

# ***MAGIC – 2018***

3<sup>rd</sup> workshop of MAGnetically Induced  
Currents in molecules

## **BOOK OF ABSTRACTS**

EDITOR

Slavko Radenković

23 – 28 September 2018, Kragujevac  
Serbia

# ***MAGIC – 2018***

3<sup>rd</sup> workshop of **MAGnetically Induced Currents in  
molecules**

23 – 28 September 2018, Kragujevac, Serbia

held under auspices of

**Faculty of Science, University of Kragujevac**

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## **Foreword**

This year MAGIC (**MAG**netically **I**nduced **C**urrents in molecules) workshop is the 3<sup>rd</sup> in the series started in 2014. The first MAGIC workshop was held in Tvärminne/Finland, and the second in Salerno/Italy.

The main purpose of the MAGIC workshop is to bring together established scientists, who made significant contributions to the field, as well as younger researchers, who are interested in future developments. Considering the success of the first two workshops, we expect that MAGIC 2018 will stimulate discussions on the state-of-the-art, open problems, new ideas, and that it will initiate and strengthen collaborations.

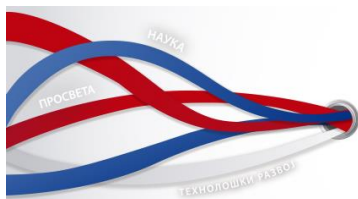
It is a great pleasure to welcome all of you and we wish you fruitful and enjoyable days in Kragujevac.

*Organizing committee of the MAGIC 2018*

## Acknowledgements



**Faculty of Science, University of Kragujevac**



Министарство просвете,  
науке и технолошког развоја



**Ministry of Education, Science and Technological Development,  
Republic of Serbia**

## **An Animated Visualisation of Orbital Angular Momentum and Spin-Orbit Coupling.**

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Visualisation of orbital angular momentum in a wavefunction may be accomplished by several methods: phase-colouring the wavefunction, plotting the current density (in the absence of magnetic field), or plotting the property density of the orbital angular momentum operator. Here, I present an additional method in which the orbital is animated by applying a time-dependent phase factor. This makes orbital angular momentum visible in a way that reflects the nature of the orbital angular momentum eigenfunction. This can be extended to examining the effects of spin-orbit coupling (SOC), which admixes higher orbital angular momentum states into the orbital; although the small extent of such admixture requires judicious scaling of one phase-component to properly visualise. The method is demonstrated using a model *p*-orbital and the singly-occupied molecular orbitals (SOMOs) of small doublet radicals. This method may prove of interest to quantum chemists whose work involves analysing properties where SOC is important, such as magnetic resonance parameters.

## Are Substituent Resonance Effects Responsible for Variations of $^1\text{H}$ NMR Chemical Shifts in Aniline and Nitrobenzene?

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While many phenomena in chemistry are explained in terms of  $\pi$ -electron effects, recent computational studies have revealed the significance of the  $\sigma$ -electronic system. Thus, for example, it was shown that  $^{13}\text{C}$  NMR chemical shifts of substituted benzenes can not be explained by the substituent resonance effects involving the  $\pi$ -electronic system, as classically suggested, but by the effects from the few nearest  $\sigma$ -orbitals [1]. Our DFT study on two substituted benzenes, possessing an electron-donating ( $\text{NH}_2$ ) and an electron-accepting group ( $\text{NO}_2$ ), showed that  $^1\text{H}$  NMR chemical shifts, too, are better explained by the  $\sigma$ -electronic effects, with the exception of *meta*- and partly *para*-protons of aniline. For *ortho*-hydrogen atoms of nitrobenzene the oxygen in-plane lone pairs are important, as well [2].

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## Magnetically Induced Current Densities in Porphycene and Porphycene Isomers

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Magnetically induced current densities have been calculated and analyzed at the density functional theory (DFT) level for a number of synthesized and yet to be synthesized porphycene and porphycene isomers using gauge-including magnetically induced current (GIMIC) method. The current pathways have been determined by numerical integration of the current flow along selected bonds. All studied molecules are aromatic according to the magnetic criterion. For all investigated molecules the current bifurcate into an outer and inner branch at the pyrrolic subring. For unsubstituted porphycene and porphycene isomers, large portion of the current takes the outer path for the pyrrolic subring which contains an inner hydrogen, whereas, the current divides almost equally for the pyrrolic subring without an inner hydrogen. For substituted porphycene, the presence of the electron-withdrawing NO<sub>2</sub> at the *meso* position does not change the ring current pattern at the pyrrolic subring, however, the current pattern at the pyrrolic subring is affected by the presence of the electron-withdrawing CF<sub>3</sub> at the  $\beta$ -carbon position of the pyrrolic ring.

