

7th European Charge Density Meeting Warsaw, Poland

Book of Abstracts





7th European Charge Density Meeting

June 26th – July 1st, 2016

Centre of New Technologies University of Warsaw

Warsaw

Poland

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The
7TH EUROPEAN CHARGE DENSITY MEETING

is organised by:

Department of Chemistry, University of Warsaw
Committee of Crystallography of the Polish Academy of Sciences
Polish Crystallographic Association

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Welcome to ECDM7!

Dear Colleagues and Friends,

Welcome to Warsaw, welcome to Poland. We are very happy that after 4 year-long break, the next European Charge Density Meeting, already the 7th in the series (ECDM7), is organised at our University of Warsaw. This is a continuation of previous meetings held in Nancy (1996, France), Sitges (1999, Spain), Sandbjerg Estate (2003, Denmark), Brandenburg on the Havel (2006, Germany), Gravedona (2008, Italy) and Štrbské Pleso (2012, Slovakia). During the previous meeting at Štrbské Pleso (2012), we offered organisation of the next ECDM conference in Poland in the year 2015. It appeared however, that quite a few important conferences in our field (Sagamore and ECA Congress in Croatia) were organised in 2015. To avoid a clash and following the advice from the IUCr Charge, Spin and Momentum Commission and from the ECA SIG2 Charge, Spin and Momentum Density members, we decided to shift organisation of ECDM7 to the year 2016.

Similarly to previous conferences, we would like to present the latest results focused on charge density studies both experimental and theoretical. However, following advices from our Committees we wanted to accent more methodological, particularly statistical problems, resulting from recent advances in experimental hardware and software development, including large scale facilities. We were doing our best to prepare interesting and rich scientific program which would contain new theoretical and experimental accomplishments in our field. We also were trying to find a balance between conference activities and free time so need for informal discussions. We are very grateful to the all invited speakers who have decided to accept our invitations and come to this Conference. We also express our warmest thanks for all suggestions we have got from the members of the Scientific and International Advisory Committees. The list of covered topics at ECDM7 includes: a brief history of charge density investigations, errors in experimental and theoretical approaches, new approaches in modelling of charge density and thermal motion, understanding dynamics of atoms and structures, challenging experiments for charge densities, charge densities in the life sciences, from conceptual quantum chemistry to properties of molecules and crystals, progress in using large scale facilities, understanding & engineering of solid state materials, electron diffraction – the future of charge density measurements?

Our ambition as organisers of ECDM7 is – among others – to present and stress prospective areas of science such as, for example, electron microscopy, to begin a possible collaboration between members of our community and experts in other areas. We would especially like to attract newcomers to our field: young PhD students, young researchers and even students, as this would strengthen foundation of our future. Therefore, we are extremely thankful to Prof. Mark Spackman and Prof. Wolfgang Scherer who have kindly agreed to present contributions on the history of charge density investigations and on the milestones in the development of charge density studies.

We wanted to avoid invited lectures by those of our colleagues who have had this opportunity at different conferences within last 2-3 years, but even so, the selection of invited talks was a very difficult task, as the whole field is very lively and rich. As the meeting venue we have chosen the Centre of New Technologies, a new institute of the University of Warsaw, well equipped in all needed facilities. The end of June in Warsaw is

usually very sunny and pleasant and there is an abundance of the historical and cultural attractions. As a part of the social program we will organise excursions showing the beauty of the city and its rich history.

It would be great if such conferences as ours could help to organise a pan-European, or maybe even World-wide research program in the field of charge density studies, following excellent example of the program once funded by the Deutsche Forschungs Gemeinschaft (DFG). Finally, we wish to thank to all sponsors of ECDM7 including Committee of Crystallography, Polish Academy of Sciences, Rigaku Oxford Diffraction, Bruker AXS GmbH, International Union of Crystallography, European Crystallographic Association, Oxford Cryosystems Ltd, STOE & Cie GmbH, AXO DRESDEN GmbH, Centre of New Technologies UW, Department of Chemistry, University of Warsaw and Dectris for their generous support.

Charge density studies (and methods going beyond charge densities) are focused on quality: quality of data, quality of work and quality of the final results. These methods will shape the future of X-ray diffraction as they can replace the 100 year old Independent Atom Model. Our feeling is that this quality has already started fighting against quantity of routine investigations. At the end of the day quality always wins:). We hope that the ECDM7 activities will show off the quality charge density investigations. We wish all of us a fruitful and interesting meeting!

On behalf of the Organising Committee

Two handwritten signatures in black ink. The first signature on the left is 'Krzysztof Woźniak' and the second signature on the right is 'Paulina Dominiak'.

Prof. dr hab. Krzysztof Woźniak and Dr hab. Paulina Dominiak Chair and Vice-chair of the Organising Committee

INTERNATIONAL UNION OF CRYSTALLOGRAPHY

IUCr Scientific Freedom Policy Statement.

The Organizing Committee of the 7th European Charge Density Meeting (ECDM7) shall observe the basic policy of nondiscrimination and affirms the rights of scientists throughout the world to adhere or to associate with international scientific activity without regard to such factors as ethnic origin, religion, citizenship, language, political stance, gender, sex or age, in accordance with the Statutes of the International Council for Science.

At this meeting no barriers will exist which would prevent the participation of bona fide scientists.

On behalf of the Organising Committees

A handwritten signature in black ink, appearing to read 'Krzysztof Woźniak', written in a cursive style.

Krzysztof Woźniak (the Conference Chairman)

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GENERAL INFORMATION

ECDM7 CONFERENCE WEB PAGE

<http://ecdm7.chem.uw.edu.pl/>

ECDM7 RECEPTION DESK OFFICE HOURS

Sunday, June 26 th	15:00 – 20:30
Monday, June 27 th & Tuesday, June 28 th	08:30 – 19:00
Wednesday, June 29 th & Thursday, June 30 th	08:30 – 17:00
Friday, July 1 st	08:30 – 14:00

ECDM7 RECEPTION DESK PHONE NUMBER

+48 723 797 646

VENUE

The Conference takes place at the Centre of New Technologies of the University of Warsaw (address: Banacha 2C, 02-097 Warszawa, Poland; www.cent.uw.edu.pl) which is located at the Ochota Campus of the University of Warsaw in close proximity to the F. Chopin Airport (ca. 10 min. by taxi) and many hotels and hostels.

ABOUT WARSAW

Warsaw (Warszawa) is the capital of Poland and its largest city. Warsaw is a modern and dynamic city, and, as a true metropolis, it has a lot to offer. Here you can discover the extraordinary history of the Polish capital, meet its culture and tradition, or just simply have fun! For more information about the Capital of Poland:

<http://www.um.warszawa.pl/en>

<http://www.warsawtour.pl/en/tourist-attractions/top-10-3930.html>

http://www.warsawtour.pl/sites/default/files/article_brouchures/top_10_gb_wyd_ii_2013.pdf

<http://www.traveladvisortips.com/top-10-things-to-do-in-warsaw-poland/>

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GETTING AROUND IN WARSAW

Centre of New Technologies is located in Ochota district, which is very close and well connected to the city centre. There are trams (lines **1**, **14**, **25** from “**Banacha**” stop and lines **7**, **9** and more from Grójecka Street stop “**OCH-Teatr**”) and buses (“**Banacha Szpital**” is the closest bus stop) which can take you from Ochota to the city center, to the **railway station** and to the **airport**. To get to the Old Town buses **128** or **175** from “**Banacha Szpital 02**” stop are a good option. Tickets for buses and trams are available in vending machines and kiosks, as well as inside most of the buses and trams (although

those might have limited methods of payment). A **single ride ticket** (up to 75-minutes including changes) inside zone 1 (most of Warsaw) costs 4,40 PLN (1 euro).

Please remember, that you need to validate your ticket when you get on!

TAXI

If you wish to choose a taxi please choose the licensed one. You can also use **MyTaxi** app and choose the taxi most suitable for you:

<https://pl.mytaxi.com/index.html>

PUBLIC TRANSPORT JOURNEY PLANNER

You can also plan your journey using the **jakdojade** journey planner. The mobile version is available for Android, iOS and Windows Phone:

<http://warszawa.jakdojade.pl/>

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999: Ambulance

998: Fire Brigade

997: Police

981: Road Assistance

986: Municipal Police

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22 - 997 to call the police in Warsaw.

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ECDM7 Program



Sunday, June 26 th	Monday, June 27 th	Tuesday, June 28 th	Wednesday, June 29 th	Thursday, June 30 th	Friday, July 1 st
	9:00 – 12:30 S1 Errors in experimental and theoretical approaches	9:00 – 12:30 S3 Challenging experiments for charge densities	9:00 – 12:30 S5 From conceptual quantum chemistry to properties of molecules and crystals	9:00 – 15:40 S6 Understanding & engineering of solid state materials	9:00 – 10:20 S7 Electron diffraction – the future of charge density measurements?
	10:20 – 10:50 Coffee Break	10:20 – 10:50 Coffee Break	10:20 – 10:50 Coffee Break	10:20 – 10:50 Coffee Break	10:20 – 10:50 Coffee Break
	S1	S3	S5	S6	S7
	12:30 – 14:00 Lunch Break	12:30 – 14:00 Lunch Break	12:30 – 14:00 Lunch Break	12:30 – 14:00 Lunch Break	12:30 – 14:00 Lunch Break
	13:15 – 13:45 Bruker AXS GmbH: The Latest Generation D8 QUEST / D8 VENTURE: Welcome to the Future	13:15 – 13:45 Rigaku Oxford Diffraction: Advances in crystallography			
15:00 – 17:00 Registration	12:30 – 17:10 S2 New approaches in modeling of charge density and thermal motion	14:00 – 17:10 S4 Charge densities in the life sciences	14:00 – 17:00 Excursions	S6	
15:40 – 16:10 Coffee Break	15:40 – 16:10 Coffee Break	15:40 – 16:10 Coffee Break		15:40 – 16:10 Coffee Break	
17:00 – 19:00 OC Opening Ceremony	S2	S4		17:00 – 17:15 Departure for Dinner	
	17:30 – 19:00 Poster Session 1	17:30 – 19:00 Poster Session 2			
		18:30 – 19:00 Closed meeting of IUCr CSMD Commission		18:00 – 23:00 Conference Dinner	
19:00 – 20:30 Welcome Party					

Sunday, June 26th		
15:00 – 17:00	Registration	
15:40 – 16:10	Coffee Break	
	Registration	
Opening Ceremony Chair: Dietmar Stalke		OC
17:00 – 18:00	A brief history of charge density analysis, Mark A. Spackman	L1
18:00 – 19:00	Past and recent developments of experimental charge density studies - a European perspective, Wolfgang Scherer	L2
19:00 – 20:30	Welcome Party	

L – Invited lecture

Monday, June 27th		
Errors in experimental and theoretical approaches		S1
Chairs: Simon Coles, Piero Macchi		
Session sponsored by Rigaku Oxford Diffraction		
09:00 – 09:40	About Fit Quality Indicators, Julian Henn	L1
09:40 – 10:00	Diffraction data analysis in Jana2006, Václav Petříček	O2
10:00 – 10:20	Empirical correction for resolution- and temperature-dependent errors caused by factors such as thermal diffuse scattering, Regine Herbst-Irmer	O3
10:20 – 10:50	Coffee Break	
10:50 – 11:30	Prediction uncertainty of density functional approximations for properties of crystals, Bartolomeo Civalleri	L4
11:30 – 11:50	Assessing the reliability of charge density parameters and derived properties, Christian Jelsch	O5
11:50 – 12:30	Aspects of single crystal neutron diffraction, Matthias Gutmann	L6
12:30 – 14:00	Lunch Break	
13:15 – 13:45	Bruker AXS GmbH: The Latest Generation D8 QUEST / D8 VENTURE: Welcome to the Future	
New approaches in modeling of charge density and thermal motion		S2
Chairs: Simon Grabowsky, Ángel Martín Pendás		
14:00 – 14:40	On hydrogen-atom treatment in high-quality single crystal structure analysis, Birger Dittrich	L1
14:40 – 15:00	Combining multipole refinements and lattice dynamics: a case-study of L-alanine, Anders Østergaard Madsen	O2
15:00 – 15:20	Is relativity the hammer in charge density of heavy elements and their compounds? How heavy is the hammer - how heavy is heavy metal? Lukáš Bučinský	L3
15:20 – 15:40	Can the X-ray constrained wave function methods extract electron correlation effects on the electron density? Alessandro Genoni	O4
15:40 – 16:10	Coffee Break	
16:10 – 16:30	X-ray wave function refinement - overcoming the limitations of the multipole model, Magdalena Woińska	O5
16:30 – 17:10	A tale of two densities, Dylan Jayatilaka	L6
17:30 – 19:00	Poster Session 1 (odd poster numbers)	

L – Invited lecture, O – Oral presentation

Tuesday, June 28th		
Challenging experiments for charge densities		S3
Chairs: Bartolomeo Civalleri, Carlo Gatti		
09:00 – 09:40	Concerning measurement errors in synchrotron X-ray charge density studies, John R. Helliwell	L1
09:40 – 10:00	The resolution dependence of aspherical core refinements: the case of light atoms, Andreas Fischer	O2
10:00 – 10:20	Probing chirality with high energy synchrotron light, Vadim Dikadkin	O3
10:20 – 10:50	Coffee Break	
10:50 – 11:30	Insights into single molecule magnetism from charge and spin density studies, Jacob Overgaard	L4
11:30 - 11:50	Experimental and theoretical electron density analysis of copper pyrazine nitrate quasi-low-dimensional quantum magnets, Leonardo H. R. Dos Santos	O5
11:50 - 12:10	Nuclear dynamics in the metastable phase of the solid acid caesium hydrogen sulfate, Matthew Krzystyniak	O6
12:10 - 12:30	Chemical bonding in boron polymorphs and boron carbide, Sander van Smaalen	O7
12:30 – 14:00	Lunch Break	
13:15 – 13:45	Rigaku Oxford Diffraction: Advances in crystallography	
Charge densities in the life sciences		S4
Chairs: John R. Helliwell, Maciej Kubicki		
14:00 - 14:40	Reproducibility in biomedical sciences, Wlodek Minor	L1
14:40 - 15:20	Using QM methods to refine biological structure, Kenneth M. Merz Jr.	L2
15:20 - 15:40	Study of the key interactions in the self-recognition of the anti-malarial drug chloroquine, Giovanni Macetti	O3
15:40 – 16:10	Coffee Break	
16:10 – 16:50	GEM, a force field based on density fitting for scalable molecular dynamics simulations, Jean-Philip Piquemal	L4
16:50 – 17:10	Crystal and enzyme environmental effects on the electron density of a cysteine protease inhibitor, Florian Kleemiß	O5
17:30 – 19:00	Poster Session 2 (even poster numbers)	
18:30 – 19:00	Closed meeting of IUCr CSMD Commission	

L – Invited lecture, O – Oral presentation

Wednesday, June 29 th		
From conceptual quantum chemistry to properties of molecules and crystals		S5
Chairs: Birger Dittrich, Anders Østergaard Madsen		
09:00 – 09:40	Information-theoretic approaches to Atoms-in-Molecules, Patrick Bultinck	L1
09:40 - 10:00	Can electrons attract each other? Lucjan Piela	L2
10:00 - 10:20	Revealing the role of spin-relativistic effects on bonding in molecules and solids, Alexey I. Baranov	O3
10:20 – 10:50	Coffee Break	
10:50 – 11:30	Some emergent scalar and vector fields in Quantum Chemical Topology, Ángel Martín Pendás	L4
11:30 – 11:50	QTAIM study of tetracoordinated IVa metal complexes, Martin Breza	O5
11:50 – 12:10	Charge density analysis of the cubic diamond→ β -Sn phase transition of group 14 elements, Olga Matthies	O6
12:10 – 12:40	Combined analysis of intra- and intermolecular chemical bonding in organometallic compounds using QTAIM and Voronoi tessellations, Anna V. Vologzhanina	O7
12:30 – 14:00	Lunch Break	
14:00 – 17:00	Excursions	

