{\pi,zz}$ -scan of (left) benzene and (right) D_{4h} -cyclooctatetraene. The distance from the molecular plane (r , the X axis) is in Å.

accounted for by the ring current model (RCM). By using a dense grid of BQs it is shown that, when close to the molecular plane, the maximum (absolute) NICS values are off center. At proximity they are located above the atoms and move towards the center as the distance between the BQ-grid and the molecular plane increases. Only at significant heights above the molecular plane (e.g., 1.2 Å for benzene, 2.4 Å for borazine) the maximal (absolute) NICS value is at the center, as should be by the RCM. A couple of mechanisms to explaining this behavior are tested. It was found that the $\text{NICS}_{\pi,zz}$ behavior is parallel to the π -electron density behavior; located at the atoms when close to the molecular plane and becomes delocalized and later fade with increasing the distance to the molecular plane.

All of the above implies that, when close to the molecular plane, $\text{NICS}_{\pi,zz}$ (and certainly less refined NICS indices) do not represent the clean effect of the ring current, namely, aromaticity. It is therefore suggested to use $\text{NICS}(1)_{\pi,zz}$ or $\text{NICS}(1.7)_{\pi,zz}$ which are extrapolated from scan data at larger distances (e.g., 2-5 Å) or the $\int \text{NICS}_{\pi,zz}$ which was recently introduced.

Off-nucleus magnetic shielding, aromaticity and bonding in cyclic and polycyclic conjugated molecules

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Computed isotropic magnetic shielding isosurfaces and contour plots provide a feature-rich picture of aromaticity and chemical bonding which is both quantitative and easy-to-visualize and interpret. These isosurfaces and contour plots make good chemical sense as at atomic positions they are pinned to the nuclear shieldings which, for electronic ground states, are experimentally measurable through chemical shifts. The applications that will be discussed include ground and excited-state aromaticity and antiaromaticity in benzene, cyclobutadiene, cyclooctatetraene and Möbius conjugated rings, the contest between aromaticity and antiaromaticity in norcorrole, the smallest cyclic tetrapyrrole porphyrin analogue synthesized so far, and modern off-nucleus shielding-based visual interpretations of Clar's aromatic sextet theory.

A simple model for describing diamagnetic ring currents in aromatic compounds and pericyclic transition structures

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In this talk, general aspects [1] associated with aromaticity in transition structures (especially in pericyclic reactions) [2] and stable molecules will be presented (Figure 1). Thermal reactions to be discussed include (3+2) [3] and (4+3) [4] cycloadditions, as well as double group transfer (type II dyotropic) reactions. [5] The differences between in-plane and out-of-plane diamagnetic ring currents will be emphasised. Finally, a recent study on aromatic phenazine dications will be presented.

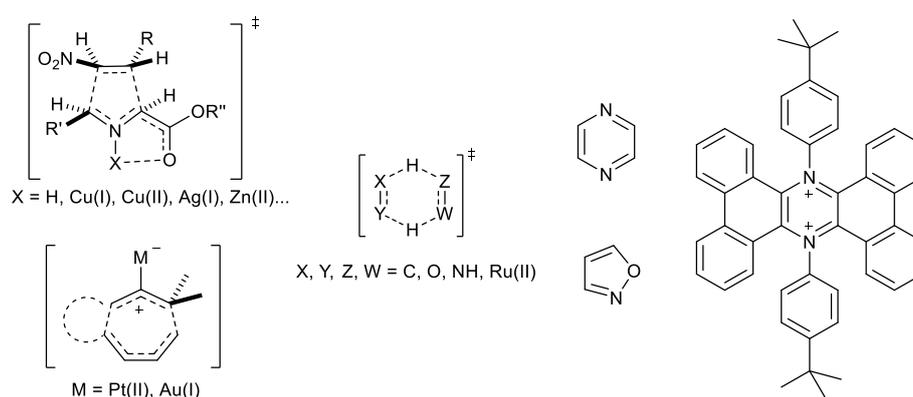


Figure 1. Selected examples of aromatic transition structures and stable heterocycles.