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## Gauge-invariant magnetic response properties from the induced current

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In this work we solve two problems related to the calculation of static and dynamical electromagnetic properties with *ab initio* theories [1,2,3]:

- 1) we show that the dependence of the dynamical magnetic dipole moment on the reference point of the multipole expansion and on the “gauge origin” of the vector potential have a clear physical significance. They are due to a dynamical electric dipole moment and an electric field, respectively. Both are fully determined by the experimental setup and do not pose any fundamental problem, contrary to what is commonly assumed.
- 2) in the static case, any dependence on the gauge origin is an artifact of the computational method. We show that the artificial dependence on the gauge origin can be removed in an elegant way by the introduction of a sum rule that puts diamagnetic and paramagnetic contributions on an equal footing.

Our approach can be applied to calculate any magnetic observable that can be derived from the current density, and can be used in combination with any *ab initio* theory from which it can be obtained.

To illustrate our method we apply it here to time-dependent current-density-functional theory for the calculation of static and dynamical magnetizabilities of molecules.

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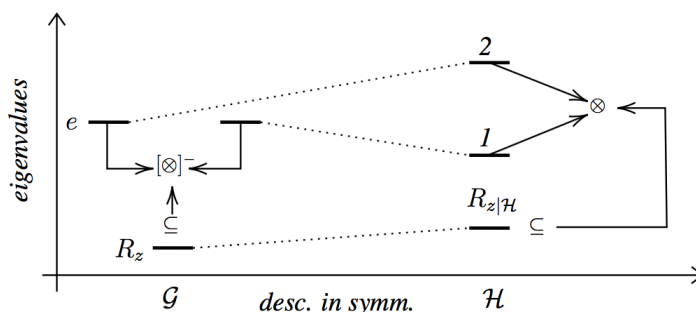
## A connection between Jahn-Teller distortion and paratropic currents by symmetry

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Group theoretical considerations show that systems that undergo first order Jahn-Teller-distortion [1] of  $E \times e$  type can be partitioned into two classes. One class gives rise to HOMO-LUMO symmetries fulfilling the selection rule for paratropic (paramagnetic) response [2]. These are found in the point groups of  $C_n$ ,  $D_n$ , and  $S_n$  type. The other class does not contain such a symmetry relation and is comprised of tetrahedral and octahedral point groups. These results shed some light on the phenomenon of anti-aromaticity and the fact that symmetry breaking is often observed in organic ring systems showing also paramagnetic response, while this connection has not been observed for metal coordination compounds.



**Scheme:** descending in symmetry retains the rotation around the main axis in the tensor product between representations.

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## Topological Ring-Currents and Bond-Currents in Some Neutral and Dianionic *Altans* of Corannulene and Coronene

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The novel series of conjugated systems called *altans*, defined nearly a decade ago,<sup>1</sup> was subsequently extended to multiple ('iterated')<sup>2</sup> *altans* and their magnetic properties were calculated by Monaco and Zanasi using the *ab initio ipso*-centric formalism.<sup>2,3</sup> Such properties of the single ('mono') *altans* of corannulene and coronene, calculated by this sophisticated *ab initio* approach, have since been compared<sup>4</sup> with those calculated *via* the rudimentary Hückel–London–Pople–McWeeny (HLPM) method<sup>4-8</sup> — a parameter-free 'topological', quasi graph-theoretical approach requiring knowledge only of the conjugated system's molecular graph and the areas of its constituent rings. These investigations are here extended to double and triple *altans*. HLPM bond-currents in several neutral mono *altans* are found to differ from those in the corresponding dianion *only in those bonds that lie on the structures' perimeters*, whilst the HLPM bond-currents in *all* bonds in the neutral double and triple *altans* of corannulene and coronene are *precisely the same as in the respective dianions*. Some rationalisation of these unexpected phenomena is offered in terms of the HOMO–LUMO nature of the role played by the lone non-bonding orbital in each of the neutral species and its respective dianion.

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## Halomethanes and CH fragments in strong magnetic fields

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The electrons in a molecule interact with an external magnetic field, affecting the electronic structure, energy and geometry. Atomic orbitals with high angular momenta lower their energy and can become the ground state. The Schrödinger equation involves an additional term, where the angular momentum operator appears, thus requiring that atomic and molecular orbitals are complex functions. We are investigating the electronic states and geometries of methane, halogenated methanes and their building blocks: H, C, H<sub>2</sub>, H<sub>3</sub>, H<sub>4</sub>, HF, HCl, CH, CH<sub>2</sub>, and CH<sub>3</sub>. We investigate the behaviour of halomethanes in magnetic fields up to one atomic unit  $B_0 = 235\,000$  T and compare the energies, geometries and the character of the excited states of the molecules. The atoms and molecules are studied in magnetic fields up to  $B_0$  using the LONDON program<sup>1</sup> at the unrestricted Hartree-Fock level using the uncontracted aug-cc-pVTZ basis set and London orbitals to ensure gauge-origin independence. The multiplicity and stability of molecules change with the increase in the magnetic field strength. The CH fragment exhibits paramagnetic bonding when  $B > 0.4B_0$  and exists as a bound sextet. CH<sub>4</sub> exists in a singlet or triplet state until  $B \approx 0.1B_0$ . Quintet states might get stabilised by paramagnetic bonding. C – H bonds preferably orient themselves to be parallel to the magnetic field vector and gradually become shorter, while C – X bonds prefer to be perpendicular to the magnetic field.