L – Invited lecture, O – Oral presentation

Thursday, June 30 th		
Understanding & engineering of solid state materials		S6
Chairs: Mark Spackman, Jacob Overgaard, Jozef Kožíšek		
09:00 – 09:40	When experimental charge and spin density data challenge ab initio and DFT calculations, Claude Lecomte	L1
09:40 – 10:00	Uncovering the electrostatic nature of host-guest assemblies, Mingwen Shi	O2
10:00 – 10:20	Inter-layer binding energies from experimental charge densities: Exploring the plastic bending in a molecular crystal, Sajesh P. Thomas	O3
10:20 – 10:50	Coffee Break	
10:50 – 11:30	Locality of intermolecular interactions in organic crystals, Tonglei Li	L4
11:30 – 11:50	Experimental and theoretical charge density study of the I···N halogen bond and F···F interactions in iodoperfluoroalkylimidazoles, Davide Franchini	O5
11:50 – 12:10	Is there a link between charge density distribution and packing motif in donor-acceptor co-crystals?, Ivan V. Fedyanin	O6
12:10 – 12:30	Electron density studies as a new volume-based approach to thermophysical properties of ionic liquids, Yulia Nelyubina	O7
12:30 – 14:00	Lunch Break	
14:00 – 14:20	100 years Lewis diagram – still valid in the light of charge density?, Dietmar Stalke	O8
14:20 – 14:40	Anions with typical cation chemistry! Understanding the curious reactivity of [B ₁₂ X ₁₁] [−] , Simon Grabowsky	O9
14:40 – 15:00	Lone electron pair dispersion? - Charge density of cubic arsenic(III) oxide, Piotr A. Guńka	O10
15:00 – 15:20	Addressing the issue of bending in certain metallocenes: A comparative study of linear MgCp* ₂ vs. bent CaCp* ₂ through theoretical and experimental electron density analysis, Rumpa Pal	O11
15:20 – 15:40	Polarizabilities of atoms in molecules: the choice of partitioning schemes, Piero Macchi	O12
15:40 – 16:10	Coffee Break	
17:00 – 17:15	Departure for Dinner	
18:00 – 23:00	Conference Gala Dinner	

L – Invited lecture, O – Oral presentation

Friday, July 1st		
Electron diffraction – the future of charge density measurements?		S7
Chair: Wolfgang Scherer		
09:00 – 09:40	Electronic cryomicroscopy: from molecules to cells, Wolfgang Baumeister	L1
09:40 – 10:20	Approaching the physical limits of electron cryomicroscopy for structure determination, Christopher J. Russo	L2
10:20 – 10:50	Coffee Break	
10:50 – 11:30	Towards the measurement of bonding in and around inhomogeneities in nano-composite materials, Philip Nakashima	L3
11:30 – 12:30	Closing Ceremony	
12:30 – 14:00	Lunch Break	

L – Invited lecture



Opening Ceremony

Chair:

Dietmar Stalke

A brief history of charge density analysis

Mark A. Spackman

School of Chemistry and Biochemistry, University of Western Australia, Perth WA 6009, Australia

The field of experimental charge density analysis is now very active – even more so than when Philip Coppens wrote a decade ago that “Charge densities come of age” [1]. But it is increasingly uncommon for modern publications to cite the early and pioneering papers that were published in the 1960s, 1970s and 1980s, let alone even earlier work. Much of that work – experimental as well as theoretical and analytical – was extremely important to the development of the field, and its importance and relevance is in danger of being forgotten. Equally important are those early papers describing developments that were never fully appreciated at the time, but which may now deserve to be revisited. This presentation will attempt to outline a history of charge density analysis, largely in the form of a timeline, but from a rather personal viewpoint. It will highlight key developments and publications from the past, with a focus on their relevance to today’s practitioners.

Bibliography:

[1] P. Coppens, *Angew. Chem., Int. Ed.* 2005, 44, 6810-6811.

**Past and recent developments of experimental charge density studies
– a European perspective**

Wolfgang Scherer

Institute of Physics, University of Augsburg, Germany

This introductory talk is intended to set the stage for the conference. It will therefore provide a brief overview from a European perspective how the field of charge density studies has emerged and developed during the past years/decades. Besides historical aspects also a short review on recent trends such as charge density studies under extreme conditions, external fields or at ultra-high resolution will be presented. The talk will end by opening a discussion on new perspectives e.g. time-resolved charge density studies and present a to-do-list for software developers and instrument scientist to overcome the present experimental hurdles.

The background of the slide is a photograph of a city skyline at sunset. The sky is a mix of orange, yellow, and light blue. The city features several tall skyscrapers, some of which are illuminated. In the foreground, there are lower-rise buildings and a road with some greenery. The overall atmosphere is hazy and serene.

SESSION 1

Errors in experimental and theoretical approaches

Chairs:

Simon Coles, Piero Macchi

Session sponsored by Rigaku Oxford Diffraction

About Fit Quality Indicators

Julian Henn

University of Bayreuth, Germany

The talk will address the following questions and topics: Why are Fit Quality Indicators (FQI) important? What is the purpose of application of FQI? What FQI can do for you and what they can't do. How FQI help to establish a powerful way of learning: The feedback-loop. A conflict between short-term goals and long-term goals in science: The feedback-loop breakdown. How FQI are used to hide systematic errors. New FQI [1-3], how they are connected and what they tell. Some illustrative examples from published data sets will be discussed.

Bibliography:

[1] J. Henn and K. Meindl (2014) "More about systematic errors in charge-density studies", Acta Crystallogr. A70, 499-513 [2] J. Henn and K. Meindl (2014) "Statistical tests against systematic errors in data sets based on the equality of residuals means and variances from control samples: theory and applications", Acta Crystallogr. A71, 203-211 [3] J. Henn and A. Schönleber (2013) "More about residual values", Acta Crystallogr. A69, 549-558

Diffraction data analysis in Jana2006

Václav Petříček and Michal Dušek

Structure Analysis, Institute of Physics, ASCR, Na Slovance 2, 18221 Praha 8, Czech Republic

The crystal structure determination for regular structures is nowadays more or less automatic procedure and with new CCD diffractometers we can achieve in relatively short time much better accuracy and higher redundancy than ever before. However, most of routinely published structures are presented with the final goodness of fit (GOF) close to one as if there would be no systematic errors necessarily imposed by the presence of chemical bonds in the crystal inducing aspheric distribution of electrons. Regrettably, such requirement is sometimes the condition for accepting a simple structural paper. This leads authors to reduce “accuracy” of the experiment either by selecting shorter exposition time or by modifying estimated standard uncertainties of measured intensities. While the first solution means that we are not fully using what diffraction experiment can offer the second method makes the data analysis based on GOF and its individual contributions useless. On the other hand, simply accepting the estimated standard uncertainties (s.u.) of reflection intensities as supplied from CCD integration, even based on carefully done experiment, may be insufficient for reliable detailed structure analysis. In this contribution we present tools implemented recently to the program Jana2006 [1],[2] which allow for comparison of s.u. from the experiment with statistical distribution of multiply measured and equivalent reflections. This can be used both for modifying the s.u. of measured reflections and/or for finding individual outliers by comparison with the average value. Moreover, the variance for each reflection as a function of diffraction angle, average intensity and the CCD frame identifier can help to find systematic error in data collection, scaling or absorption procedure. An analogical method can be used during the refinement process but here we compare weighted differences of observed and calculated intensities. This can help to find systematic errors caused by incomplete structural model. An interactive graphic interface has been developed to facilitate all above mentioned possibilities. The presentation will demonstrate features of this interface based on several examples.

Acknowledgments: We acknowledge support of the Czech Science Foundation project 14-03276S.

Bibliography:

[1] V. Petříček, M. Dušek & L. Palatinus, (2014). *Z. Kristallogr.* 229(5), 345-352. [2] K. Fries, A. Grzechnik, J.M. Posse & V. Petříček, (2013). *High Pressure Research*, 33, 196-201.

Empirical correction for resolution- and temperature-dependent errors caused by factors such as thermal diffuse scattering

Regine Herbst-Irmer, Benedikt Niepötter and Dietmar Stalke

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Germany

Charge density investigations of several compounds we conducted at multiple temperatures show two disturbing features. First, the models derived from these high resolution datasets at different temperatures differ significantly. Additionally, residual density appears close to or even at the atomic positions, especially for datasets measured at 100 K. This indicates significant errors that could be caused by thermal diffuse scattering (TDS). TDS mainly results in an underestimation of the atomic displacement parameters. However, smaller but nevertheless important errors occur in other parameters as well.[1] Hence the heights of the maxima in the electron density are changed at the same location.[2,3] First order TDS leads to peak broadening in the diffraction experiment. A reduction of the integration box size leads to a substantial improvement in quality and diversity of the models. At the same time it indicates TDS to cause these errors. However, this method turns out to be very time-consuming and an alternative is needed. As shown by Jennings [4] it is possible to estimate the TDS contribution by analyzing the peak profile. Blessing [5] as well as Stash and Zavodnik [6] extended this idea and developed programs to assess the TDS contribution to the measured intensities for data collected with point detectors. In our endeavours to improve the method, we noticed that refining resolution-dependent scale factors can be employed as a validation tool to detect such errors. In a nested interval approach a correction factor ($\alpha = a \cdot (\sin(\Theta)/\lambda)^2 + b \cdot (\sin(\Theta)/\lambda)^3$) [7] is determined that minimizes these errors and improves the model quality, which is now based on only a single scale factor refinement.[8]

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Prediction uncertainty of density functional approximations for properties of crystals

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An increase in computing power has allowed the replacement of personal experience with databases. In the realm of density functional theory, these have become a valuable tool for both tuning and tailoring new methods and, in particular, to assess the performance of density functional approximations. Ultimately, benchmarks should help computational chemists in choosing the best method to be adopted in a new study. The large amount of available data then requires synthetic and reliable indicators capable of providing a ranking based on the quality of the approach. However, these indicators might be insufficient and a more careful analysis is needed. Some pitfalls in ranking indicators [1,2] will be discussed for the prediction of band gaps, bulk moduli, and lattice constants of cubic semiconductors and insulators [2,3]. In addition, for a proper validation of DFAs accurate reference data must be available from either higher-level theory or experiment. In some cases, further approximations are needed for a consistent comparison with experimental data (e.g. thermal effects) as it will be shown for molecular crystals [4]. All reported results were computed by means of the periodic ab-initio program CRYSTAL14 [5,6].

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Assessing the reliability of charge density parameters and derived properties

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A new methodology based on perturbed structures and charge density models is proposed within the MoPro software [1]. Random numbers are generated to create molecular structures at standard deviation. Root mean square deviations (rmsd) of values can be computed from a sample of models. Reliability of topological and electrostatic properties can be fully assessed this way. Some charge density features, such as electron lone pairs are finer and more difficult to observe properly from an experimental charge density study [2]. Results from theoretical and experiments do not always agree, due to atomic thermal motion. Helium cryostat temperature is sometimes required to observe the proper electron density features. The configuration of electron lone pairs on oxygen atoms varies greatly with the chemical functional group. Alcohols and phenols show for example fine differences which have important consequences on the directionality of the hydrogen bonds they form, as demonstrated in an extensive survey of Cambridge Structural Database [2]. The effect of the lone pairs charge density on the hydrogen bond stereochemistry is strongest for the short interactions. An alternate model to the multipoles is proposed in MoPro to describe the bonding and lone pair electron density using spherical scatterers [3]. The Hansen & Coppens multipoles yield better R-factor values and residual electron densities than the spherical virtual atoms as the larger number of parameters gives more flexibility. Electrostatic properties are however well reproduced by spherical atoms and additional charges.

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S1-L6

Aspects of single crystal neutron diffraction

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Neutron single crystal diffraction ideally complements X-ray experiments. The scarcity of neutron sources and sometimes difficulty to obtain beamtime tends to render this possible only for relatively few select problems. Even when granted beamtime, relatively large crystals need to be obtained and experiment time is limited. Here, I will present various aspects of a neutron experiment, including details of data analysis procedure and more.



SESSION 2

New approaches in modeling of charge density and thermal motion

Chairs:

Simon Grabowsky, Ángel M. Pendás

On hydrogen-atom treatment in high-quality single crystal structure analysis

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We have recently described how anisotropic displacement parameters (ADPs) of hydrogen atoms can be obtained for conventional (and high-quality/resolution) diffraction data i.e. by combining transferable internal displacements obtained from quantum chemical frequency computations of invariom model compounds with segmented-body Translation Libration Screw (TLS-fit) for a molecule of interest [1]. These “TLS+INV” hydrogen ADPs have been used in re-refinement of several high-resolution diffraction data sets of some of the naturally occurring amino acids [2], where revision of the data reduction procedure has eliminated some known systematic errors. These data sets are now even better suited as reference or test structures for method development. We are here concerned with hydrogen-atom treatment in “high-quality single crystal structure analysis” [3] and suggest the following procedures that provided convincing results in our hands: 1. Initially a refinement with transferable aspherical scattering factors (e.g. using [4], the invariom database) should be carried out. When [4] is used it also provides gas-phase quantum chemical bond distances to hydrogen atoms. 2. Refinement results with ADPs de-convoluted from electron density can then be used as starting structures in estimating hydrogen ADPs. 3. For good data free refinement of the hydrogen positional parameters with fixed ADPs then yields remarkably good results: Bond distances are in favorable agreement to results from quantum chemical/force field QM/MM computations initiated with the X-ray structures prior to free positional refinement of hydrogen atoms or with neutron diffraction. Bond distance to hydrogen atoms are also compared to Hirshfeld-atom refinement [5], where simultaneous refinement of H-ADPs and positions may lead to non-physical H-ADPs, which we think would be due to over-parameterization. Another advantage of the TLS+INV procedure is that estimated H-ADPs do not require the computational effort of HAR. Other applications of TLS+INV estimated H-ADPs are to reduce the number of parameters in free multiple refinements, since the isotropic displacements become obsolete. All these tools combined, the invariom approach provides H-ADPs, aspherical scattering factors and most recently point charges that reproduce gas-phase electrostatic potentials [6] in a rapid manner. In summary we think to have found a convincing way to treat hydrogen atoms in the absence of disorder for obtaining high-quality structures that could be used on a regular basis.

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Combining multipole refinements and lattice dynamics: a case-study of L-alanine

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Thermal motion in crystals is normally modelled using atom-centered harmonic motion. We have recently shown how a lattice-dynamical model derived from periodic DFT calculations can provide an alternative description, and how this approach have certain virtues, such as providing a sensible description of H atom motion, and the possibility of deriving thermodynamic properties [1-2]. In this contribution, we combine this approach with the refinement of a multipole-model, as implemented in the XD program, in an X-ray diffraction study of L-alanine at 23 K [3] and 123 K. We test the influence of the level of theory, such as the DFT functional and basis-set size, and we propose a way to extend the lattice-dynamical model to include dispersion of the acoustic phonons.

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Is relativity the hammer in charge density of heavy elements and their compounds? How heavy is the hammer - how heavy is heavy metal?

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Different relativity approaches for treating the charge density of heavy elements will be presented. Starting with the Dirac Hamiltonian, its simplified versions leading to the quasirelativistic Hamiltonians will be examined. In the case of our investigation, we will focus on the Infinite Order Two Component (IOTC) approach [1], exploring the relativistic effects (scalar and spin-orbit ones), picture change of the quasirelativistic wave function [2-6] as well as finite nucleus effects [7] in electron density first at the nucleus as well as for complexes of metals (including Laplacians and structure factors) [4-6]. Subsequently, a recent study on Hg(phenyl)₂ and Bi(phenyl)₃ compounds will be presented [8]. We focus on the comparison of relativistic effects on one hand and the electron correlation on the other hand. This includes latest developments in the Tonto package [9] with respect to relativistic X-ray Constrained Wave function (XCW) [10] and Hirshfeld Atoms Refinement (HAR) [11] and the fission of both aforementioned approaches XCW + HAR = XWR (X-ray Wavefunction Refinement) [12]. The essential question whether relativistic effects can be detected with the help of diffraction experiments will be discussed, with pointing out the ultimate challenges on the experimental side and limitations on the theoretical one.