These examples of aromaticity will be discussed in terms of a very simple ring current model that permits to describe σ -, π^1 and π^2 aromaticity by analysing the behaviour of the diamagnetic shielding along the axis that intersects the ring point of electron density of the cyclic structure and is perpendicular to the average molecular plane.

References

- [1] F. P. Cossío, *Aromaticity in molecules and transition structures: from atomic and molecular orbitals to simple ring current models*. In *Aromaticity: Modern Computational Methods and Applications*. I. Fernández, Ed. Elsevier, 2021, pp 1-40. DOI: 10.1016/C2019-0-04193-3.
- [2]. P. v. R. Schleyer, J. I. Wu, F. P. Cossío, I. Fernández, *Chem. Soc. Rev.* 2014, 43, 4909-4921.
- [3]. A. de Cózar, F. P. Cossío, *Phys. Chem. Chem. Phys.* 2011, 13, 10858-10868.
- [4] I. Fernández, F. P. Cossío, A. de Cózar, A. Lledós, J. L. Mascareñas, *Chem. Eur. J.* 2010, 16, 12147-12157.
- [5] I. Fernández, M. A. Sierra, F. P. Cossío, *J. Org. Chem.* 2007, 72, 1488-1491.
- [6] J. Dosso, B. Bartolomei, N. Demitri, F. P. Cossío and M. Prato, *J. Am. Chem. Soc.* 2022, 144, 7295-7301.

Exploring the frontiers of the Woodward-Hoffmann rules with induced ring currents

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Abstract

Woodward-Hoffmann rules, in rationalizing the selectivity of pericyclic reactions, are one of the greater successes of Physical Organic Chemistry. Their definition of allowed and forbidden paths for these processes through the conservation of orbital symmetry can also be recast in terms of the aromaticity/antiaromaticity of the corresponding concerted transition states. As a result, the association of aromaticity to induced currents allows for the magnetic characterization of pericyclic transition states. In this presentation, modulating the bold statement "There are none!" of the original reports, we will use the study of magnetic properties of transition states to guide our exploration of the frontiers of application of Woodward-Hoffmann rules in situations where the occurrence of radicals, polarization, stepwise paths or dynamic effects lead to unexpected results.

Real-time time-dependent electronic structure methods for modelling strong-field interactions

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Electron dynamics in intense laser fields provide immense information for understanding complex phenomena such as light-harvesting, charge migration, and strong-field interactions like in high-harmonic generation and above threshold ionization processes. Due to the attosecond time scale of the electronic motion, experimental methods based on photoelectron techniques have recently been developed to measure the electron dynamics in molecular systems. For instance, RABBIT (reconstruction of attosecond beating by interference of two-photon transitions), high harmonic spectroscopy, and time-resolved photoelectron spectroscopy.

Real-time time-dependent electronic structure methods, on the other hand, are efficient approaches for modelling electron dynamics in both ultrafast and strong-coupling regimes – yielding information and potential new insights into the electronic behaviour of atoms and molecules.¹ Recent studies have highlighted interesting features of the electronic structure of atoms and molecules in strong magnetic fields in both their ground and excited states.²⁻⁴ In this work, we present our recent development of real-time time-dependent electronic structure methods implemented in the QUEST code⁵ for modelling electron dynamics of molecules in both intense laser fields⁴ and strong oscillating magnetic fields⁶ – describing strong-field interactions of molecules with externally applied electric and magnetic fields.