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## Local aromaticity in phosphorus and nitrogen analogues of acenaphthylenes

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A several different criteria of aromaticity were used to perform a detailed study in a series of phosphorus and nitrogen analogues of acenaphthylenes. The analysis was performed by means of the following aromaticity indices: the energy effect (ef), multicenter delocalization indices (MCI), harmonic oscillator model of aromaticity (HOMA) index, nucleus-independent chemical shifts (NICS) and ring current maps. As expected, all these methods show that the extent of aromaticity of the five membered ring in all derivatives of phosphorus and nitrogen analogues of acenaphthylene is quite small. In the previous studies it was shown that cyclic conjugation of the five membered ring depends on the size of the polyacenic part and on the position of the five membered ring along the polyacenic part of the given acenaphthylene derivatives. In this paper we report that according to our results most of the aromatic indices predict increase of cyclic conjugation in the five membered ring in phosphorus and nitrogen analogues of acenaphthylenes.

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## Theoretical studies of magnetically induced currents as a tool for understanding the aromatic character of novel compounds

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An overview over different theoretical approaches to study the aromatic character of novel compounds with the focus on magnetically induced current densities will be given.[1, 2] The current densities presented are obtained with the gauge including magnetically induced current density method (GIMIC).[3-5] Observed trends as well as new visualization features for current densities are presented.[6] It is shown that new insights can be obtained by complementing experimental work with computed current densities.[7,8] A thorough current density analysis can lead to novel viewpoints and detailed interpretations of experimental findings as compared to many other approaches.

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## Methods for partitioning the $\pi$ -electrons by rings in polycyclic aromatic hydrocarbons as parameters for the qualitative elucidation of ring currents

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Partition of  $\pi$ -electrons by the rings in polycyclic aromatic compounds had been introduced fifteen years ago by M. Randić and A. T. Balaban [1,2]. Nowadays, several methods for calculating the electron contents of rings (*EC*) of various polycyclic compounds have been devised [3]. All of them are based on the valence-bond method and their calculations are not computer-demanding. Nonetheless, these *EC*-values might be used for the quite accurate qualitative description of ring-current maps of large benzenoid systems. In this talk, some of the methods for the distribution of  $\pi$ -electrons by the rings in benzenoid hydrocarbons and phenylenes will be outlined.

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## Are aromatic molecules suitable candidates for high dielectric materials?

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High dielectric materials are interesting for their application in electronic devices. Especially of interest are high dielectric materials for the use in organic photovoltaic devices. It has been proposed that a high dielectric constant reduces exciton recombination and enhances exciton dissociation. The high dielectric constant is related to the polarisability of molecules, and in turn, the polarisability has been connected to aromaticity [2,3]. For identification of aromaticity, the ring current criterion is used. We now started a study to relate the aromaticity of molecules to their dielectric constant, with the aim to search for materials that can be used in organic photovoltaic devices. In this presentation, our first results are presented.

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## Closed-Shell Molecular Paramagnetism

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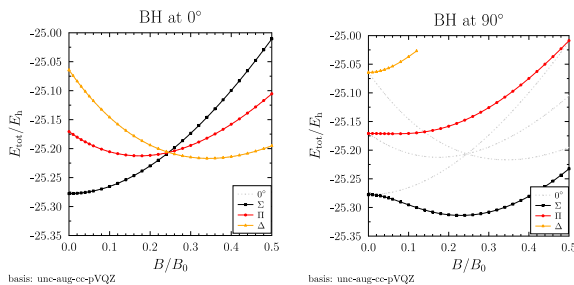
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In a magnetic field, atoms and molecules behave in a complicated and often fascinating manner, challenging both our understanding of electronic structure and our computational methods. For example, the evolution of electronic states with increasing field strength is characterized by a complicated competition between para- and diamagnetism. As a result, all open-shell molecules are paramagnetic, whereas most closed-shell molecules are diamagnetic. However, some closed-shell molecules such as BH are paramagnetic for certain field orientations; see Figure 1. In the talk, para- and diamagnetism are discussed with emphasis on closed-shell paramagnetism, illustrated by high-quality molecular calculations at the coupled-cluster level of theory [1].