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Can the X-ray constrained wave function methods extract electron correlation effects on the electron density?

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The development of methods to determine wave functions from experimental data has been an open and stimulating field of research for about fifty years. Nowadays, among all the modern strategies devised in this context, the X-ray constrained wave function (XC-WF) approach proposed by Jayatilaka is by far the most promising and it can be also considered as a plausible alternative to the wave function-based and DFT techniques for the investigation of many-electron systems. Relying on the Henderson & Zimmermann idea [1], the Jayatilaka method [2,3] enables to successfully extract single Slater determinants that not only minimize the molecular electronic energy but that also reproduce as much as possible sets of experimental structure factor amplitudes, namely sets of data directly related to the electron density. For this reason the original XC-WF technique and all its later developments [4-6] can be considered to merge the features of the wave function-based and DFT strategies and, in principle, they should automatically introduce electron correlation effects. Understanding if and to what extent the Jayatilaka-type approaches capture the effects of the correlation on the electron density is thus of paramount importance and this could also open new interesting perspectives in the search of alternative density functionals, since X-ray structure factors are not usually exploited to this purpose. To accomplish this task, we have recently performed X-ray constrained Hartree-Fock calculations for a series of small/medium-size molecules considering theoretical Coupled Cluster structure factor amplitudes as external constraints and, afterwards, to roughly determine the amount of “recovered correlation”, we have compared the obtained charge distributions with other correlated electron densities [7]. This investigation and its main results will be presented in detail, especially highlighting the optimal conditions under which (namely, the optimal resolution at which) the XC-WF approaches significantly allow to capture the electron correlation effects.

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X-ray wave function refinement - overcoming the limitations of the multipole model

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High resolution X-ray crystallography allows to reconstruct experimental electron density and is a source of information about properties of molecules in crystals and interactions between them. However, extracting reliable information requires not only good quality experimental data, but also advanced data processing methods based on sophisticated models of electron density. To date, the most popular of such techniques is the multipole refinement (MM), which, due to certain drawbacks, such as insufficient flexibility, is known to yield electron density characterized by many flaws [2]. An alternative method presented in this contribution is X-ray wave function refinement (XWR) [3] in which the model aspherical atomic scattering factors are based on Hirshfeld partition of electron density. The full XWR procedure consists of two steps: Hirshfeld atom refinement (structural refinement) and the fitting of experimentally constrained wave function (refinement of electron density) [4][5]. The final electron density is restrained to the quantum mechanical minimum of energy and is influenced by interactions with the crystal environment. XWR is free from serious limitations of MM, which should result in improvement of the reconstructed electron density. In this contribution we present the comparison of XWR nad MM for a set of high resolution X-ray data for the crystals of 4 amino acids and 6 tripeptides. The analysis of the refined electron density is based on the QTAIM formalism [6] and quantities such as integrated atomic properties and properties at the bond critical points (BCPs). QTAIM properties obtained from experimental electron density refined with MM and XWR are compared to the benchmark values derived from periodic DFT calculations. The analysis of bond lengths and ADPs of atoms in the crystals is also performed. The selected compounds allow to study certain types of C, N, O and H atoms and bonds linking them, which are common in biological molecules and in many organic compounds. Our study reveals the advantage of XWR over MM in the description of experimental electron density. MM underestimates atomic charges of N, O and C and incorrectly describes polar bonds such as C-N or C-O, overestimating electron density and Laplacian at the BCPs. XWR eliminates or reduces these problems, moreover it results in QTAIM properties in significantly higher agreement with the theoretical values and in better quality of the data refinement compared to MM.

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S2-L6

A tale of two densities

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The charge density is actually two densities - the negatively charged electron density and the positively charged nuclear density. In X-ray diffraction it is not possible to obtain the former without assumptions about the latter. In the talk I will review the Hirshfeld atom refinement (HAR) method for obtaining information about the nuclear density, including a review of the results for rubrene, compared with the multipole refinement. I will describe a new method for structure refinement (KMAR) based on a reduction of the Koritsanzsky-Michael variance-covariance matrix in a gaussian basis set; the link to Tanaka's thermal averaging method will be pointed out. I will present results for this method, which is more efficient than HAR. I will also present results concerning the anharmonic density distribution, and will argue that refinements such as these are better done in the cartesian system.

The background of the slide is a photograph of a city skyline at sunset. The sun is a bright, glowing orb in the center of the horizon, casting a warm, orange and yellow light across the sky. Several tall, modern skyscrapers are visible, their silhouettes and some lit windows contrasting against the bright sky. In the foreground, there are lower-rise buildings and some greenery, all slightly hazy from the distance and the atmospheric light. The overall mood is serene and urban.

SESSION 3

Challenging experiments for charge densities

Chairs:

Bartolomeo Civalleri, Carlo Gatti

Concerning measurement errors in synchrotron X-ray charge density studies

John R. Helliwell

University of Manchester, Manchester M13 9PL, UK

In synchrotron X-ray charge density studies I learnt at ECDM5 that there was an issue concerning measurement errors in synchrotron X-ray charge density studies. I recall mentioning that in my view, built on the experience of a totally different field admittedly, multi-wavelength anomalous dispersion (MAD), ESRF BM14 [1] has proved highly successful in the number of its Protein Data Bank deposits and working with low anomalous signal cases. At the root of our thinking in proposing BM14 for MAD (R Fourme and J R Helliwell 1990s) was that this was the most stable beam intensity possibility, at least for the then knowledge of X-ray optics cooling at the time. Since ECDM5 I have continued my thinking about ESRF and the possibility of a dedicated beamline there for charge density measurements. I note also that a recently published synchrotron radiation X-ray charge density analysis has shown that the lower resolution intensities were the main source of errors in that study at APS [2]. A possible way to address that type of error could be to utilise the continual crystal sample rotation measurement method, conceived of for monochromatic time-resolved work [3,4]. In summary this abstract is concerned with sharing ideas for reducing errors in synchrotron radiation X-ray charge density data. I offer two ideas; firstly, the use of a 3rd generation SR source bending magnet capable of delivering high photon energies and, secondly a continual rotation of the single crystal sample. There may of course be other possible sources of measurement errors!

Acknowledgments: I am grateful to Dr Jon Wright at ESRF for discussions.

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The resolution dependence of aspherical core refinements: the case of light atoms

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The enormous advances in the development of highly intense and brilliant X-ray sources even for short X-ray radiation triggered the charge density community to explore the performance of these tools in the field of ultra-high resolution X-ray diffraction studies. With data well above the classical charge density limit of $\sin\theta/\lambda \geq 1.0$, the limitations of the frozen core approximation could be overcome to model even the contraction/expansion and polarization of the core and outer-core electron density distribution of atoms by an Extended Hansen Coppens (EHC) multipolar model. [1] Recent experimental studies on diamond, BN and silicon have in the meantime demonstrated the necessity and applicability of the EHC to model high-resolution data. [2] However, the refinement of aspherical core density deformations requires the acquisition of high-order data of uttermost precision. The aim of this theoretical study is to identify criteria (e.g. the minimal data resolution) to model and interpret reliably the core and outer-core electron distribution in solids and molecules. [1,3]

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Probing chirality with high energy synchrotron light

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Absolute structure determination using hard x-rays is considered as problematic because of the small resonant contributions for many chemical elements. Here we show that even small resonant contributions can be safely detected at high energy. This is due to the large number of the observable Bijvoet differences which are available, and that the signal increases with Q due to the form factors, so that absolute structure determination becomes possible. The absolute structure has been determined for a crystal of MnSi with data collected using synchrotron radiation with $E = 78.3$ keV. At this energy, the resonant scattering contribution from MnSi is very small $f'(\text{Mn}) = -0.0397$, $f''(\text{Mn}) = 0.0385$, $f'(\text{Si}) = -0.0197$, $f''(\text{Si}) = 0.0027$. A comparison with the data collected at $E = 18$ keV ($f'(\text{Mn}) = 0.2858$, $f''(\text{Mn}) = 0.6739$, $f'(\text{Si}) = 0.0653$, $f''(\text{Si}) = 0.0646$) for the same crystal shows the correctness of the absolute structure measured at the high energy. Similar data collections have also been carried out for crystals with known absolute structures: $\text{Fe}_{0.7}\text{Co}_{0.3}\text{Si}$ at $E = 65.2$ keV; in all the cases, the absolute structure was correctly determined by analyzing the statistical distribution of the chirality measure. Statistical descriptors of the refinements, Flack parameter, and the distribution of Parsons quotients are discussed for all presented experiments.

Insights into single molecule magnetism from charge and spin density studies

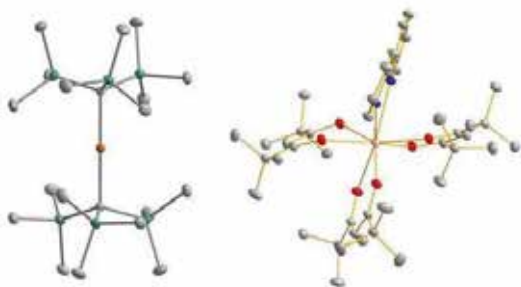
Jacob Overgaard^a, Maja Thomsen^a, Phil Bunting^b, ShangDa Jiang^c, James Walsh^d
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The atoms are depicted as 50% probability ellipsoids. Pink, orange, blue, red, petrol blue and grey refer to dysprosium, iron, nitrogen, oxygen, silicon and carbon, respectively. Hydrogen atoms have been omitted for clarity.

abundant metals such as iron have been found to be useable by clever engineering of the ligand field. In this talk, I will outline very recent results from electron density studies of the premier mononuclear transition metal-based SMM so far discovered which combines two unusual features of an iron complex, namely two-coordinate Fe(I), $2 [\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$ (left Figure). This complex has a record high effective relaxation barrier ($U = 226(4) \text{ cm}^{-1}$). It had been suggested that the low coordination number and the low oxidation state combine to give a very weak ligand field with the d_{z^2} -orbital lowest in energy of the d-orbitals. To study this we have modeled the experimental electron density of this compound, as well as its di-valent analogue, and use these to discuss the molecular magnetic properties. If time allows, I will also address the magnetic anisotropy of a Dy-based SMM (right Figure) based on polarized neutron single crystal data and the local susceptibility tensor approach.[3] Figure caption: ORTEP drawings of (left) the $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$ anion obtained from 100 K X-ray data measured on a $[\text{K}(\text{crypt-222})][\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]$ (crypt-222 = 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane), and (right) $\text{Dy}(\text{2,2'-bipyridine})(\text{t-Bu-acac})_3$.

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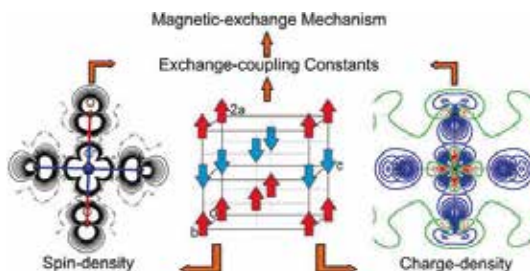
Experimental and theoretical electron density analysis of copper pyrazine nitrate quasi-low-dimensional quantum magnets

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In this work, the accurate electron density distribution and the magnetic properties of two metal-organic polymeric magnets, the quasi-one-dimensional $\text{Cu}(\text{pyz})(\text{NO}_3)_2$ and the quasi-two-dimensional $[\text{Cu}(\text{pyz})_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$, have been investigated by high-resolution single-crystal X-ray diffraction and by density functional theory calculations on the whole periodic systems and on selected building-block subunits [1]. Topological analyses, based on quantum theory of atoms in molecules, enabled the characterization of possible magnetic exchange pathways, and the establishment of relationships between the electron (charge and spin) densities and the exchange-coupling constants. In both compounds, the experimentally observed antiferromagnetic coupling can be quantitatively explained by the intrachain Cu–Cu superexchange pathway mediated by the pyrazine bridging ligands, via a sigma-type interaction. From a careful examination of the ellipticity profile along the Cu–pyz bond path, we show for the first time that the pyrazine tilt angle with respect to the plane of the magnetic d-orbital does not play a role in determining the strength of the magnetic interaction, at variance from what has been previously thought based on Hatfield's proposal [2]. Furthermore, taken in combination with molecular orbital analysis and spin density calculations, our results also show a synergy between the spin-delocalization and the spin-polarization mechanisms on determine the total spin density of the magnets, and that both mechanisms influence the bulk magnetic behavior of these Cu(II)–pyz coordination polymers. Even though the complete, quantitative understanding of the magnetic behavior of a material can only be achieved by the knowledge of its spin-density, this work constitutes an example of how the determination and analysis of the position electron-density alone, either theoretical or experimental, directly impacts our understanding of superexchange mechanisms, as it plays an invaluable role in advancing chemical bonding theory.



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Nuclear dynamics in the metastable phase of the solid acid caesium hydrogen sulfate

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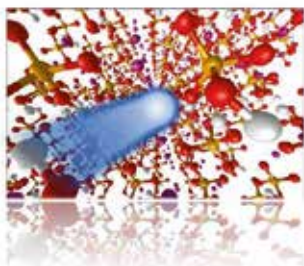
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High-resolution spectroscopic measurements using thermal and epithermal neutrons and first-principles calculations within the framework of density-functional theory are used to investigate the nuclear dynamics of light and heavy species in the metastable phase of caesium hydrogen sulphate. Within the generalised-gradient approximation, extensive calculations show that both ‘standard’ and ‘hard’ formulations of the Perdew–Burke–Ernzerhof functional supplemented by Tkatchenko–Scheffler dispersion corrections provide an excellent description of the known structure, underlying vibrational density of states, and nuclear momentum distributions measured at 10 and 300 K. Encouraged by the agree-

ment between experiment and computational predictions, we provide a quantitative appraisal of the quantum contributions to nuclear motions in this solid acid. From this analysis, we find that only the heavier caesium atoms reach the classical limit at room temperature. Contrary to naive expectation, sulphur exhibits a more pronounced quantum character relative to classical predictions than the lighter oxygen atom. We interpret this hitherto unexplored nuclear quantum effect as arising from the tighter binding environment of this species in this technologically relevant material.

Acknowledgments: The authors gratefully acknowledge the UK Science & Technology Facilities Council for financial support and access to beam time at the ISIS Facility, as well as its e-Science Facility for access to supercomputing resources on the SCARF cluster at the Rutherford Appleton Laboratory. K.D. acknowledges partial support from the PL-Grid Infrastructure under grant Solidstate2015-KD, and the Ministry of Science and Higher Education of Poland for a mobility grant to fund his stay at the ISIS Facility in 2015.

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Chemical bonding in boron polymorphs and boron carbide

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Boron carbide unites a series of useful properties, including extreme hardness, low density, high melting point and remarkably good chemical stability. Explaining the chemical stability, reactivity and properties in terms of chemical bonding in elemental boron and boron-rich solids has remained a major challenge in boron research. We have used low-temperature high-resolution single-crystal X-ray diffraction with synchrotron radiation for the determination of the electron density in alpha-boron (α -B₁₂), the high-pressure polymorph γ -B₂₈ and stoichiometric boron carbide B₁₃C₂ by multipole refinements and the Maximum Entropy Method (MEM) [1, 2, 3]. Our results on α -B₁₂ [2] are essentially different from an earlier study by the MEM [4], and they have been recently confirmed by x-ray powder diffraction [5]. Presently studied B₁₃C₂ is free of intrinsic defects, in agreement with an independent study on the high-pressure behavior of non-stoichiometric B_{12.17}C_{2.83} [6]. Here we present the variety of chemical bonds formed in boron polymorphs and boron carbide, and we will show that they can be derived from a unified orbital picture. Analysis of the electron densities reveals a unified picture for the B₁₂ icosahedral groups present in all three materials. These groups participate in several unique two-center-two-electron, two-center-one-electron and three-center-two-electron chemical bonds, which explain bonding in these solids.