References

1. X. Li, N. Govind, C. Isborn, A. E. DePrince, and K. Lopata, *Chem. Rev.* **2020**, *120*, 9951.
2. K. K. Lange, E. I. Tellgren, M. R. Hoffmann, and T. Helgaker, *Science* **2012**, *337*, 327.
3. S. Sen, K. K. Lange, and E. I. Tellgren, *J. Chem. Theory Comput.* **2019**, *15*, 3974.
4. M. Wibowo, T. J. P. Irons, and A. M. Teale, *J. Chem. Theory Comput.* **2021**, *17*, 2137.
5. QUEST, A rapid development platform for Quantum Electronic Structure Techniques, <https://quest.codes>.
6. M. Wibowo, B. Ennifer and A. M. Teale, submitted 2022.

Bridging between the magnetic and molecular orbital pictures of excited-state aromaticity

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Excited-state aromaticity has gained prominence as a design strategy for tuning the photophysical properties of molecules. Its particular appeal lies in the fact that it can be applied independently from the more traditional strategies of variations in delocalisation and introduction of electron donating/withdrawing substituents. Enhanced discussions of excited-state aromaticity raise new questions in terms of how it can be understood within the molecular orbital (MO) picture.

This talk will explore aromaticity in electronically excited and charged states in polyaromatic hydrocarbons and macrocycles. Specific attention will be paid to the interplay between the magnetic ring-current and MO pictures. For the visualisation of magnetic properties the visualisation of chemical shielding tensors (VIST)^[1] method – based on the nucleus-independent chemical shift – will be used as it provides a way for viewing magnetic anisotropy in non-planar systems (cf. Figure 1). Connections to the MO picture will be studied based on a rigid rotor model.^[2] This toolbox will be used to study the properties of biphenylene derivatives explaining dramatic differences in excitation energies between isomeric structures.^[2] Subsequently, the photo-redox properties of macrocycles with formally antiaromatic ground states will be discussed.^[3,4]

In a final part, two more formal questions will be discussed. First, we highlight that the MO-based view of excited-state aromaticity presents a natural route of defining excited-state aromaticity of singlets or higher lying triplets. Second, the connection between excited-state aromaticity and Platt's electron loop model^[5] will be explored.

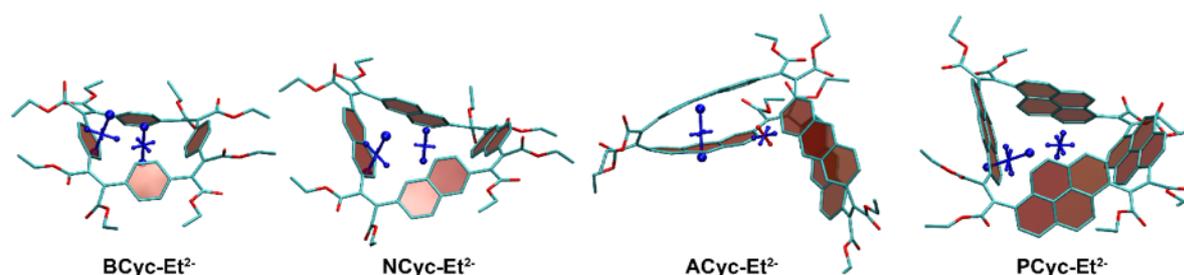


Figure 1: Visualisation of local and global aromaticity of the dianions of a set of macrocycles.^[3]

References

- [1] F. Plasser, F. Glöcklhofer, *European J. Org. Chem.* **2021**, 2021, 2529–2539.
- [2] F. Plasser, *Chem.* **2021**, 3, 532–549.
- [3] M. Pletzer, F. Plasser, M. Rimmele, M. Heeney, F. Glöcklhofer, *Open Res. Eur.* **2021**, 1, 111.
- [4] M. Rimmele, W. Nogala, M. Seif-Eddine, M. M. Roessler, M. Heeney, F. Plasser, F. Glöcklhofer, *Org. Chem. Front.* **2021**, 8, 4730–4745.
- [5] J. R. Platt, *J. Chem. Phys.* **1949**, 17, 484–495.

Effect of benzo-annulation on local aromaticity: to what extent do different aspects of aromaticity agree?