**Figure 1.** The CCSD (EOM-CCSD) energy of the three lowest states of the BH molecule plotted against the magnetic field strength with the field vector parallel (left) and perpendicular (right) to the molecular axis. One atomic unit of field strength  $B_0 = 2.35 \cdot 10^5$  T.

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## What is the Multiplicity of the Bonds in C<sub>2</sub> and S<sub>2</sub>N<sub>2</sub> and Can We Say that S<sub>2</sub>N<sub>2</sub> is Aromatic?

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The carbon-carbon and sulfur-nitrogen bonds in the ground states of C<sub>2</sub> and S<sub>2</sub>N<sub>2</sub>, at their equilibrium geometries, are characterised by analysing the changes in the off-nucleus magnetic shielding tensor within the space surrounding each of these molecules. A wide range of quantum-chemical approaches, including full-valence CASSCF-GIAO, CCSD(T)-GIAO and CCSDT-GIAO, all with the cc-pVQZ basis set, as well as HF-GIAO and MP2-GIAO, with the cc-pVQZ, cc-pV5Z and cc-pV6Z basis sets, show that the surroundings of the carbon-carbon bond in C<sub>2</sub> are more shielded than those of the triple carbon-carbon bond in C<sub>2</sub>H<sub>2</sub>. The additional shielding of the carbon-carbon bond in C<sub>2</sub> is found to be due to a larger paramagnetic contribution to component of the shielding tensor which is perpendicular to the molecular axis. The analysis of the off-nucleus shielding data indicates that the carbon-carbon bond in C<sub>2</sub> is “bulkier” and, therefore, of a higher multiplicity, but weaker than the corresponding bond in C<sub>2</sub>H<sub>2</sub> [1]. CASSCF-GIAO/cc-pVTZ shielding data for S<sub>2</sub>N<sub>2</sub> indicates bonding consistent with a 2π electron system of rather low aromaticity. However, the CASSCF-GIAO/cc-pVTZ analyses of the lowest singlet and triplet excited states of S<sub>2</sub>N<sub>2</sub> suggest strong antiaromaticity, similar to that observed in the corresponding states of benzene [2]. According to these results, disulfur dinitride provides the first example of an inorganic ring for which theory predicts a switch in aromatic character upon excitation.

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## Gauge invariance and origin independence of electronic charge density and current density induced by optical fields

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Expressions for the first order polarization charge density  $\rho^{(1)}$  and current density  $\mathbf{J}^{(1)}$ , induced in the electrons of a molecule by the optical fields of a monochromatic plane wave, have been obtained. Within the (long wavelengths) dipole approximation, the electric field  $\mathbf{E}$  and its time-derivative  $\dot{\mathbf{E}}$  (assumed spatially uniform) fully determine  $\rho^{(1)}$  and  $\mathbf{J}^{(1)}$  respectively. To the next higher quadrupole approximation, in which the magnetic field  $\mathbf{B}$  and the electric field gradient  $\nabla\mathbf{E}$  are assumed uniform, a contribution to  $\rho^{(1)}$  from the time derivative of  $\mathbf{B}$ , and a contribution to  $\mathbf{J}^{(1)}$  from the time derivative  $\nabla\dot{\mathbf{E}}$ , are found. Within the quadrupole approximation, the first-order densities are shown to be invariant in a gauge transformation of the scalar potential  $\phi$  and vector potential  $\mathbf{A}$ , induced by the generating function  $f = -(1/2)\mathbf{B} \times d\dot{\mathbf{Y}}r$ . The gauge-transformed densities involve terms depending on  $\mathbf{B}$ ,  $\nabla\mathbf{E}$  and their time derivatives, which cannot be separated: gauge invariant properties are only obtained by mixing them, e.g., both  $\mathbf{B}$  contributions and  $\nabla\dot{\mathbf{E}}$  contributions are to be included in  $\mathbf{J}^{(1)}$ . At variance with the case of a static magnetic field, in which the transformation induced by  $f$  can be described as a translation of coordinate system, a shift of origin of the time dependent densities is shown to depend also on contributions arising from the electric field  $\mathbf{E}$ , which is no longer uniform in the quadrupole approximation. The relevant conclusion is that, within the quadrupole approximation, the three current densities induced by  $\dot{\mathbf{E}}$ ,  $\nabla\dot{\mathbf{E}}$  and  $\mathbf{B}$  cannot be treated separately and should be considered as a whole to preserve the translational invariance of their sum. Whereas the space integral of  $\mathbf{J}^{(1)}$  vanishes identically for a static magnetic field, implying charge conservation, integrals  $\int \mathbf{J}^{(1)} d^3r$  for the various contributions arising from  $\dot{\mathbf{E}}$ ,  $\mathbf{B}$  and  $\nabla\dot{\mathbf{E}}$  are nonzero, giving contributions to the time derivative of the electric dipole moment induced in the electron cloud via terms depending on electric dipole polarizability, mixed electric dipole-electric quadrupole polarizability, and mixed electric dipole-magnetic dipole polarizability. In addition, integrals  $\int \mathbf{J}^{(1)} d^3r$  are equal to corresponding time-derivatives of integrals involving moments of the polarization charge density,  $d/dt \{ \int \rho^{(1)} \mathbf{r} d^3r \}$ . An expression for the magnetic-field induced time-dependent current density obtained by continuous translation of the origin of the coordinate system, formally killing the diamagnetic contribution, has been arrived at, finding that its sum with the conventional paramagnetic contribution is separately origin independent.