Acknowledgments: We thank Carsten Paulmann for assistance with the x-ray diffraction experiments at beamline F1 of Hasylab at DESY, Hamburg, Germany. Financial support has been obtained from the German Science Foundation (DFG—“Deutsche Forschungsgemeinschaft”) under project No. Sm 55/24-1 and Project No. DU 954-8/1. N.D. thanks the DFG for financial support through the Heisenberg Program. N.D. and L.D. gratefully acknowledge the Federal Ministry of Education and Research (BMBF, Germany) for funding.

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SESSION 4

Charge densities in the life sciences

Chairs:

John R. Helliwell, Maciej Kubicki

Reproducibility in biomedical sciences**Wladek Minor***University of Virginia, Charlottesville, VA, 22908-0736, USA*

Experimental reproducibility is the cornerstone of scientific research, upon which all progress rests. The veracity of scientific publications is crucial because subsequent lines of investigation rely on previous knowledge. Several recent systematic surveys of academic results published in biomedical journals reveal that a large fraction of representative sets of studies in a variety of fields cannot be reproduced in another laboratory. Big Data approach and especially NIH Big Data to Knowledge (BD2K) program is coming to the rescue. The goal of the presented research is to provide the biomedical community with a strategy to increase the reproducibility of reported results for a wide range of experiments by building a set of “best practices”, culled by extensive data harvesting and curation combined with experimental verification of the parameters crucial for reproducibility. Experimental verification assisted by the automatic/semi-automatic harvesting of data from laboratory equipment into the already developed sophisticated laboratory information management system (LIMS) will be presented. This data-in, information out paradigm will be discussed.

Using QM methods to refine biological structure

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The starting point for structure-based drug design (SBDD) efforts is a high quality structural model obtained using X-ray crystallography or NMR spectroscopic techniques. In most instances classical tools are used as structural surrogates in X-ray and NMR refinement protocols in order to improve the parameter to observation ratio realized from these experimental techniques. While classical approaches are useful structural surrogates, they do suffer from a number of issues that affect their performance including: electrostatic modeling, parameter defects and missing parameters. The way in which these issues can be mitigated is to use more robust structural theories like quantum mechanical (QM) methods, which have had a tremendous impact on our understanding of “small” chemical and biological systems. In this talk we will focus on the application of ab initio QM methods to refine protein/ligand complexes for use in SBDD applications using NMR and X-ray methods. We will discuss the computational details and describe several uses of QM in structure refinement efforts using NMR and X-ray datasets. The strengths and weaknesses of a QM approach in structure refinement will be discussed as well as future prospects of this strategy.

Study of the key interactions in the self-recognition of the antimalarial drug chloroquine

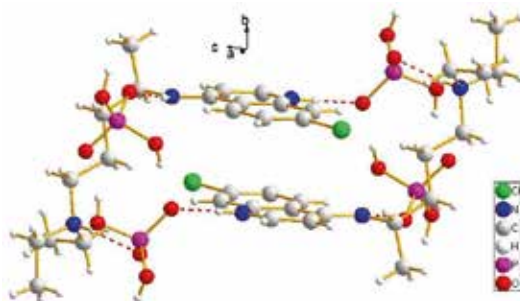
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Malaria is a parasitic disease that causes thousands of deaths every year, especially in undeveloped countries. The Plasmodium protozoa, responsible of the infection, kill human red blood cells by digesting hemoglobin. Many compounds have been employed in the last century against malaria, but nowadays the increasing resistance of Plasmodium is becoming a very serious problem. New drugs are required and to this end it is desirable to quantitatively understand the role of different functional groups in determining effective pharmacophores. This work focuses on chloroquine (CQ), a 4-aminoquinoline antiplasmodial whose effectiveness is now hampered by evolved parasite resistance. It is accepted that CQ interferes with a crucial detoxification process of the parasite [1], namely the inhibition of heme bio-crystallization, but several details of this process still remain rather obscure. In the acidic digestive vacuole of Plasmodium, CQ is supposed to interact in its diprotonated form directly with the monomeric heme in two possible ways: 1) π - π stacking interactions between quinoline ring and heme proto-porphyrin [2] or 2) a direct Fe-N quinoline coordinative bond, supported by strong charge-assisted hydrogen bonds (CAHBs) between the tertiary amine of CQ and the propionate groups of heme [3-4]. In this work, the self-recognition of chloroquine diphosphate dihydrate salt was studied both theoretically and experimentally. High-resolution single crystal X-ray data were collected at low temperature (20–103 K) and complemented by quantum simulations with CRYSTAL14 [5] at the BP86/6-311G(p,d) theory level. The salt crystallizes in a P21/c structure, with phosphate ions forming infinite chains parallel to the b axis. CQ molecules and phosphates are connected through strong N-H...O CAHBs, while a π - π interaction is present between the quinoline rings (see figure). The topological analysis of the primary charge density, performed according with the Quantum Theory of Atoms in Molecules [6], along with the ab-initio energy decomposition, show that the coulombic interactions between the charged hydrocarbon chain of CQ and the phosphate ions seem to provide the dominant features in the molecular self-recognition, while the π - π stacking between the quinoline moieties has just an ancillary role. These evidences suggest that, in agreement with our previous DFT/EXAFS results [3], the protonated tertiary amine of CQ is an essential component of the drug pharmacophore.



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GEM, a force field based on density fitting for scalable molecular dynamics simulations

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In this contribution, I will present the Gaussian Electrostatic Model (GEM) a force field based on electron density using hermite gaussians fitted through resolution of the identity (i.e. density fitting) techniques. As the theoretical basis of the model will be explained, I'll present its high performance implementation within the context of the massively parallel Tinker-HP package, a software suite dedicated to high performance polarizable molecular dynamics. (<http://www.ip2ct.upmc.fr/tinkerHP>).

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Crystal and enzyme environmental effects on the electron density of a cysteine protease inhibitor

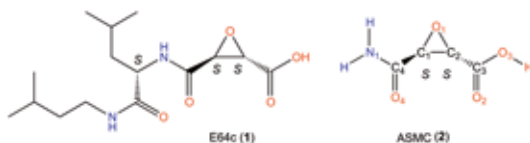
Florian Kleemiß^a, Ming W. Shi^b, Scott G. Stewart^b, Kuniyoshi Sugimoto^c
and Simon Grabowsky^a

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Loxistatin acid (E64c (1), see figure) is a biologically active molecule of high interest, since its possibility to irreversibly inhibit cysteine protease enzymes leads to many applications in medicinal and pharmaceutical science. There have been many derivatizations with subsequent investigations of their effect on protease inhibitors [1, 2]. The interaction between E64c and



the enzyme (cathepsin B) was studied using different theoretical methods [3, 4]. In these studies it was shown that only the epoxysuccinyl amid moiety is important for the binding of E64c inside the enzyme, so that we reduced the size of the molecule to include only the relevant hydrogen bonding donors and acceptors (O1 to O4, N1) yielding epoxysuccinyl amide as the active site model compound (ASMC (2), see figure). This was necessary because in the recently obtained crystal structure of E64c [5] lots of disorder hampers an experimental electron density study, but it was possible to obtain a data set of sufficient quality and sufficiently high resolution for experimental electron-density modelling of ASMC at the synchrotron SPring-8, beamline BL02B1, Japan. In addition to experimental electron-density investigations on ASMC employing the multipole model, both enzyme and crystal induced differences will be investigated using QM/MM methods to receive reliable electron density data from wavefunctions resulting from high level calculations. This approach makes it possible not only to look at effects predicted by theoretical calculations of the structure in the crystal and in the enzyme but to compare it to the crystallographically measured data as well.

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The background of the slide is a photograph of a city skyline at sunset. The sky is a mix of orange, yellow, and light blue, with the sun low on the horizon. Several tall skyscrapers are visible, including a prominent one on the right. In the foreground, there are lower-rise buildings and some greenery.

SESSION 5

From conceptual quantum chemistry to properties of molecules and crystals

Chairs:

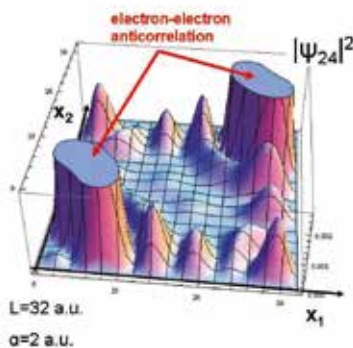
Birger Dittrich, Anders Ø. Madsen

Information-theoretic approaches to Atoms-in-Molecules**Patrick Bultinck^a, Farnaz Heidar-Zadeh^{a,b,c}, Paul W. Ayers^c and Toon Verstraelen^b**^a *Inorganic and Physical Chemistry, Ghent University, Belgium*^b *Center for Molecular Modeling, Ghent University, Belgium*^c *Chemistry and Chemical Biology, McMaster University, Canada*

Many population analysis methods are based on the precept that molecules should be built from fragments (typically atoms) that maximally resemble the isolated fragment. The resulting molecular building blocks are intuitive (because they maximally resemble well-understood systems) and transferable (because if two molecular fragments both resemble an isolated fragment, they necessarily resemble each other). Information theory is one way to measure the deviation between molecular fragments and their isolated counterparts, and one that lends itself to analysis. For example, one can analyze the relative importance of electron transfer and polarization of the fragments. We present key features, advantages, and disadvantages of the information-theoretic approach. We also codify existing information-theoretic partitioning methods in a way that clarifies the enormous freedom one has within the information-theoretic ansatz.

Can electrons attract each other?

Lucjan Piela

Department of Chemistry, University of Warsaw, Poland

Electrons repel each other by Coulombic force. This creates a Coulomb, or correlation hole, about each electron position (for all other electrons). Electrons that have the same spin coordinate repel each other also due to the Pauli exclusion principle, thus creating in addition the Fermi, or exchange electronic hole. When in molecules, electrons are attracted by the nuclei. According to the common knowledge a compromise is achieved: the largest amplitude of the electronic wave function corresponds to the electronic positions close to the nuclei, with the mean interelectronic distances being as large as possible. As a consequence the mean electron-electron distance calculated by using an exact electronic wave

function (the Fermi and Coulomb hole correctly included) is larger than the electron-electron distance computed by the Hartree-Fock method (the Fermi hole included, the Coulomb hole neglected). It is shown [1], using an example of two electrons moving in 1D boxes (with the Coulomb interaction), that indeed in the ground electronic state the electron-electron distance increases as expected, when compared to that for independent electrons. It is demonstrated however that there exist excited states (often of low energy), in which the electrons, while having a lot of empty space, choose to be close to each other in their motion (a kind of electronic anticorrelation). Their mean distance is shorter than that corresponding to non-interacting electrons, as if the electrons mutually attracted each other. Figure above shows the probability density of finding the two electrons (with coordinates x_1 and x_2) in two parallel 1D boxes of length $L=32$ a.u. (separated by $\alpha=2$ a.u.), for one of the singlet excited states. The two highest maxima of the probability density occur at $x_1 = x_2$. The reason of this phenomenon is of quantum-mechanical nature: it stems from orthogonality of the corresponding two-electron wave functions. It will be shown that such two-electron states represent analogs of the experimentally observed "low-field seeking molecules", with the molecular dipole oriented, anti-intuitively, opposite to the external electric field [2]. Some attempts of using this mechanism to obtain the Cooper-like pairs in a solid state model will be reported.

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Revealing the role of spin-relativistic effects on bonding in molecules and solids

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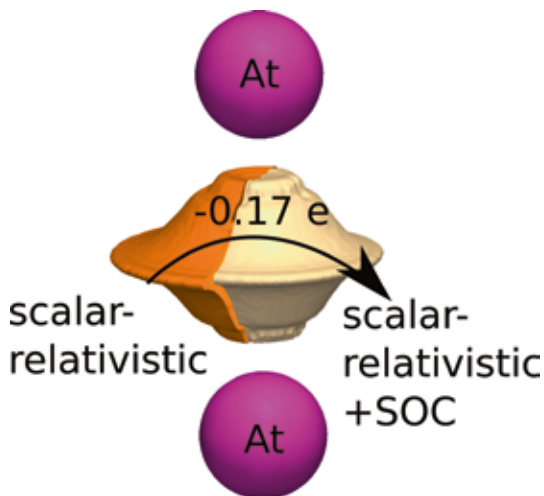
The spin-relativistic effects, the most pronounced and known among which is spin-orbit interaction, become essential for the compounds of heavy elements [1]. They are responsible for many important physical properties and emerging novel physical phenomena, which are actively studied now, and also may affect chemical bonding. Taking them into account turns the wavefunctions into complicated multicomponent spinor objects, which are cumbersome to analyse, and makes spin to cease to be a good quantum number. Similar situation appears for a noncollinear magnetism. In the same time, many useful chemical bonding indicators are based on spin-related properties and thus can not be applied directly in this case. The relativistic extension of electron localizability bonding indicator [2], capable to reveal shell structures, is presented in this work. Its formalism is well defined for both multicomponent spinor and scalar wavefunctions and is based on the densities of spatially antisymmetrized electron pairs. This indicator has been employed for the analysis of the effects of spin-orbit coupling (SOC) in molecules and crystals and have clearly revealed known relativistic effects like bond weakening in homonuclear dimers. A comparison with the results of analysis employing some shell structure indicators based solely on total electron density [3 - 4] is also reported.

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Acknowledgments: Financial support from DFG grant BA-4911/1-1 is gratefully acknowledged

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Some emergent scalar and vector fields in Quantum Chemical Topology

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Several potentially useful scalar and vector fields that have been scarcely used to date in Quantum Chemical Topology are defined, computed, and analyzed for a few small molecules. The fields include the Ehrenfest force derived from the second order density matrix, the exchange-correlation (xc) potential, the potential acting on one electron in a molecule, and the additive and effective energy densities. The basic features of the topology of some of these fields are also explored and discussed, paying attention to their possible future interest.

QTAIM study of tetracoordinated IVa metal complexes

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All Pb(IV) structures in the Cambridge Structural Database have a holodirected coordination geometry in which the lead–ligand bonds are distributed throughout the surface of an encompassing globe (such as tetrahedral PbL_4 structures). Pb(II) compounds for low coordination numbers (2-5) are prevalingly hemidirected, i.e. the lead–ligand bonds are directed throughout only a part of an encompassing globe and there is an identifiable void in the distribution of lead–ligand bonds (such as pyramidal PbL_4 structures) [1]. The stability of the hemidirected Pb(II) structures has been explained by the so-called “inert-pair effect” of $6s^2$ lone-pair electrons. MP2 studies of tetracoordinated Pb(II) complexes [1] show that their stable hemidirected structures have not a tetragonal principal axis (corresponding to C_4 or C_{4v} symmetry point groups) and their symmetry is lower. This symmetry descent cannot be explained by an electrostatic repulsion of the Pb lone electron pair. Alternatively, the stability of less-symmetric hemidirected PbL_4 structures might be explained by pseudo-Jahn–Teller effect [2]. The role of relativistic effects might be studied on a series of similar metal complexes with various central atoms of the same group of the periodic table. We have performed MP2 calculations of $[\text{ML}_4]^q$ complexes in their ground singlet spin states, $M = \text{Pb}, \text{Sn}$ or Ge in +II and +IV oxidation states, $L = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{OH}^-, \text{SH}^-, \text{H}_2\text{O}, \text{NH}_3$ or PH_3 , q being the charge of the complex. We have optimized their geometries within various symmetry groups and analyzed their imaginary vibrations and excited electron states from the point of view of the Jahn–Teller effect. We have shown [3] that the stable $[\text{M(II)L}_4]^q$ hemidirected structures of lower symmetry originate in the pseudo-Jahn–Teller effect. On the other hand, the problem of the stability of the high-symmetric $[\text{M(IV)L}_4]^q$ holodirected structures of T_d , D_{2d} or S_4 symmetry point groups cannot be explained by excited states of too high energies for an effective pseudo-Jahn–Teller interaction. The aim of our recent study is a QTAIM analysis of the above mentioned complexes in order to explain the differences between the structures of various symmetries and oxidation states of their central atoms.