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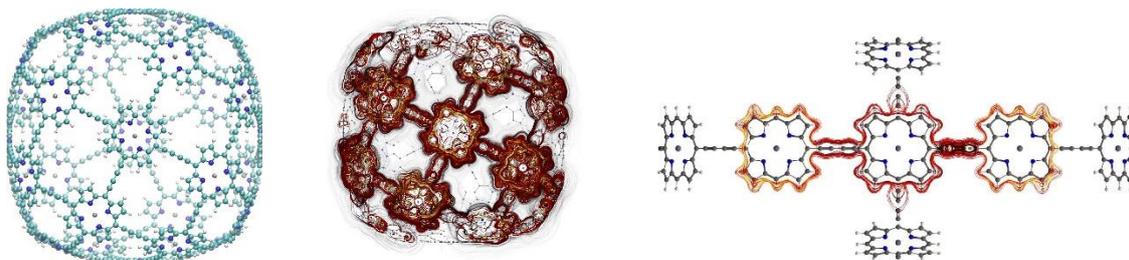
Recent systematic studies demonstrated that the intensity of cyclic electron delocalization in the six membered rings of benzenoid hydrocarbons can be significantly altered by means of benzoannulation. In particular, linear (resp. angular) benzo-annulation was found to decrease (resp. increase) the intensity of cyclic electron delocalization. These regularities were initially observed using the energy effect (ef) which is a graph-theory-based quantity calculated at the level of the simple HMO theory. Eventually, the ef-based results were corroborated at higher levels of calculations by means of the multi centre delocalization index (MCI) and harmonic oscillator model of aromaticity (HOMA) index. On the other hand, the nucleus independent chemical shifts (NICS) index does not support the results obtained by the other employed aromaticity indices. Our aim is to provide a better understanding of the found disagreement between the NICS, as a magnetic index, and the electronic-, energy- and geometry-based aromaticity indices. Here we employed the integrated current strength (current strength susceptibility) to quantify the local aromaticity of individual rings in anthracene and acridine benzo-annulated derivatives. The magnetic aspect of the local aromaticity in the studied molecules was found to be not related to the electronic, geometric and energetic aspects, findings that underline earlier observations on differences between the various aspects of the aromaticity phenomenon.

Induced current densities in porphyrin nanostructures

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Magnetically induced current densities (MICD) of Zn-porphyrinoid nanostructures have been studied at the density functional theory (DFT) level using the B3LYP functional. Six of the studied Zn-porphyrinoid nanostructures consist of two crossing porphyrinoid belts and one is porphyrinoid nanoball belonging to the octahedral (O) point group. The Zn-porphyrin units are connected to each other via butadiyne linkers as in a recently synthesized porphyrinoid cross-belt structure.^[1,2] We have also studied a nanotube and a nanocylinder with the neighbors connected via ethyne bridges at their meso carbon atoms.^[3,4] A clam-like molecule has porphyrin units connected on one side via butadiyne linkers and on the other side they are fused. The MICDs are calculated using the gauge-including magnetically induced currents (GIMIC) method.^[5,6] Current-density pathways and their strengths were determined by numerically integrating the MICD passing through selected planes that cut chemical bonds or molecular rings. The current-density calculations of the cross-belts and the nanoball show that they are globally non-aromatic but locally aromatic sustaining ring currents in the individual porphyrin rings. The ring-current strengths of the individual porphyrin rings are 20% weaker than in Zn porphyrin, whereas oxidation leads to globally aromatic cations sustaining ring currents that are somewhat stronger than for Zn porphyrin. Calculations of the current densities show that there is a paratropic ring current around the nanotube, whereas sealing the ends leads to an almost non-aromatic nanotube. Fusing porphyrinoids as in the fully fused clam-shell molecule results in complicated current-density pathways that differ from the ones usually appearing in porphyrinoids. The neutral fused molecule is antiaromatic, whereas the dication is non-aromatic.