## Investigation of Magnetically Induced Current Density on Helicene compounds

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Helicene compounds are very interesting molecules that combine a helical conformation and  $\pi$ -electron delocalization. In order to investigate the aromaticity of these systems, different magnetic criteria have been investigated: the NICS values, the magnetically induced current density as well as its integration through a plane cutting the different chemical bonds. For that, Gaussian 16 program together with the GIMIC code [1] have been used. Starting from [6]Helicene molecule, we have investigated larger and larger helicenes up to 20 fused benzene rings. Among the interesting features, we have noticed that the two extrema rings bear the largest induced current values as well as the smallest NICS(0) values. From [7]Helicene, we have substituted 1, 3 and 4 benzene rings by either pyrrole or thiophene moieties. Results have shown that the 5-membered rings were having the smallest current value.

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## A mystery of a through-space indirect NMR spin-spin coupling

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Indirect nuclear spin-spin coupling constants are amongst the most important magnetic resonance parameters, invaluable in establishing molecular structure from NMR spectroscopy. Their detailed understanding in terms of molecular and electronic structure is thus of central importance in many fields of research and has been pursued since the beginnings of NMR spectroscopy. Nowadays quantum-chemical calculations can offer a variety of tools for the interpretation of couplings including visualization of spin-spin coupling pathways by real-space functions [1-3].

In this presentation we will show how visualization of NMR spin-spin coupling pathways has been used for interpretation of the experimentally detected “through-space” indirect spin-spin couplings between protons formally separated by 18 covalent bonds.[4] The bilinear response of the total electron density to the nuclear magnetic moments of the interacting nuclei will be analyzed.

### **Acknowledgment.**

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## Visualization of EPR Hyperfine Structure Coupling Pathways

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Paramagnetic compounds represent an important class of technologically relevant materials. They can be used as contrast agents for enhancing NMR imaging, molecular magnets, materials for spintronics and advanced information storage, transition-metal battery materials and many others. Paramagnetic NMR spectra contain a wealth of information about paramagnetic compounds but their interpretation is often challenging.[1,2] One of the most interesting questions in the analysis of pNMR shifts concerns the pathways of the contact and pseudocontact shifts which help to understand the structure-property relations for paramagnetic compounds. [3]

In the present work we propose a new tool for visualization of hyperfine coupling pathways based on our experience with visualization of NMR indirect spin–spin couplings.[4] The plotted 3D-function is the difference between the total electron densities when the magnetic moment of the nucleus of interest is parallel and antiparallel to the external magnetic field and as such is an observable from the physical point of view. In contrast to the widely used visualization of spin density, our new approach depicts only the part of the electron cloud of a molecule that is affected by the interaction of the unpaired electron(s) with the desired nuclear magnetic moment.

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## Topological Ring-Currents and Clar Sextets in Fully Benzenoid Hydrocarbons

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It is well-known that the very special family of conjugated systems described as ‘fully benzenoid hydrocarbons’ have a unique Clar structure that causes all their rings to be classified as either ‘full’ or ‘empty’.<sup>1</sup> In this work,  $\pi$ -electron ring-currents in several dozen such structures are calculated by means of the quasi-graph-theoretical, parameter-free Hückel–London–Pople–McWeeny method.<sup>2–4</sup> In the case of benzenoid hydrocarbons, the calculated values of such ‘topological’ ring-currents depend only on the carbon–carbon connectivity of the system in question.<sup>2</sup> It is found that, until a certain fully benzenoid hydrocarbon comprising 17 rings is examined, all ring currents in *full* rings are seen to be *larger* in intensity than the ring current in benzene while such currents in *empty* rings are *less* than the benzene value. There is an indication that this distinction might break down when ‘giant’ fully benzenoid structures are considered. Accordingly, these studies are extended to a selection of fully benzenoid hydrocarbons containing up to 43 rings. It is still found that *all* full rings in all structures bear ring currents that are *greater* than the ring current in benzene but in several of the larger systems empty rings are found to bear ring currents greater than the benzene value. In the very largest structures examined, the ring currents in some of the empty rings are greater than the currents in as many as *half* of the symmetrically non-equivalent full rings. Furthermore, the full ring(s) with the largest current and the empty ring(s) with the largest current are both to be found at or near the centre of the fully benzenoid system in question.