Acknowledgments: This work is supported by Slovak Grant Agency VEGA under the contract No. 1/0598/16.

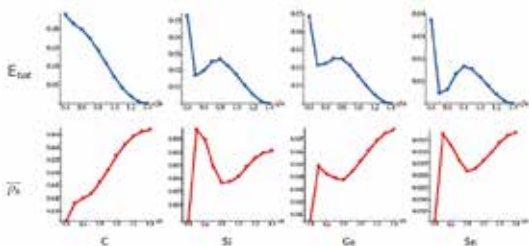
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Charge density analysis of the cubic diamond $\rightarrow \beta$ -Sn phase transition of group 14 elements

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The combined analysis of the change of two electron density (ED) based indicators, namely the number of bond critical points and the ED values at those points (ρ_b), along the transition pathway helps to rationalize the fact that the cubic diamond (cd) $\rightarrow \beta$ -Sn phase transition exists for Si, Ge and Sn, but isn't observed for the carbon. The geometry driven changes of the electron density are highlighted by the comparison of the optimized densities with the procrystal ones. Additionally, de-

localization indexes and interaction energies are used as measures of the bond strength. Both cd and β -Sn structures can be described by the body-centered tetragonal lattice, where $c/a = \sqrt{2}$ for the cd and $c/a \approx 0.5$ for the β -Sn phase. The cd $\rightarrow \beta$ -Sn transition can therefore be simulated by a smooth decrease of the c/a ratio. It was shown that, although the change in the ED topology during the transition is caused by the change of the symmetry, in terms of energy, the increase of the number of bond critical points around the atoms corresponds to the increase of the atomic coordination. The stability of the structures is a result of the interplay between the primary bond weakening, caused by their elongation, and the new bond formation. The ρ_b value is a suitable measure of a bond strength for these structures, the sum of them being correlated with the energy. To have a β -Sn-like energy minimum, the sum of the ρ_b values for procrystals should have a local maximum at $c/a \approx 0.5$. This is possible only if the volume decreases substantially (around 20%) between the cd and β -Sn structures, which is not fulfilled for carbon. This reveals the low compressibility of the carbon structures as a main factor of the absence of the phase transformations.

Combined analysis of intra- and intermolecular chemical bonding in organometallic compounds using QTAIM and Voronoi tessellations

A. V. Vologzhanina, A. A. Korlyukov and A. F. Smolyakov

A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia

The Voronoi tessellation has found diverse applications in crystallography of organic, inorganic, organometallic and macromolecular compounds in recent years. It applies an idea of Voronoi partitioning of crystal space, based on atomic coordinates, in order to construct atomic and molecular domains inside the crystal. Hence, it is not an electron-density-analysis technique, however, this model can give qualitative, quantitative and visual representation of intra- and intermolecular interactions, atomic and molecular domains, and crystal voids. Correct application of this method to various objects requires better understanding of its limitations, and accuracy of quantitative descriptors. We compared how the Voronoi approach and the QTAIM theory would perform for a number of organometallic compounds. Not only covalent and coordination bonds, but also metal-metal bonding and multicentered interactions were considered as examples of intramolecular bonding. Intermolecular bonding was studied on the example of hydrogen, dihydrogen and halogen bonds. Qualitative and quantitative similarity of two approaches was demonstrated. The Voronoi tessellation was proved to be suitable for understanding of the interplay between intermolecular strong and weak interactions and to be applicable to a large number of objects.

Acknowledgments: Authors acknowledge the Russian Science Foundation (grant 14-13-00884) for financial support.



SESSION 6

Understanding & engineering solid state materials

Chairs:

Mark A. Spackman, Jacob Overgaard, Jozef Kožíšek

When experimental charge and spin density data challenge ab initio and DFT calculations

Claude Lecomte^a, Bolivar Voufack^a, Mohamed Souhassou^a, Nicolas Claiser^a, Slimane Dahaoui^a, Alessandro Genoni^b, Marco Marazzi^b, Zeyin Yan^c, Jean Michel Gillet^c and Béatrice Gillon^d

^a CRM2, Institut Jean Barriol, Université de Lorraine and CNRS, France

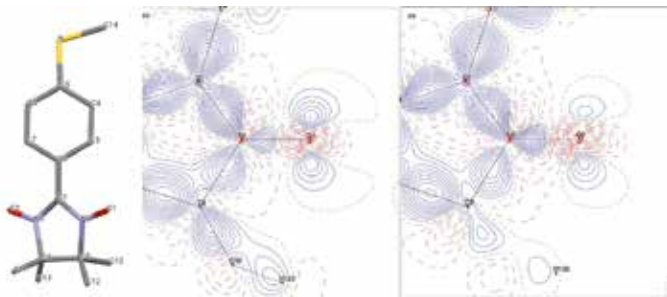
^b SRSMC, Institut Jean Barriol, Université de Lorraine and CNRS, France

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^d Laboratoire Leon Brillouin CNRS CEA Saclay, France

X-ray diffraction (XRD) and polarized neutron diffraction (PND) are powerful tools for exploring respectively experimental charge density and magnetic moment distributions. Recently we proposed a new method (coded in Molly-NX program) for jointly refining these two quantities, giving access to very precise models of spin resolved electron density. This has been first applied to magnetic coordination compounds but never to organic radicals. The aim of this talk is to discuss the molecular or collective origins of the magnetic properties of 2-(4-thiomethylphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide commonly known as Nit(SMe)Ph on the basis of experimental X-ray and polarized neutron diffraction data and of theoretical, DFT and CASSCF calculations. It will be shown that the resulting theoretical maps calculated with DFT do not agree with experiments whereas the high level ab initio CASSCF do. These results demonstrate the utmost importance of experimental charge and spin density determinations to calibrate theoretical results.

Acknowledgments: Agence Nationale de la recherche (ANR), CNRS and Université de Lorraine are greatly acknowledged.



Uncovering the electrostatic nature of host-guest assemblies

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and Mark Spackman^a

^a *The University of Western Australia, Australia*

^b *Aarhus University, Denmark*

Host-guest chemistry has attracted great attention since its discovery in late 1960's. Before that, it was hard to connect the concepts and chemical interpretations from small-molecule crystallography with those from macromolecular crystallography. Due to the low resolution and universal disorder problems, the electrostatic information in macromolecular crystallography has remained unreachable. Sitting between small molecules and macromolecules, host-guest complexes provide fruitful amount of information in non-covalent interactions, molecular electric moments, electrostatics etc. Although disorder, weak diffraction power and large size remain as general problems for solving host-guest complexes' structures, with recent advance in "Dectris" detectors and cooling devices and application of intense synchrotron beam many non-disordered host-guest complexes became feasible to high-resolution X-ray diffraction study and modern charge density analysis [1]. This enables us to carefully evaluate the non-covalent interactions which play crucial roles not only in host-guest and supramolecular complexes but also in biological macromolecules. Our recent research has extensively focused on the interactions between crown ether/calixarene derivatives with small neutral guest molecules. Preliminary results have shown the strong host-guest binding energy ($> 90 \text{ kJ.mol}^{-1}$) between 18-crown-6 and sulfonamide derivatives [2]. Such strong binding commonly exist in crown ether: neutral guest complexes. Moreover, due to the strong electric field from the crown ethers the dipole moments of those guest molecules are dramatically enhanced. Meanwhile, we also evaluated the properties of guest molecules with zero dipole moment (e.g. CCl_4 , CS_2 , etc.) in calixarene host environment. Based on our substantial electron density studies in various host-guest complexes, I will present our results in studying the nature and functions of non-covalent interactions in the formation of supramolecular assemblies.

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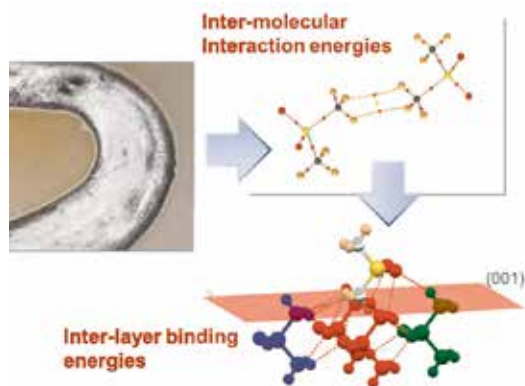
Inter-layer binding energies from experimental charge densities: Exploring the plastic bending in a molecular crystal

Sajesh P. Thomas, Ming Wen Shi, Dylan Jayatilaka and Mark A. Spackman

School of Chemistry and Biochemistry, The University of Western Australia, Australia

The study of mechanical properties of organic crystals is a burgeoning interest in crystal engineering.[1] Bending/shearing phenomena are often correlated with the anisotropy of intermolecular interactions in crystals. However, quantitative studies that rationalize mechanical behaviour of organic crystal are rare.[2] In this context, the ‘Energy Framework’ tool recently introduced by us has been found useful for the visualization and understanding of crystal packing in terms of intermolecular interaction energy topology.[3] Thus it becomes possible to correlate the anisotropy in the strengths of crystal packing which manifests as the anisotropy in the ‘energy frameworks’, making it an efficient tool to predict bending/ shearing behaviour in crystals.

Bending property exhibited by several crystals have been explained in terms of anisotropic energy frameworks. Here, we present an intriguing observation of plastic bending in an organic crystal that defies this trend, and exhibits nearly isotropic energy framework. In order to rationalize the observed bending behaviour of the crystal, we performed X-ray charge density analysis on this crystal. The interaction energies and inter-layer binding energies, derived from the experimental charge density model, are discussed in conjunction with the CE-B3LYP energy values from the energy framework module of CrystalExplorer. The structural origin of the observed plastic bending phenomenon has been rationalized in terms of these energy values. The argument has been further substantiated by the electrostatic potentials mapped on Hirshfeld surfaces. In addition, some initial results on the interaction energy values from the X-ray wavefunction refinement will also be discussed in this context.



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Locality of intermolecular interactions in organic crystals**Tonglei Li***Industrial & Physical Pharmacy, Purdue University, West Lafayette, Indiana, USA*

Intermolecular interaction plays a critical role in crystallization of molecular crystals. Not only is a crystal structure the result of competition and complement of various types of intermolecular interactions that a molecule forms, but the crystallization process is also controlled by the interactions established among solute and between solute and solvent molecules. Importantly, the molecular interactions of a molecule are highly anisotropic, resulting in unique crystal structure(s) when it crystallizes. The goal of our research is thus to probe and predict such anisotropy of a molecule's interacting capabilities with another molecule (of the same or a different compound). We have investigated this locality of molecular interactions with electronic calculation, in particular, conceptual density functional theory (CDFT). The essence of our efforts lies in calculating, analyzing, and quantifying electron densities of a molecular system. We have sought to identify local electronic properties capable of characterizing local softness and hardness. The local electronic quantities are believed to be deterministic of intermolecular interactions. According to the HSAB (hard and soft acids and bases) principle, proper matching between local soft-ness or hardness indices governs the locality of intermolecular interactions that a molecule develops. Our results support this notion and our long-term goal is to develop CDFT concepts that can better characterize the locality of intermolecular interactions and apply for systemically examining major intermolecular interactions found in organic crystals.

Experimental and theoretical charge density study of the I...N halogen bond and F...F interactions in iodoperfluoroalkylimidazoles

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Halogen bonding (XB), namely any non-covalent interaction involving halogens as electrophilic sites, is a relatively new item in the supramolecular toolbox and shares numerous properties with the better known hydrogen bonding. The X...N(O) halogen bond has been thoroughly investigated by means of several experimental and theoretical techniques, including the topological analysis of the X-ray multipole refined charge density [1]. Fluorine-Fluorine interactions [2] are much less explored intermolecular interactions, though F...F contacts below or just above the sum of van der Waals radii of the fluorine atoms are ubiquitous in fluorinated organic structures. We present here the results obtained on two iodotetrafluoroethylimidazole derivatives, whose crystal structure is dominated by formation of I...N halogen bonds between equivalent molecules, and stabilized by the presence of F...F and other weak (C-H...F, C-H... π and π ... π) interactions. The experimental charge densities have been derived from X-ray data collected at 100 K, using the aspherical atom formalism of Stewart [3] as implemented in VALTOPO [4], as well as by accurate M062X/6-311++G(d,p) and MP2/6-311++G(d,p) calculations in gas phase, and M062X/6-311G(d,p) calculations in solid state [5]. The topological analysis of charge density and its Laplacian allowed to elucidate the role exerted on the XB properties by the alkyl/aryl moiety bonded to the iodine atom through comparison with previous results [1a]. Moreover, an Interacting Quantum Atoms (IQA) analysis [6] on the M062X/6-311++G(d,p) optimized halogen bonded dimer revealed the nature essentially electrostatic for this interaction. Selected dimers extracted from the crystal structure were as well submitted to IQA analysis in order to investigate the nature of the F...F interactions and in particular the relative electrostatic/exchange contributions. Both Type I ($\theta_1 \cong \theta_2$) and Type II ($\theta_1 \cong 180^\circ$ and $\theta_2 \cong 90^\circ$, where $\theta_1 = \text{C-X1}\cdots\text{X2}$ and $\theta_2 = \text{X1}\cdots\text{X2-C}$ angles) geometries have been considered. All interactions in the presently investigated systems follow the relationship recently suggested by Spackman et al [7].

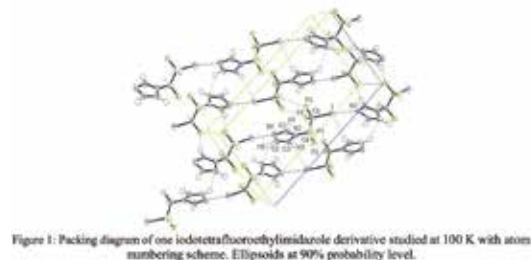


Figure 1: Packing diagram of one iodotetrafluoroethylimidazole derivative studied at 100 K with atom numbering scheme. Ellipsoids at 90% probability level.

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Is there a link between charge density distribution and packing motif in donor-acceptor co-crystals?

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Co-crystals have various applications in design and production of new pharmaceuticals, energetic and optical materials. Much efforts have been made to understand and control supramolecular organization in multicomponent crystalline systems, however, studies of electronic structure of co-crystals and its relation to their structural characteristics are scarce. In this work, we report charge density study of binary donor-acceptor complexes of nitro- and cyano-bearing aromatic compounds (2,4,6-trinitroaniline, 1H-3,5-dinitropyridin-2-one, tetracyanotophene, etc.) with polyaromatic hydrocarbons. Single crystals of these systems are easy to obtain, but only some of them are suitable for high-resolution X-ray diffraction studies due to static or dynamic disorder of components. To have a possibility to analyze the electronic structure of the whole sets of co-crystals formed by particular donor and/or acceptor, we compare different approaches that allow obtaining approximate charge density distribution; those include multipole refinement of high-resolution X-ray diffraction data, use of multipole parameters transferred from pure components, invariom modeling and ab initio calculations of crystals. For all the co-crystals analyzed, local and integral charge density descriptors are compared, which include characteristic sets of critical points, values of charge density and its derivatives in critical points, atomic charges and overall charge transfer between the components. A special attention has been paid to the contribution of different types of donor...acceptor, donor...donor and acceptor...acceptor interactions into hereto-association and into the formation of a crystal packing of a particular type. Our results allowed us to make some useful suggestions for prediction of packing motifs in crystal and directed engineering of co-crystals with desired mutual disposition of its components optimal for physical property of interest.