The magnetically induced current density in the nanoball and in a cross-belt porphyrinoid structure.

References:

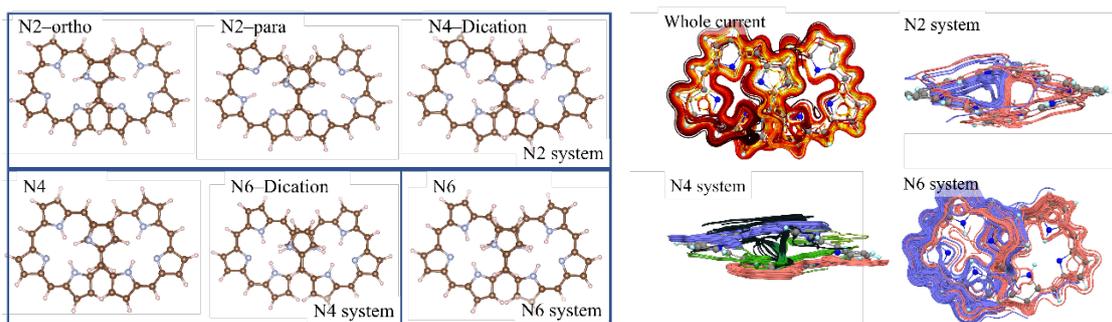
1. Cremers J., Haver R., Rickhaus M., Gong J. Q., Favereau L., Peeks M. D., Claridge T. D. W., Herz L. M., Anderson H. L. *J. Am. Chem. Soc.* **2018**, *140*, 5352.
2. Fliegl H., Valiev R., Pichierri F.; Sundholm D. *In Chemical Modelling.* **2018**, *14*, Chapter 1, 01.
3. Dimitrova M., Sundholm D. *In Aromaticity.* **2021**, Chapter 5, 155.
4. Mahmood A., Dimitrova M., Wirz L. N., Sundholm D. *J. Phys. Chem. A.* **2022**, *126*, 1936.
5. Sundholm D., Dimitrova M., Berger R. *J. Chem. Comm.* **2021**, *57*, 12362.
6. Jusélius J., Sundholm D., Gauss J. *J. Chem. Phys.* **2004**, *121*, 3952.

Magnetic properties of 8-shaped porphyrinoids

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We have studied the current density induced by an external magnetic field of complex eight-shaped porphyrinoids. The studied porphyrinoids can be divided into three classes based on the number of the inner hydrogen atoms (N2, N4 and N6 as shown below). The ring current flows along the frame of the molecules from the outer side of one half of the molecule to the inner side of the other half and vice versa, which is similar to infinitene.[1] However, the current-density pathways have many branching points. The porphyrinoids and their dications have similar current densities when they have the same number of electrons, whereas current-density pathways of N2, N4 and N6 having different number of electrons differ. We also observe vertical through-space current-density pathways through the plane in the middle of the molecule. There are two isolated current-density loops in the two halves of N2, while for N4 there are two independent current-density loops in the upper and lower halves of the molecule (see below). N6 has a porphyrin-like ring current with a significant through-space pathway from the upper to the lower half. Integration of the ring-current strength shows that N2 is weakly antiaromatic with ring-current strengths of -2.38 nA/T in ortho-N2 and -6.29 nA/T in para-N2.[2,3] The dication of N4 is antiaromatic with the ring-current strengths of -8.54 nA/T. The dication of N6 and N4 are weakly aromatic or practically non-aromatic with ring-current strengths of 4.22 nA/T and 3.20 nA/T, respectively. N6 is aromatic with ring-current strengths of 7.57 nA/T. The current densities of the studied porphyrinoids depends on the number of electrons. However, the aromatic character does not follow the expected alternating aromaticity when adding two electrons.



The molecular structures of the studied porphyrinoids. The total ring current is shown for N4. The isolated ring-current pathways are shown for N2, N4 and N6.