These conclusions are consistent both with chemical intuition and earlier studies connecting Clar aromatic sextets with NICS calculations.

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## AACID: the Anisotropy of the Asymmetric magnetically Induced Current Density tensor

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Molecular magnetic properties, such as the magnetizability, the magnetic shielding, and the current strength, all stem from the asymmetric current density tensor. The anisotropy of that tensor (known by the metathesized acronym of the Anisotropy of the magnetically Induced Current Density tensor), was previously defined from its symmetric component only [1-2]; it is a scalar field expected to bear useful information on molecular structure. Criticisms to the physical meaning of ACID have appeared in literature [3-4]. A more general anisotropy has been recently defined [5], considering the full asymmetric tensor and its eigenvalues in the complex plane. Published and new results show that the latter anisotropy, called AACID (by the still metathesized acronym of the Anisotropy of the Asymmetric magnetically Induced Current Density tensor), is sensibly different from the previously defined ACID, and promises to be a useful tool in the study of molecular structure and aromaticity.

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## Magnetic properties in the Frozen Density Embedding framework – lessons from the topological data analysis perspective

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In this contribution we discuss the application of various tools from the rich scientific visualization domain to study the magnetically-induced current density and magnetic property densities (such as the NMR shielding density and the magnetizability density) calculated with the Frozen Density Embedding (FDE) scheme [1-4] in the 4-component relativistic framework. In particular, we will focus on applying the topological data analysis tools [5] to the data from FDE calculations in order to address the following questions: (i) how does the topology of various densities of a molecular system change upon embedding this system in an environment and (ii) is FDE able to account for that change? Additional motivation in these studies is to clarify what information can be extracted from plots of different densities and to propose a visualization pipeline that can accompany the FDE calculations.

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## On Triplet State Baird (Anti)Aromaticity in Polycyclic, Macrocyclic and Through-Space Conjugated Hydrocarbons

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In the first  $\pi\pi^*$  triplet state ( $T_1$ ) the rule for aromaticity and antiaromaticity is opposite to Hückel's rule, as shown by Baird,<sup>[1]</sup> *i.e.*, annulenes with  $4n$   $\pi$ -electrons are aromatic in  $T_1$  while those with  $4n + 2$  are antiaromatic. Today, Baird's rule has been confirmed by a range of quantum chemical calculations and by experiments.<sup>[2]</sup> Yet, the scope and limitations of Baird's rule need to be assessed. First, how does it apply to polycyclic conjugated hydrocarbons? We found that  $T_1$  state antiaromaticity of many polycyclic aromatic hydrocarbons tend to localize to certain hexagons.<sup>[3]</sup> Conversely, in polycyclic antiaromatic hydrocarbons, having central  $4n\pi$ -electron units, the  $T_1$  state aromaticity localizes to the  $4n\pi$ -electron unit provided that Hückel-aromatic  $\pi$ -sextets can form in the benzene rings that are disjoint with the central  $4n\pi$ -electron unit.<sup>[4]</sup> Thus, Baird's rule can be combined with Clar's rule. On the other hand, in some  $\pi$ -conjugated macrocycles in their  $T_1$  states, *e.g.*,  $[n]$ cycloparaphenylenes, we observed a tug-of-war between global macrocyclic Baird-aromaticity and local Hückel-aromaticity in individual monocycles. Finally, we discovered the existence of  $T_1$  state homoaromaticity, *i.e.*,  $T_1$  aromaticity involving one or several through-space conjugated linkages, yet, the strength varies significantly between different molecules.<sup>[5]</sup>

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## Link between aromatic polycyclic aromatic hydrocarbons and boron hydrides

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A direct connection is established between three-dimensional aromatic *closo* boron hydride clusters and planar aromatic [*n*]annulenes for medium and large boron clusters.<sup>[1]</sup> In particular, the results prove the existence of a link between the two-dimensional Hückel rule, as followed by aromatic [*n*]annulenes, and Wade–Mingos' rule of three-dimensional aromaticity, as applied to the aromatic [*BnHn*]<sup>2-</sup> *closo* boron hydride clusters. The *closo* boron hydride clusters can be categorized into different series, according to the *n* value of the Hückel (4*n*+2)  $\pi$  rule.<sup>[2,3]</sup> The distinct categories studied in this work correspond to *n*=1, 2, and 3. Each category increases in geometrical difficulty but, more importantly, it is possible to associate each category with the number of pentagonal layers in the structure perpendicular to the main axis. Category 1 has one pentagonal layer, category 2 has two, and category 3 has three.