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Electron density studies as a new volume-based approach to thermophysical properties of ionic liquids

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Ionic liquids (ILs), low-melting organic salts, have found use in many areas of science and industry owing to their unique properties[1]. By an appropriate choice of cation and anion, ILs can be tailored to a specific application; however, the number of such combinations is so huge that their experimental screening is unrealistic. This triggers the search for methods to predict properties of an IL from the knowledge of its constituents: among them, volume-based approaches are gaining an increasing attention[2]. They use empirical relations between melting points[3] or other properties of ILs and their molecular volumes that are accessible by X-ray diffraction. As another approach to ionic volumes, we suggest electron density studies from high-resolution X-ray diffraction, which are very helpful in addressing important chemical problems in material science[4]. They are, however, nearly impossible for ILs, as collecting X-ray diffraction data of suitable quality or growing single crystals for them is a real challenge. A solution to the former problem may be found in a concept of invariums (aspherical atomic scattering factors computed for an atom in a given covalent environment within the multipole formalism[5]), and to the latter problem, in search for correlations between some features of ILs made accessible by the invarium approximation (such as ionic volumes) and their physicochemical behavior. The invarium approximation, which produces 'experimental' electron density from X-ray diffraction data of lower resolution or compromised otherwise and is applicable to any organic compound (as missing invariums can be easily calculated), has recently been pushed beyond molecular crystals for which it has been introduced – into the realm of organic salts[6]. Although ignoring charge redistribution between ions, it gives chemical bonding features that are very similar to those obtained from electron density studies based on high-resolution X-ray diffraction. After the successful transfer of the invarium approximation to ILs[7], we probed the applicability of ionic volumes from thus derived electron densities for volume-based description and prediction of thermophysical behavior of ILs. Tested on a series of salts with 1-tetradecyl-3-methylimidazolium cation and ten anions (most of them commonly used in ILs) with different size, shape and coordination ability, this approach allowed observing some general trends and proposing guidelines for the design of new ILs.

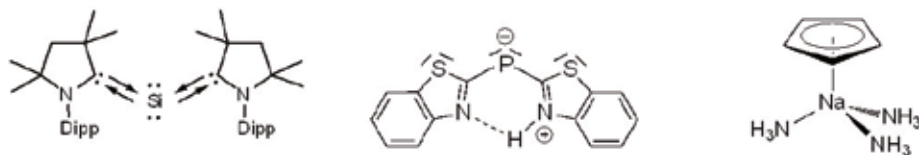
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100 years Lewis diagram – still valid in the light of charge density?

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Ever since G. N. Lewis invented the dash between two elements to define the two-centre two-electron bond 100 years ago this concept proves to be most resilient among the various disciplines of chemistry.[1] It is the lowest common denominator and works best in organic chemistry. Even the reactivity of substrates and the variety of products can to a certain extent be explained and predicted by weighting the canonical forms. Anyhow, there is no dash in nature and the chemical bonding is wide open to discussion, prone to implement various codes for interactions like the arrow for donor bonds and the dotted line for weak interactions, e. g. hydrogen bonding. The electron deficient bonds e. g. in boron compounds are particularly difficult to rationalise. The talk will provide some physically meaningful insights from charge density investigations and discuss the chemical re-translation to reactivity, among them low valent silicon,[2] (hetero)aromatic systems[3] and reactive organometallics.[4] Some of these cases can be covered by Lewis diagrams, others not. They are a good start to explain bonding, but certainly anticipated, mostly too limited in others.

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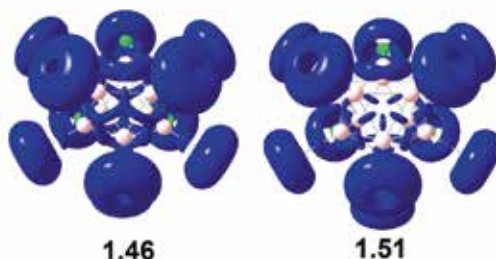
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Anions with typical cation chemistry! Understanding the curious reactivity of $[\text{B}_{12}\text{X}_{12}]^-$

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Polyhedral closo-dodecaborate dianions ($[\text{B}_{12}\text{X}_{12}]^{2-}$, $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) attracted attention in the past due to their application as weakly coordinating anions in synthetic chemistry.[1] This main property, their extraordinary resistance against electrophilic attack, may be deeper understood by investigations of the $[\text{B}_{12}\text{X}_{12}]^-$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) anions. $[\text{B}_{12}\text{X}_{12}]^-$, although being anionic, have to offer a remarkable electron deficiency at the vacant boron atoms keeping abstracted anionic ligands like halogenides in place. As a consequence, there is no evidence in the literature that $[\text{B}_{12}\text{X}_{12}]^-$ was detected in any experiment performed in condensed phase. In mass spectroscopic experiments, we created $[\text{B}_{12}\text{X}_{12}]^-$ anions and investigated their reactions with the nucleophiles water H_2O and nitrogen N_2 . These reactions were referenced against the reaction of the phenyl cation C_6H_5^+ with the same nucleophiles.[2] Interestingly, the anion $[\text{B}_{12}\text{X}_{12}]^-$ reacted as readily with both nucleophiles as the cation C_6H_5^+ , but preferring N_2 . In order to understand this behavior of $[\text{B}_{12}\text{X}_{12}]^-$, we performed theoretical calculations of all involved species and investigated their real-space bonding indicators based on an electron-density analysis and on an analysis of the Electron Localizability Indicator ELI-D [3]. We compared the results with molecular orbital and electric field properties. All results confirm that there is a positively charged region at the vacant boron atom that is isolated from the delocalized electronic system of the remaining eleven boron atoms and creates a reactive channel. This reactive channel is ideal for the attachment of unpolar species such as N_2 , but less ideal for polar species such as H_2O . We can explain the attachment mechanism with the combination of descriptors used, and predict that the unpolar carbondioxide molecule CO_2 will also be attached and activated. Hence, $[\text{B}_{12}\text{X}_{12}]^-$ is not only interesting for its unusual, counterintuitive reactivity, but will also be investigated for its catalytic properties in a forthcoming study.

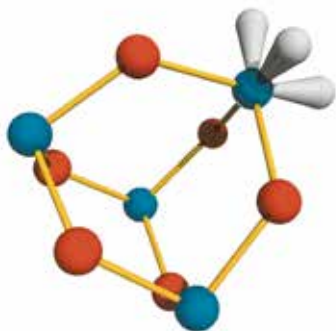


Isosurface representations of the ELI-D of $[\text{B}_{12}\text{X}_{12}]^-$ for two different isovalues (1.46 and 1.51).

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Lone electron pair dispersion? – Charge density of cubic arsenic(III) oxide

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Stereoactive lone electron pairs (LEPs) situated on arsenic atomic cores in arsenic(III) compounds are responsible for a number of their interesting structural features. Thanks to their presence, arsenic may be involved in weak interactions such as As...O and As...X (X stands for halogen).[1] It is the directional As...O interactions that cause the sphere-like As₄O₆ molecules to pack in a diamondoid network in the cubic polymorph of arsenic(III) oxide, arsenolite, rather than in the closest-packed-sphere-type structure. We have carried out precise high-angle diffraction experiments on arsenolite single crystals using both laboratory X-ray source and synchrotron X-ray radiation. The obtained diffraction data have been analysed utilising the Hansen-Coppens multipolar model[2] and X-ray constrained wavefunction refinement.[3] CDD resulting from

both models has been analysed within the QTAIM (Quantum Theory of Atoms in Molecules) framework.[4] Additionally, the experimental results have been compared with benchmark calculations performed within the Wien2k program suite utilizing the linearized augmented plane wave method.[5] Both experimental and computed charge density indicate departure of the LEP symmetry from the expected cylindrical symmetry to the symmetry of threefold axis, accompanied by the LEP dispersion (as shown in the Figure above).

Acknowledgments: Authors thank National Science Centre for financial support of this work (DEC-2012/05/N/ST5/00283). ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under grant number NSF/CHE-0822838. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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Addressing the issue of bending in certain metallocenes: a comparative study of linear MgCp^*_2 vs. bent CaCp^*_2 through theoretical and experimental electron density analysis

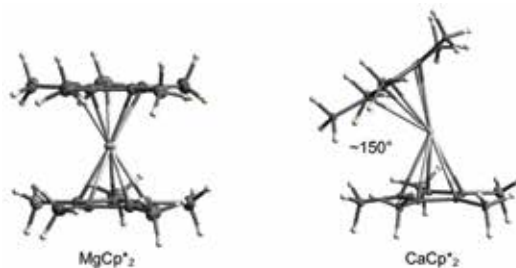
Pal, R.^a, Shi, M. W.^b, Krzeszczakowska, J. M.^c, Jayatilaka, D.^b, Beckmann, J.^a and Grabowsky, S.^a

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In the family of metallocenes, MgCp^*_2 (Cp^* , pentamethylcyclopentadienyl) exhibits a regular sandwich structure; i.e., two Cp^* rings are parallel in the gas phase and in the crystal geometry.[1] In contrast, CaCp^*_2 is bent in both gaseous and solid state with the ring centroid - metal - ring centroid angle being 154 deg obtained from gas phase electron diffraction (GED)[1] and 147.7 deg (146.3 deg) for the two independent molecules in the asymmetric unit of the crystal structure (see figure).[2] The retaining of the bent geometry even in the gas phase suggests that the root cause of bending must have intramolecular origin. Three factors accounting for bending in these complexes have been put forward; (i) ligand induced charge concentration (LICC) at the metal centre,[3] (ii) attractive van der Waals or dispersive forces between the methyl groups[4] and (iii) optimum metal...ring interaction[5] which is an integral part of structure and bonding properties in metallocenes. To investigate the role of dispersive interaction, high level ab-initio calculations on isolated molecules MgCp^*_2 and CaCp^*_2 (experimental and optimized geometries) and MgCp_2 and CaCp_2 (optimized geometries) using both B3LYP and B3LYP-D methods were carried out. The electronic properties have been analysed using Electron Localizability Indicator (ELI), Hirshfeld surface combined with electrostatic complementarity analysis and studies within the framework of Quantum Theory of Atoms in Molecules (QTAIM) approach. Theoretical findings have been supported by experimental charge density determinations on MgCp^*_2 and CaCp^*_2 . The comparison between the two closely related alkaline earth metal ions Mg^{2+} and Ca^{2+} in their Cp^* complexes serve as a case study to explore which electronic effects cause the bending in such systems without any lone pair at the metal centre.

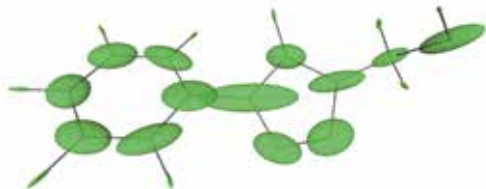


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Polarizabilities of atoms in molecules: the choice of partitioning schemes

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Department of Chemistry and Biochemistry, University of Bern, Switzerland

The methods to partition the molecular polarizability into atomic terms are revised and critically discussed. The pro's and cons of space or fuzzy partitioning are compared. The focus is on the interpretation of the two components of the atomic polarizabilities, the inherent (or intrinsic) and the charge transfer, and on the similarities between polarizabilities of atoms with same chemical environments and therefore on their transferability. Methods to improve the calculations of crystal dielectric constants from distributed atomic polariz-

abilities on building blocks of organic and organometallic crystalline materials are also presented.

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The background of the slide is a photograph of a city skyline at sunset. The sun is low on the horizon, creating a warm, orange glow that fills the sky. Several tall skyscrapers are visible, their silhouettes softened by the light. In the foreground, there are lower-rise buildings and some greenery, all appearing slightly hazy. The overall mood is serene and modern.

SESSION 7

Electron diffraction – the future of charge density measurements?

Chair:

Wolfgang Scherer

Electronic cryomicroscopy: from molecules to cells**Wolfgang Baumeister***Max Planck Institute of Biochemistry, Germany*

Today's biomolecular electron microscopy uses essentially three different imaging modalities: (i) electron crystallography, (ii) single particle analysis and (iii) electron tomography. Ideally, these imaging modalities are applied to frozen-hydrated samples to ensure an optimum preservation of the structures under scrutiny. Electron crystallography requires the existence of two-dimensional crystals. In principle, electron crystallography is a high-resolution technique and it has indeed been demonstrated in a number of cases that near-atomic resolution can be attained. Single-particle analysis is particularly suited for structural studies of large macromolecular complexes. The amount of material needed is minute and some degree of heterogeneity is tolerable since image classification can be used for further 'purification in silico'. In principle, single particle analysis can attain high-resolution but, in practice, this often remains an elusive goal. However, since medium resolution structures can be obtained relatively easily, it often provides an excellent basis for hybrid approaches in which high-resolution structures of components are integrated into the medium resolution structures of the holocomplexes. Electron tomography can be applied to non-repetitive structures. Most supramolecular structures inside cells fall into this category. In order to obtain three-dimensional structures of objects with unique topologies it is necessary to obtain different views by physical tilting. The challenge is to obtain large numbers of projection images covering as wide a tilt range as possible and, at the same time, to minimize the cumulative electron dose. Cryoelectron tomography provides medium resolution three-dimensional images of a wide range of biological structures from isolated supramolecular assemblies to organelles and cells. It allows the visualization of molecular machines in their functional environment (in situ) and the mapping of entire molecular landscapes.

Approaching the physical limits of electron cryomicroscopy for structure determination

Christopher J. Russo

Laboratory of Molecular Biology, MRC, UK

In spite of recent advances in electron cryomicroscopy (cryo-EM), the structures of many proteins cannot be determined by cryo-EM because the individual protein molecules move during electron irradiation. This blurs the images so they cannot be aligned with each other to calculate a 3D density map. I will discuss the types of movement at various length scales that occur in biological specimen during high energy electron irradiation, and show how reducing this movement leads to improved micrographs and density maps. Further, I will discuss several physical limits important to cryo-EM and how they determine the types of specimen which will ultimately be amenable to atomic resolution imaging with electrons.

Towards the measurement of bonding in and around inhomogeneities in nano-composite materials

Philip Nakashima^a and Laure Bourgeois^b

^a *Department of Materials Science and Engineering, Monash University, Australia*

^b *Monash Centre for Electron Microscopy and Department of Materials Science and Engineering,
Monash University, Australia*

Most commercially important nano-composite materials are designed so that the nanoscale particulate phases impart desirable properties on the composite material without compromising other beneficial properties inherent in the host matrix. It is well-known that chemical bonding and electron distribution are the dominant determinants of all materials properties (except radioactivity). Therefore, the question is posed as to whether it is possible to measure bonding electron distribution within nano-particles contained in a host matrix as well as at the particle/matrix interfaces. This would open a window onto a fundamental understanding of the origins of the hybridized properties of nano-composite materials. This work takes advantage of the situation in some nano-composites where the host matrix and secondary nano-particulate phases are crystallographically coherent. This allows convergent beam electron diffraction patterns taken through volumes of material containing a particle, under specific geometric conditions, to be analysed with the multislice formalism for electron scattering [1]. It is shown here that quantitative convergent beam electron diffraction (QCBED) [2], applying the multislice formalism, can measure bonding-sensitive structure factors on both side of a nano-scale void in aluminium. This has led to the commencement of work on intermetallic precipitates in aluminium alloys, which will also be discussed here.

Acknowledgments: All data were collected at the Monash Centre for Electron Microscopy. Some of the analyses were carried out together with Mr. Tianyu Liu and Mr. Yao Qiu. This work was funded by the Australian Research Council (FT110100427).

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The background of the entire page is a faded, artistic image of a city skyline at sunset. The sun is low on the horizon, creating a warm, orange and yellow glow that fills the sky. Several tall skyscrapers are visible, their silhouettes softened by the light. In the foreground, there are lower-rise buildings and some greenery, also appearing in a hazy, blue-tinted style. The overall effect is a serene and professional-looking backdrop for the text.