References:

- [1] M. Orozco-Ic, R. R. Valiev, D. Sundholm, *Phys. Chem. Chem. Phys.*, **24** (2022) 6404.
- [2] D. Sundholm, F. Heike, B. Raphael, *WIREs Comput Mol Sci*, **6** (2016) 678.
- [3] J. Jusélius, D. Sundholm, J. Gauss, *J. Chem. Phys.*, **121** (2004) 3952.

Revealing Structure-Property Relationships in Polybenzenoid Hydrocarbons using Interpretable Machine- and Deep-Learning Methods

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Polybenzenoid hydrocarbons (PBHs) – molecules made up of multiple benzene rings – are the quintessential polycyclic aromatic species. The structure-property relationships of PBHs have both conceptual and practical implications and, because they serve as model systems for the much larger and more heterogeneous space of polycyclic aromatic systems, understanding them can enable design of new functional compounds and elucidation of reactivity in a broader context.

We interrogated these compounds using a combination of traditional computational techniques, including characterization of their aromatic character in the S_0 and T_1 states (as described with the NICS metric), their spin density in the T_1 state, and their S_0 – T_1 energy gaps. Regularities were revealed that allowed for simple and intuitive design guidelines to be defined.¹

To verify these guidelines in a data-driven manner, we generated a new database – the COMPAS Project²– which contains the calculated structures and properties of all PBHs consisting of up to 11 rings. Further, we developed and implemented two types of molecular representation to enable machine- and deep-learning models to train on the new data: a) a text-based representation³ and b) a graph-based representation.⁴

In addition to their predictive ability, we demonstrate the interpretability of the models that is achieved when using these representations. The extracted insight in some cases confirms well-known “rules of thumb” and in other cases contradicts common wisdom and sheds new light on this classical family of compounds. In addition to corroborating domain-experts’ interpretation, the different models also highlight additional relationships that are harder for the human eye to discern.

(1) Markert, G.; Paenurk, E.; Gershoni-Poranne, R. Prediction of Spin Density, Baird-Antiaromaticity, and Singlet–Triplet Energy Gap in Triplet-State Polybenzenoid Systems from Simple Structural Motifs. *Chemistry – A European Journal* **2021**, *27*, 1–14. <https://doi.org/10.1002/chem.202100464>.

(2) Wahab, A.; Pfuderer, L.; Paenurk, E.; Gershoni-Poranne, R. The COMPAS Project: A Computational Database of Polycyclic Aromatic Systems. Phase 1: Cata-Condensed Polybenzenoid Hydrocarbons. *J. Chem. Inf. Model.* **2022**. <https://doi.org/10.1021/acs.jcim.2c00503>.

(3) Fite, S.; Wahab, A.; Paenurk, E.; Gross, Z.; Gershoni-Poranne, R. Revealing Structure-Property Relationships in Polybenzenoid Hydrocarbons with Interpretable Machine-Learning. **2022**. <https://doi.org/10.26434/chemrxiv-2022-6dd6n>.

(4) Weiss, T.; Wahab, A.; Bronstein, A. M.; Gershoni-Poranne, R. Interpretable Deep-Learning Unveils Structure-Property Relationships in Polybenzenoid Hydrocarbons. **2022**. <https://doi.org/10.26434/chemrxiv-2022-krng1>.

Exploring the Size Limits of Global Aromaticity

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Identifying large globally aromatic molecules is very important for molecular electronics – in such systems, π -electrons are coherently delocalized around the whole molecular ring, leading to efficient charge and energy transport. Butadiyne-linked porphyrin nanorings with Hückel circuits containing up to 162 π -electrons have been experimentally shown to be globally aromatic or antiaromatic when charged,¹ but lack global aromaticity in the more chemically stable electrically neutral state. Fully fused porphyrin nanorings (Figure 1) benefit from a stronger coupling between the porphyrin subunits, and are thus prime candidates for exploring the limits of global aromaticity.