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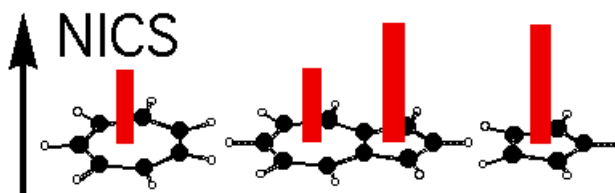
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## Nucleus Independent Chemistry by Schleyer

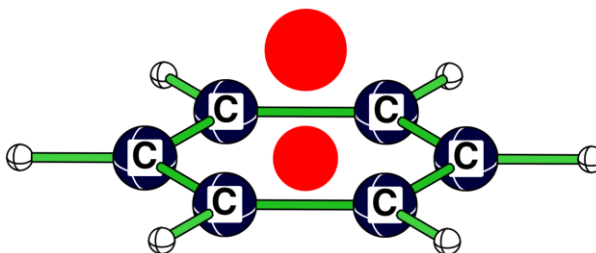
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Aromaticity is one of the most fundamental concepts originated in organic chemistry and today applied in all chemical disciplines. While Hückel's theory of aromaticity is taught already in school, the fully understanding of aromaticity is still a recent topic in theoretical oriented chemistry.



In 1996, 22 years before, the research team of Paul von Ragué Schleyer published a new criterion for aromaticity called NICS (Nucleus-Independent Chemical Shift). According to the citations of the most relevant manuscripts related to this method, NICS is the most common used criterion for investigation of aromaticity. In this contribution we will follow the process leading to NICS and the impact of NICS-calculations on different topics, not always directly connected to aromaticity.



## Double aromaticity and ring currents in triple-layered beryllium-boron clusters

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In the recent papers [1,2]  $\text{Be}_6\text{B}_{11}^-$  and  $\text{Be}_6\text{B}_{10}^{2-}$  clusters were theoretically examined.  $\text{Be}_6\text{B}_{11}^-$  and  $\text{Be}_6\text{B}_{10}^{2-}$  were found to be the triple-layered clusters having a  $\text{B}_{11}/\text{B}_{10}$  central ring being sandwiched by two  $\text{Be}_3$  rings. In the present study the double aromatic nature of the studied systems was analyzed using current density maps computed by means of the BLYP functional using the diamagnetic-zero variant of the continuous transformation of origin of current density (CTOCD-DZ) method [3,4]. It was shown that the double aromaticity of the examined Be-B clusters arises from the presence of two orthogonal, cyclically delocalized electronic systems. The pattern of current density distribution in the triple-layered Be-B clusters was found to be analogous to the monocyclic  $\text{C}_{10}$  cluster.

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## Visualization of current densities calculated by means of the relativistic two- and four-component electron dynamics

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We present an implementation and application of electron dynamics (real-time time-dependent DFT) based on non-relativistic as well as relativistic 2-component (X2C) and 4-component (Dirac–Coulomb) Hamiltonians to the calculation of various spectroscopic properties, such as electron absorption (EAS) [1], electron circular dichroism (ECD) or optical rotatory dispersion (ORD) [2]. The spectra are obtained by the Fourier transform of the time-dependent induced electric/magnetic dipole moment recorded during a real-time propagation of the electronic density matrix perturbed by an external electric/magnetic field. In addition, we also show how the electron dynamics approach allows to access the charge and current densities associated with the spectroscopic properties. Visualization of the densities provides an additional tool for the analysis of processes that occur at atto- and femto-second time scale. We believe that these results support (relativistic) electron dynamics as a viable and perspective tool for molecular property calculations and visualizations [3].

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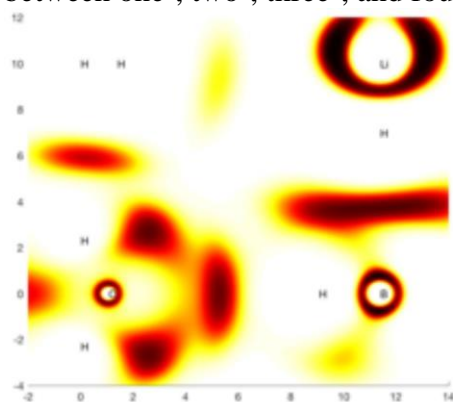
## A local tensor that unifies kinetic energy density and vorticity dependent exchange-correlation functionals