POSTER SESSIONS

Session 1

Monday, June 27th 2016, 17:30 – 19:00

odd poster numbers

Session 2

Tuesday, June 28th 2016, 17:30 – 19:00

even poster numbers

Validation of charge density refinement strategies

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Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Germany

Modern experimental charge density investigations require the most accurate data, the highest possible resolution and an optimized refinement strategy [1,2]. As stated in the XD2006 manual [3] the complexity of the model should be increased in a stepwise manner and the final data to parameter ratio should not fall below a value of 10. However, following these guidelines does not guarantee a reasonable model or, more precisely, all refined parameters to be reasonable. Common criteria such as residuals of the linear least squares refinement tend to decrease with increasing number of parameters. The statistical method of cross-validation helps to decide whether the addition of parameters increases model quality or introduces bias. This method is well established in macromolecular crystallography, known as the Rfree concept [4]. A fraction of the measured data is excluded from the refinement process and residuals are calculated against the unused data. In charge density investigations there are two concerns that need to be addressed: Firstly, the changes in R-values are small compared to the precision of the Rfree value. Therefore, k-fold cross-validation is utilized. The data set is divided into k subsets. One set acts as validation set, while the remaining sets determine the model. The refinement is repeated k times with each of the subsets serving once as Rfree set [5]. Hence, every single reflection is used for validation. Secondly, the omission of particular reflections may introduce severe bias to the model. This can be monitored by an inspection of the parameter distribution of the k refinements. This approach is automated for charge density refinement procedures using the XD2006 program suite [3]. The application of this procedure is herein demonstrated and validated.

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The role of the hydrogen atom model in crystallographic studies

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and Krzysztof Woźniak^a

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^b Synchrotron Radiation Research Section, National Cancer Institute, Argonne, IL, USA

$$RMSD = \sqrt{\frac{\sum_{t=1}^n (\hat{y}_t - y)^2}{n}}$$

Hydrogen bond (HB) is the most important stabilization interaction for proteins. Thermodynamic measurements showed that energies associated with HB formation in the liquid and solid states are similar [1], so single crystal diffraction methods

are an efficient tool supplying not only geometry of a given interaction but also information on its relative strength. However, truly quantitative studies of both geometry and electron density distribution in organic crystals are also possible when experimental charge density approach is applied [2]. The proper description of the H atom in the charge density model must take into account two factors: thermal motion of atoms (which can be approximated using SHADE server [3]) and– in case of refinement with the Hansen-Coppens model - the expansion-contraction coefficients of the valence density (κ). The role of the second factor is usual underestimated, however there are three theoretical approaches to its modelling: Volkov-Abramov-Coppens (VAC) model [4], UBDB databank [5] and theoretical κ parameters obtained from Crystal 09 calculations [6]. Referential energies were calculated with the program Tonto [7], where wave functions for isolated molecule and for molecule in the crystal field, were simulated with cluster charges and dipoles. The results were used as an input for computations of electrostatic energy EES of dimer interactions in the SPDFG program. [8] A comparison of the interaction energy of hydrogen bonds in all three models indicates: • different types of κ and κ' values for the hydrogen atoms introduce variation in the values of the electrostatic interaction energy • κ and κ' derived for H atoms from VAC model and UBDB give the best results in comparison to the reference model and the highest differences in resulting energies are obtained for the κ and κ' set to 1.0 or derived from refinement against theoretical structure factors • the modeling of the κ and κ' for H-atoms is apparently only a small amendment in relation to other problems with multipole model parameterization, and the differences obtained in the sum of dimer EES show that current model had trouble with the correct estimation of energy based on experimental data. The RMSDs values for all dimers electrostatic energies were calculated from formula presented above, with the spdf-polarized method EES values as a reference model \hat{y}_t and the results are presented in Table 1.

theoretical F ²			experimental F ²				SPDFG	
refined	UBDB	VAC	$\kappa=1$	Crystal09	UBDB	VAC	promolecule	cluster
17	16	16	32	31	27	23	21	0

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Towards precise and accurate determination of hydrogen positions with X-ray diffraction data utilizing hydrogen maleate salts

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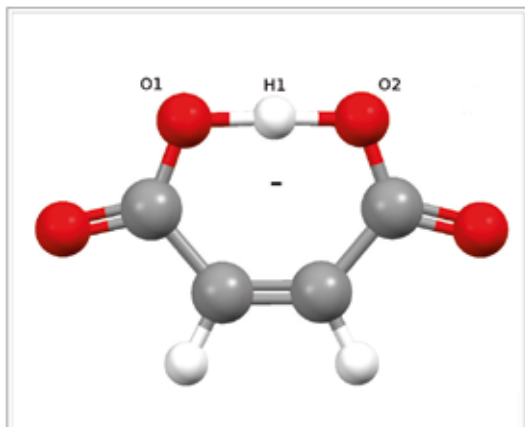


Figure 1: Hydrogen maleate anion

Hydrogen maleate salts offer the unique opportunity to follow a pseudo-reaction pathway of a proton transfer not only in theoretical simulations but also experimentally because the hydrogen position in the strong and short intramolecular O-H-O hydrogen bond is highly flexible dependent on the cation (Figure 1). There are numerous crystal structures of hydrogen maleate salts in the literature showing that the O-O distance is constant around 2.45 Å, but the O-H distances vary from 0.88 Å[1] and 1.37 Å[2] in highly asymmetric hydrogen bonds to 1.22 Å[3] in symmetric hydrogen bonds with a large variety of intermediate distances. This means that snapshots along a pseudo-reaction pathway can be measured and with the symmetric hydrogen bonds, even a model for a possible transition state is accessible. For these aims, it is crucial to obtain the precise and accurate position and displacement parameters of the hydrogen atoms, which can only be achieved using neutron-diffraction techniques or new quantum crystallographic techniques based on X-ray data (such as Hirshfeld Atom Refinement, HAR). HAR's capability will be shown using synchrotron data sets of the compounds 4-aminopyridine, 8-hydroxyquinoline, barium, calcium, potassium, lithium, magnesium, sodium and phenylalanine[4] hydrogen maleates. It is common to all structures that intermolecular hydrogen bonds are responsible for the packing directed along the molecular plane. These intermolecular interactions seem to govern the position of the H1-atom in the intramolecular hydrogen bond. All structures can be sorted into three groups when considering the position of the H1 atom, one where the position is highly symmetric, one intermediate position and one highly non-symmetric position. Hirshfeld surface analyses and "fingerprint" plots[5] show that O-H bonds are responsible for over 41% of all interactions between the cation and anion, in particular O2...H-D bonds, which represent over 13% of these interactions for all the compounds. Possible correlations between various properties and the position of the hydrogen atom H1 in question will be discussed.

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A library for multipolar model structure factor calculations with CPU and GPU

Michał Chodkiewicz^a, Paulina Dominiak^a, Szymon Migacz^b, Witold Rudnicki^b,
Anna Makal^a and Krzysztof Woźniak^a

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^b *ICM, University of Warsaw, Poland*

A library for calculation of scattering factor for charge density described with Hansen-Coppens [1] formalism is presented. The library is designed for use with both small molecule and macromolecular crystallography software. In the former case the structure factor calculation step can be a performance bottleneck, therefore a multithreaded versions of the code for CPU and GPU were developed. The library uses notion of atom type since one of its possible applications would be extension of the existing crystallographic codes to use aspherical pseudoatoms databanks. Performance tests for macromolecules parameterized with the theoretical databank of aspherical pseudoatoms (UBDB) [2] are provided. Steps needed for structure factor calculations are separated and exposed in the library application programmer interface (API) therefore it can be used for calculations involving modified versions of Hanse-Coppens model.

Bibliography:

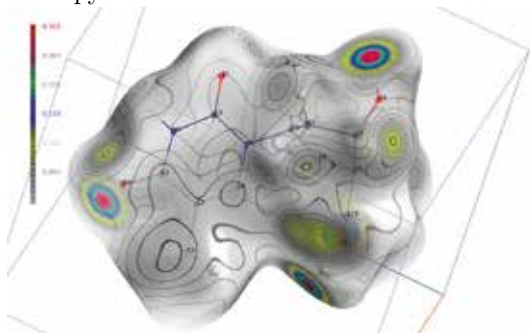
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Hirshfeld partitioning of dynamic electron densities

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Hirshfeld partitioning is a widely used and accepted technique to get individual properties of atoms or molecules in crystals[1]. It is a computationally easy fuzzy partitioning based on a simple independent atom model. We present a way to partition thermal smeared dynamic electron densities. Dynamic electron densities are for example the result of a Maximum Entropy Method calculation.



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Charge density study: comparison of data from two diffractometers on salicylate-copper complex

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This work deals with the study of experimental and theoretical electronic structure of (5-chloro-salicylate)-(2,9-di-methyl-phenanthroline)-(aqua) copper complex. Beside this, the comparison of data sets from two diffractometers are presented. Experimental X-ray data for compound under study were collected at 100(1) K on an Oxford Diffraction Gemini R diffractometer equipped with a Ruby CCD detector and a graphite monochromator, using Mo-K α radiation and on Stoe Stadi Vari diffractometer with Ag microsource and Pilatus300K detector. In the experimental electron density distribution, the multipole formalism of Hansen and Coppens [1] as implemented in the XD program suite [2] was used to represent the multipole model of charge densities. The program Gaussian09 [3] was used to perform the quantum mechanical single molecule calculations based on the experimentally observed geometry using the BLYP [4] (or B3LYP) functional and a 6-311G** basis set [5].

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Molecular interactions in the polymorphs of pyrazinamide from thermal diffuse scattering

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In charge density studies the thermal displacement of the atoms is an error source, which is minimized by reduction of temperature. The effect of atomic thermal motion is easily seen in the intensity changes of a Bragg reflection when recording at multiple temperatures. Thermal diffuse scattering (TDS) is a related phenomenon, which arises from the lattice vibrations, and implicating that the atomic vibrations not can be assumed independent. However, TDS have mostly been regarded as a nuisance contributing to the background. This contribution, which is not uniform, but has its largest contribution near the Bragg peaks, may alter the charge density model. But very little is known about the consequences of ignoring the TDS effect. Furthermore, to understand many of the fundamental properties of crystalline materials such as phase transitions, and elastic, acoustic and thermal properties [1], the lattice vibrations cannot be neglected. An unambiguous phonon dispersion determination is a ambitious task demanding access to either specialized neutron or synchrotron facilities [2-3]. Despite the vast amount of data collected, the data analysis often rely on calculated phonon dispersions. Alternatively, TDS also provides information on the phonon dispersion but in a convoluted form: All data points contain intensity contributions from all phonons. However, the current state of computers combined with the least squares refinement technique permits an extraction of the phonon dispersion. The advantages are fast data acquisition, simplistic experimental setup and small sample volume [4]. In the current study we investigate the phonon dispersion of the polymorphic forms of pyrazinamide. It is possible to determine the atomic displacement parameters, if the full phonon dispersion is known. This provides an alternative method to deconvolute the thermal motion. Further, the decomposition of the average motion into the constituent phonon contributions provides an alternative insight into the molecular interactions. Thus, investigating the TDS pattern near a solid-to-solid phase transition will provide information on the interactions in the crystal, but from a dynamical point of view, rather than the traditional static point taken in charge density analysis. Ultimately, this will contribute to the understanding of the relative stability and the phase transitions of pyrazinamide.

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Thermal analysis of 2,6-diaminopurine crystals with the help of charge density**Urszula Budniak and Paulina M. Dominiak***Department of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Poland*

The aim of the project was to analyze temperature evolution of 2,6-diaminopurine (DAP) crystal structure. DAP is a nucleobase, a derivative of adenine present in nucleic acids, which can be used to compare Watson-Crick pairing in DNA. Investigating the properties of analogues of nucleobases may contribute to our knowledge about nucleic acid properties in general and give an opportunity to find novel ligands binding to DNA, what is essential for drug design. The main part of the project was based on the single-crystal X-ray diffraction experiments. The single crystals of DAP were measured in different temperatures ranging from 100 to 320 K. Due to the temperature rise, subtle, untrivial changes in diffraction pattern were observed. The structures were refined using three methods – Independent Atom Model (IAM), Transferable Aspherical Atom Model (TAAM) and Multipole Model (MM). What essential, charge density is strongly correlated with thermal motion of atoms, thus the proper de-convolution is needed. Measurements in low temperature reduce thermal vibrations and hence increase the resolution limit, up to which the data can be collected. More accurate charge density model allows to obtain better thermal motion model. For this reason, high-resolution charge density measurement at 100 K was conducted. Obtained data were then refined using MM. Unit cell parameters and atomic displacement parameters variations within temperature changes were noticed. The accurate analysis of observed variations was performed using the parameters transferred from MM. To complement X-ray measurements, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) experiments were also performed. Existence of phase transition was confirmed, what can be correlated with changes in diffraction pattern. Preliminary results suggest that DAP crystals have commensurate structure, which can be also described as a superstructure.

One electron properties of YTiO_3 refinement from multi experimental and theoretical investigations

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Experimental and theoretical investigations of the electronic and magnetic properties of YTiO_3 have been conducted. In position space, the charge and spin densities are determined using high resolution X-ray diffraction and polarized neutrons diffraction, while in momentum space, directional magnetic Compton profiles, measured by the polarized X-ray incoherent inelastic scattering, are used to reconstruct two dimensional spin momentum density. This project is an ANR grant which aims to combine X-ray, polarized neutron diffraction and Compton scattering experiments on YTiO_3 perovskite structure whose magnetic properties are due to an unpaired electron on Ti 3d orbitals. The quasi octahedral oxygen environment around Ti lead to the energy of d_{xy} , d_{xz} , d_{yz} to be less than that of $d_{x^2-y^2}$ and d_{z^2} . The resulting electron density in position (diffraction experiments) and momentum space (Compton scattering), compared to that obtained by means of periodic DFT calculations, will be used to reconstruct by an experimental first order density matrix.

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Role of the diagonal and extra diagonal terms of the 1-RDM in the responses to an applied electric field

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Theoretical investigations have been conducted on Para Nitro Aniline (PNA) to determine linear and non-linear responses of its one-electron reduced density matrix (1-RDM) to an electric field. Induced effects on diagonal terms of 1-RDM have been previously determined by means of ab-initio calculations at Hartree-Fock level. This project aims to determine the polarization and the hyper-polarization coefficients of the molecule respectively. Since the emitted radiation vector potential is directly related to the induced probability current, determination of PNA linear and non linear responses are expected to involve changes in both diagonal and extra diagonal terms of the 1-RDM. Thus, we have investigated the extra diagonal terms and to what extent they contribute to the potential vector of the remitted radiation.

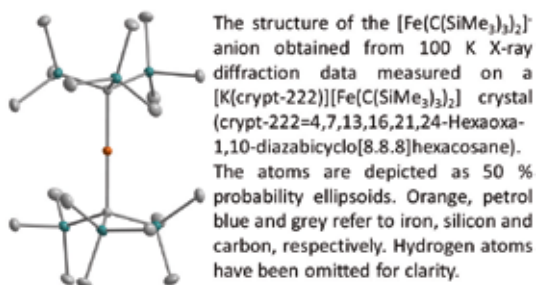
Relationships between electron density and magnetic properties in a two-coordinate iron(I) single-molecule magnet

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A single-molecule magnet (SMM) preserves its magnetization even in the absence of an external magnetic field, much like a bulk magnet does. These tiny magnets have potential technological applications in e.g. spin-based electronics. Lanthanide-based SMMs offer promising candidates for this purpose. Nevertheless, cheap and earth-abundant metals such as iron are obviously desirable as alternatives to the lanthanides. The conservation of magnetization in SMMs occurs due to a bistable magnetic ground state ($\pm|MJ|$ ground state) separated by an energy barrier to magnetic relaxation. The origin of this barrier lies in the magnetic anisotropy, which can be tuned in a transition metal complex by

varying the ligand field. In 2013, Zadrozny et al. discovered the best mononuclear transition metal-based SMM to date, a linear two-coordinate iron(I) complex, $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$. This low-coordinate and low oxidation state iron complex has a record high effective relaxation barrier ($226(4) \text{ cm}^{-1}$) derived from magnetic susceptibility data. Based on *ab initio* calculations, Zadrozny et al. found that this complex has a very weak ligand field with the d_{z^2} -orbital being energetically stabilized with respect to the other d-orbitals. This is opposite to what would be expected from basic crystal field theory. In the present study, we examine the experimental electron density and its connection to the magnetic anisotropy of the $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$ anion.