Here, we computationally investigate the global (anti)aromaticity in fully fused porphyrin nanobelts. As shown in recent correspondence between Anderson and Matito,^{2,3} the choice of an appropriate method, and especially the proportion of HF exchange in hybrid functionals, is critical in the evaluation of these systems. To minimize bias, we use double hybrid functionals and nonempirically tuned hybrid functionals to investigate these systems. Double hybrid functionals, which add a portion of MP2 correlation to the standard DFT correlation, have been shown to be more robust and accurate than regular hybrids,⁴ and they are especially well-suited for calculating chemical shielding.⁵ In a separate approach, we tune hybrid functionals for each system by making them obey Koopmans' theorem (nonempirical tuning). Together, these methods identify some of the largest neutral globally aromatic and antiaromatic systems known thus far (Figure 1).

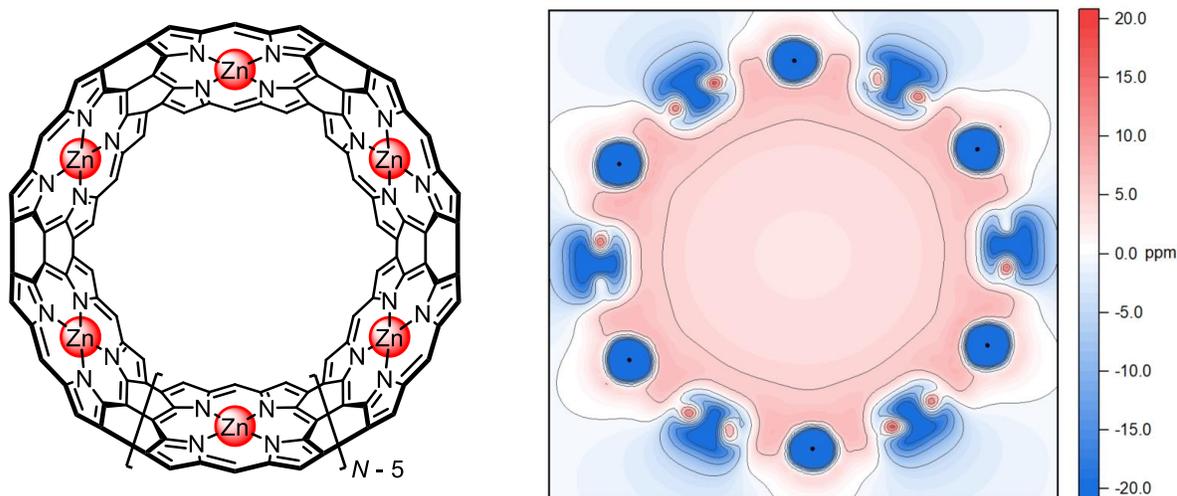


Figure 1. Left: General structure of fully fused porphyrin nanorings. Right: NICS(0)_{iso} plot for a fully fused 6-porphyrin nanoring, obtained using a nonempirically tuned PBE-based hybrid functional, showing a global antiaromatic current (zinc atoms are shown in black).

References:

1. Jirásek, M.; Anderson, H. L.; Peeks, M. D. *Acc. Chem. Res.* **2021**, *54*, 3241–3251.
2. I. Casademont-Reig, I.L Guerrero-Avilés, R.; Ramos-Cordoba, E.; Torrent-Sucarrat, M.; Matito, E. *Angew. Chem., Int. Ed.* **2021**, *60*, 24080–24088.
3. Deng, J.-R.; Bradley, D.; Jirásek, M.; Anderson, H. L.; Peeks, M. D. *Angew. Chem. Int. Ed.* **2022**, e202201231.
4. Kozuch, S.; Martin, J. M. L. *J. Comput. Chem.* **2013**, *34*, 2327–2344.
5. Stoychev, G.L; Auer, A.A.; Neese F. *J. Chem. Theory Comput* **2018**, *14*, 4756–4771.