Sangita Sen\*, Erik Tellgren

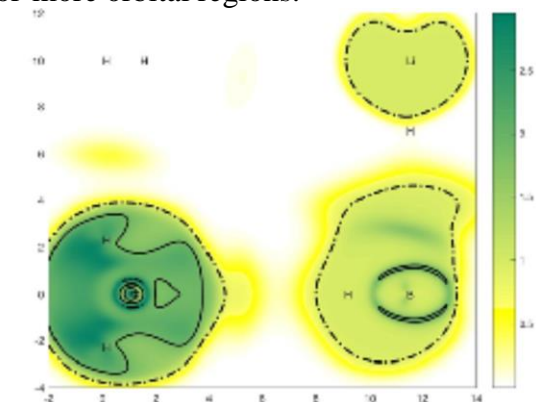
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We present a kinetic energy tensor that unifies a scalar kinetic energy density commonly used in meta-Generalized Gradient Approximation (mGGA) functionals and the vorticity density that appears in paramagnetic current-density-functional theory (CDFT). Both types of functionals can thus be subsumed as special cases of a novel functional form that is naturally placed on the third rung of Jacob's ladder. Moreover, the kinetic energy tensor is related to the exchange hole curvature, is gauge invariant, and has very clearcut Nrepresentability conditions. The latter conditions enable the definition of effective number of non-negligible orbitals. Whereas quantities such as the Electron Localization Function (ELF) can discriminate effective one-orbital regions from other regions, the present kinetic energy tensor can discriminate between one-, two-, three-, and four-or-more orbital regions.



ELF plot for the H<sub>2</sub>-LiH-BH-H<sub>2</sub>O system.



Effective rank estimates for the H<sub>2</sub>-LiH-BH-H<sub>2</sub>O system from our kinetic energy tensor,  $\mathbf{Q}$ . Contour lines are displayed for visual support at the levels 0.9 (dash-dot), 1.9 (solid), and 2.9 (dashed).

## The Gauge-Including Magnetically Induced Currents Method

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Recent developments and applications of the gauge-including magnetically induced currents (GIMIC) method will be presented.[1,2,3] The GIMIC method and its applications on porphyrinoids have recently been reviewed.[4,5] Studies of the GIMIC method on hydrocarbon rings and carbon nanostructures will be discussed.[6,7,8] Current-density studies on carbon nanotori yield information about how the ring pattern of the carbon structures determines the ability of the tori to sustain strong magnetically induced ring currents. Calculations on helical molecules show that they might sustain current densities with one ring-current component flowing around the main ring and one component perpendicular to it, which gives rise to interesting magnetic response properties. Recent GIMIC studies will also be presented in the talks by Benkyi, Dimitrova, Fliegl, Valiev and Wirz.

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## Magnetically Induced Currents in Strong Fields

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Recently, several programs have been developed for the treatment of molecules in magnetic fields up to 1 a.u. (~235,000 Tesla) [1, 2, 3]. I will discuss implementations in the QUEST program [3], which allow for the determination of magnetically induced currents (MAGICs) in strong fields via Hartree-Fock, current-density-functional, Moller-Plesset and coupled-cluster theories.

For all these methods MAGICs, bond currents and bond current profiles can be determined as a function of field strength. Connections to response currents available from the GIMIC program [4] will be discussed. The importance of open-shell  $\beta$ -spin ground states is highlighted for large field. Finally, MAGICs for excited states will be presented by using the maximum-overlap method [5].

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## The spectroscopic and magnetic properties of antiaromatic porphyrinoids and [8]circulenes

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Magnetic and spectroscopic properties of antiaromatic carbaporphyrins, carbathiaporphyrins, isophlorins, neutral and double charged hetero[8]circulenes have been investigated at density functional theory and *ab initio* levels of theory [1,2]. The calculations show that the paratropic contribution to the magnetically induced ring-current strength susceptibility and the magnetic dipole-transition moment between the ground and the lowest excited state are correlated. In the case of porphyrinoids the vertical excitation energy (VEE) of the first excited state decreases with increasing ring-current strength susceptibility, whereas the VEE of the studied higher-lying excited states are almost independent of the size of the ring-current strength susceptibility. Also, it was shown that the strong antiaromatic closed shell porphyrinoids are paramagnetic [3]. In the case of hetero[8]circulenes, it was shown that their dications are antiaromatic, dianions are aromatic and neutrals are nonaromatic [2].

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## Magnetically induced ring-current strengths in twisted annulenes

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Qualitative rules for the describing the aromaticity or antiaromaticity and hence magnetically induced electric currents in planar or Möbius-twisted molecules have been known for over 50 years.[1] However, no rules are known for general surfaces or the influence of the geometry for molecules with a given topology.

We are using the gauge including magnetically induced current (GIMIC) method[2] to explore the electric currents in a number of molecular model systems. We employ all-trans-[40]-annulene as a physical realisation of a closed twisted ribbon and explore the effect of different degrees of twist and geometries of those ribbons on the induced electrical current strength.[3]

This study not only serves a more complete understanding of the electronic structure of molecules with non-standard topologies but has potential applications, as for example very large para-/diatropic current strengths or the switching of magnetic properties through deformation of molecular systems.

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