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The charge density study of platinum precursor of anticancer complexes

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A wide range of medicinal applications of the platinate (II) complexes makes them interesting subjects for the research. The potassium tetrachloroplatinate (II) complex is convenient starting material for the preparation of a large number of platinum (II) complexes. These complexes can be prepared in two isomer forms. The biological active cis-isomers and non-active trans-isomers [1]. Our ambition is to understand these properties by studying the experimental electron structures. For this aim some Pt-complexes will be prepared and studied. Experimental electronic structures of $K_2[MC_2]$ ($M = Re, Os, Pt$) were studied at 120 K by Takazawa et.al. [2-4] in 1990. As crystallographic techniques improved significantly, we would like to see whether the improved diffraction data could bring a qualitatively new results. Preliminary X-ray data collection for $K_2[PtCl_2]$ was performed on an STOE STADI VARI four circle diffractometer equipped with a PILATUS 300K detector, using the microsource Ag-K α radiation at 100(1) K. Data reduction was done by STOE X-Red32 and an average redundancy of 36.8 gives R_{int} of 0.0318. For the anisotropic secondary extinction correction direction cosines were applied. The results of multipole refinement and the topological analysis were performed using both XD2006 and JANA2006. Experimental results obtained with different scattering factors [5] will be discussed.

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Source Function applied to experimental densities reveals subtle electron delocalization effects and appraises their transferability properties in crystals

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The Source Function (SF) [1] enables the electron density (ED) to be seen at a point as determined by source contributions from the atoms of a system, and it is therefore well linked to the chemist's awareness that any local property and chemical behaviour is to some degree influenced by all the remaining parts of a system [1-3]. The key feature of the SF is that its evaluation requires only knowledge of the ED of a system, enabling a comparison of *ab initio* and X-ray diffraction derived ED properties on a common, rigorous basis. We here apply the SF descriptor to X-ray derived EDs as a mean to reveal electron-delocalization effects (EDEs) in crystals. Use of the SF to detect them has been firmly assessed for isolated molecules and for theoretically-derived EDs [2,4-5], but extending to crystals and experimental EDs, although being reported at two conferences [6-7] and in two papers discussing heteroaromaticity in a benzothiazol-substituted phosphane [8] or antiaromaticity in cyclopentadienone derivatives [9] needs to be fully demonstrated. Still unanswered questions are whether the EDs from X-ray data may be accurate enough to reveal the subtle features caused by electron pairing and whether these are not only detectable, but also reproducible and transferable, whenever appropriate. To provide an answer we analyse the experimental SF patterns in benzene (BZ), naphthalene (NT) and (\pm)-8'-benzhydrylideneamino-1,1'-binaphtyl-2-ol (BAB) molecular crystals. We find that the SF tool recovers the characteristic SF% patterns caused by π -electron conjugation in the first two paradigmatic aromatic molecules in almost perfect quantitative accord with those from *ab initio* periodic calculations [10]. Moreover, the effect of chemical substitution on the transferability of such patterns to the BZ- and NT-like moieties of BAB is neatly spotted by the observed systematic deviations, relative to BZ and NT, of only those SF contributions from the substituted C atoms [10]. The capability of the SF to reveal EDEs by using a promolecule ED (PED), rather than the "true" ED, is then tested; the PED seems unable to reproduce the SF trends anticipated by the increase of electron delocalization [10]. The SF has wider applications than those related to the nature of chemical bonds in more or less conventional situations [2-3]. Detection of EDEs is one such new direction, another being the extension of the SF machinery to retrieve the atomic sources of the spin ED [5,11].

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Electron and spin density of $(\text{CH}_3\text{P}(\text{Ph})_3)[\text{NibdtCl}_2)_2]$

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This study is part of the ongoing project with an aim of mutual comparison of the theoretical and experimental spin densities. For the study, the complex $(\text{CH}_3\text{P}(\text{Ph})_3)[\text{NibdtCl}_2)_2]$ (methyl triphenylphosphonium bis (3,6-dichlorobenzene-1,2-dithiolato) nickelate(1-)) was selected. It is square planar with Nickel in oxidation state III. Ligands can have radical character (so-called non-innocent ligands). Crystal structure consists of two anions $(\text{NibdtCl}_2)^-$ in special position and counter cation $(\text{CH}_3\text{P}(\text{Ph})_3)^+$. Three different techniques were used: neutron diffraction (ND), X-Ray Diffraction (XRD) and polarised neutron diffraction (PND). XRD data collection was performed on an Oxford Diffraction Gemini R four circle diffractometer, using Mo-K α radiation at 100(1) K, data collections for ND and PND were performed at 2 K on D19 and D3 respectively at Institut Laue-Langevin, Grenoble. Multipole refinement and the topological analysis were performed using XD2006 program package. Spin density analysis was performed with Fullprof and JANA2006.

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Recent advances in source and detector technology for experimental charge density investigations

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Modern laboratory equipment with their high performance X-ray sources and sensitive detectors facilitates in-house charge density experiments, making synchrotron trips unnecessary in many cases. The recent improvements in the 3rd generation microfocus sealed tubes significantly increase the primary beam intensities for Mo as well as Ag radiation, boosting diffraction from your crystals especially at higher resolution. At even higher energies, the brand-new X-ray mirrors for the METALJET extend the available wavelengths for home-lab instruments to indium (In K α 0.51359 Å). The higher energy X-rays of the Ag and In beams improve the reachable resolution of the experiment and strongly reduce absorption, extinction, and scattered X-ray background. High energy X-rays - including Mo - challenge modern detectors, and especially Si-sensor based HPAD detectors. Besides detection non-linearity at high count rates, HPAD detectors suffer from low DQE, charge sharing and parallax effects due to the thick sensors employed. The latest generation of CPAD (charge integrating pixel area detector) on the other hand, with their thin and extremely efficient high Z-element scintillators, overcome these shortcomings, and provide the ideal solution for high quality experiments. This presentation will focus on new X-ray sources and detector technologies for in-house charge density investigations including first experimental results.



Experimental electron density of low barrier hydrogen bonds in $\text{H}_3\text{Co}(\text{CN})_6$

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Hydrogen bonding is the most important directional intermolecular interaction with importance in a wide range of fields across natural science. Electron density studies may quantify hydrogen bonding behavior in compounds with very strong hydrogen bonds and explain their importance for particular properties. Recent PDF studies on $\text{H}_3\text{Co}(\text{CN})_6$, which has one of the shortest N-H-N hydrogen bonds known in the literature, has shown a significant effect of isotope substitution on the negative thermal expansion (NTE) behavior of the crystals, i.e. the protonated compound has a significantly larger NTE than the deuterated compound [1]. In this study, the experimental electron density distribution in $\text{H}_3\text{Co}(\text{CN})_6$ is evaluated using synchrotron single crystal X-ray diffraction and neutron powder diffraction. Single crystal X-ray diffraction were measured at BL02B1, Spring8, Japan on both protonated and deuterated samples at 20K and 100K with resolutions up to 1.67 \AA^{-1} . These are combined with powder neutron diffraction data to get a better description of the hydrogen position and thermal parameters. The X-ray data have been modelled with the extended Hansen-Coppens multipole formalism [2] and the resulting density is analyzed by the Quantum Theory of Atoms in Molecules. The Co-CN interaction is found to be of intermediate character, with very similar properties as those reported for transition metal carbonyls in the literature [3]. This is interesting, since the formal charges are very different in two cases. The properties along the bond path for the hydrogen bond is very dependent on the position of hydrogen. A symmetric arrangement as proposed for hydrogen at low temperature, gives two shared interactions very similar to the ones seen for the O-H-O low-barrier hydrogen bond in Benzoylacetone [4], explaining the origin of the negative thermal expansion as arising from a covalently bonded network. An asymmetric arrangement gives more shared character to the donor atom bonding and more closed shell character to the acceptor atom, making the crystal more molecular of nature.

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Designing optimal multilayer mirrors for a new generation of X-ray sources

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The performance of new X-ray sources and synchrotrons in terms of photon flux and spot size has improved continuously in the last decades. At the same time, the requirements for advanced measurement techniques have risen. Thus, optimized X-ray mirrors are required for beam conditioning to achieve the best beam parameters at the sample and detector position. An X-ray mirror can only achieve its maximum performance when it is designed and adjusted optimally to a source equally selected depending on experimental needs. Experience, laboratory tests and dedicated simulation and raytracing software help to find and fabricate the best solutions. Two aspects of an X-ray optical device have to be regarded with respect to the experimental task. The mirror geometry (size, shape, contour, slope, slope errors, roughness) has the largest influence on the beam size and convergence. On the other hand, the mirror coating (usually a multilayer) not only affects the flux, monochromaticity, spectral resolution, peak reflectance and angular bandwidth. Due to its inherent selectivity it also defines how much of the source is “seen” (and thus used) and can suppress unwanted parts of the spectrum or radiation emitted from areas outside the main focal spot on the anode. Thus, only an optimal combination of mirror geometry and multilayer coating can provide sufficient beam performance for challenging measurement tasks. Several examples for applications of high performance source optics combinations, simulations and measurement results will be presented.

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Structure-function studies of organellar proteins with FAST and RAP domainsMatthew Merski^a, Jan Kutner^a, Jakub Skrzeczkowski^b and Maria Górna^a^a *Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Poland*^b *College of Inter-Faculty Individual Studies in Mathematics and Natural Sciences, University of Warsaw, Poland*

We study the structure of two putative non-canonical RNA-binding domains, FAST and RAP, found in the mitochondrial FASTKD (Fas-activated serine/threonine kinase domain) and the chloroplast OPR (octotricopeptide repeat) protein families. We propose that FAST is a helical-repeat domain which overlaps with two conserved sequence motifs, FAST-1 and FAST-2. RAP (RNA-binding domain abundant in Apicomplexans) is a globular domain of 60 residues which is found at the C-terminus of a subset of RNA-binding OPR and FASTKD proteins. The remarkably small size of RAP makes it an attractive target for protein engineering, and we present our efforts at expression, purification and structural characterisation of the RAP domains. We analyse also the phylogenetic distribution of RAP throughout the kingdoms of life and its association with predicted physicochemical properties.

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Crystal structures of vitamin D analogues

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The term vitamin D refers to a group of fat-soluble secosteroids. Two major forms of vitamin D are D2 – ergocalciferol - which is found in plants and yeasts, and D3 – cholecalciferol - which is found in animals and humans. The Vitamin D Receptor (VDR) also known as NR1H1 is a transcription factor. Due to the activation by calcitriol, the VDR and retinoid-X receptors form a heterodimer which changes its conformation. The heterodimer bonds to hormone response elements on DNA, which enables regulation of transcriptional response.¹ Moreover, VDR is involved in microRNA-directed post-transcriptional mechanism which is connected with the influence of calcitriol on human bones.² VDR could be found in many tissues, where plays various roles. So vitamin D has a lot of applications including regulation of calcium-phosphate metabolism, antiproliferation action, decreasing possibility of developing tumor and many others. I will discuss structural differences between vitamin D analogues and factors influencing these differences. The crystal structures of 1,25-dihydroxyergocalciferol and 1,25-dihydroxycholecalciferol analogues have been determined and the result of this research will be presented. The crystal and molecular structures of these compounds were solved and refined using single crystal X-ray diffraction. Two of analogues crystallize in the P212121 space group and one analogue crystallize in P21212 space group of the orthorhombic crystal system with the unit cell parameters: $a=9.62082(8)$ Å, $b=14.18309(12)$ Å, $c=31.7987(2)$ Å; $a=6.6492(5)$ Å, $b=9.9013(9)$ Å, $c=38.811(3)$ Å and $a=38.0952(3)$ Å, $b=12.95430(10)$ Å, $c=11.07290(10)$ Å, respectively. One of analogues crystallizes in the C2 space group of the monoclinic system, with the unit cell parameters $a=33.410(2)$ Å, $b=6.3780(4)$ Å, $c=12.2329(8)$ Å.

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The charge density analysis of ferrocene taxol analogue

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The ferrocene analogue of taxol (named TAX1) was investigated. The most important fragment in the investigated molecule is a β -lactam ring. It constitutes the core of the structure of many antibiotics families (for example penicillins, cephalosporins, carbapenems, and monobactams)[1]. The compound is also considered as a candidate for cancer treatment. The high resolution single crystal X-ray diffraction data were collected at 100 K and 90 K, respectively and analysis of the experimental electron density distribution was performed. [2] Five different approaches were tested in order to characterize the distribution of the electron density. Electron density distributions for the molecule with local symmetry imposed on atoms or without symmetry were modelled (while the iron atom was assigned an initial charge of either zero or plus two). For the last model, in which the UBDB bank was applied, electron density distributions were calculated for the molecule with local symmetry imposed on atoms when all multipole populations were allowed and the iron atom had a neutral valance. Preliminary results suggest that the model without imposed local symmetry, in which the iron atom has zero valance population was the best. In all models the iron atom has positive charge, but the exact value of the charge is different in each model. It is worth to notice, that some of the populations of multipole parameters prohibited due to the local symmetry were statistically significant when the model without imposed symmetry was tested. The atomic charges in the current best model are negative on both oxygen atoms and, on nitrogen atom, while the carbon atoms in the β -lactam ring have positive charges. The distribution of the electrostatic potential around the TAX1 molecule and the details of intermolecular hydrogen bonds will be presented.

Acknowledgments: Financial support within the Polish NCN MAESTRO grant: DEC-2012/04/A/ST5/00609.

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Pseudoatoms databank (UBDB) extension for parameterizing drug-like molecules

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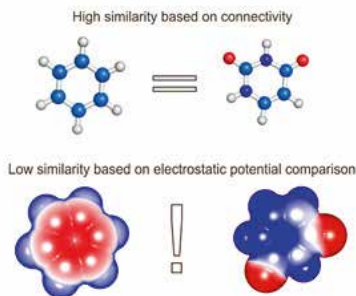
The theoretical databank of aspherical pseudoatoms (UBDB) [1] has been significantly extended recently and it contains now more than 250 atom types sufficient for refining structures or modeling electron density and calculating various properties using Transferable Aspherical Atom Model for small and biological molecules. The goal of this project is to parameterize small molecules present in DrugBank [2] and small ligands from the Protein Data Bank [3] to facilitate refinement of structural parameter or calculation of physical properties on high-throughput scale. To group atom types not present in UBDB a clustering procedure was applied to find various functional groups that are present in 7097 molecules obtained from DrugBank. Good quality experimental molecular geometries of model molecules were obtained from Cambridge Structural Database (CSD) [4]. Thereafter theoretical structure factors were obtained from single-point wave function computed at B3LYP/6-31G** level [5-8] to which the Hansen and Coppens pseudoatom model [9] was fitted following the standard procedure of UBDB extension [1].

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Application of aspherical atom model in ligand based drug discovery

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The Hansen-Coppens aspherical atom model [1] is the most widely used formalism in the analysis of charge density distribution. In this model the electron density distribution in molecule is modelled using the atom centered spherical harmonic functions. Currently, the most ambitious studies are to compute intermolecular interaction energies of drug-receptor complexes using point-charges approach [3], and it is envisaged that future studies will benefit from recent method developments.[4-7] Such charge density model is also commonly used to obtain other physical prop-

erties such as molecular electrostatic potential (MEP), dipole, etc. For example MEP surfaces, created around molecules are very useful for analyzing and predicting molecular reactive behavior as proposed by Politzer and co-workers. [8, 9] Electrostatic potential has been also applied successfully to study of interactions that involve a certain optimum relative orientation of the reactants, such as between a drug and its cellular receptor. [10, 11] In this study we propose an application of MEP's obtained from aspherical atom databank (UBDB). [12] Our approach offers a quantitative comparison of field and potential differences between molecules through molecular structural alignments followed by comparison of electrostatic potential mapped on van der Waals surface by calculating Tanimoto coefficient (T), thus quantitative structure activity relationships (QSAR).

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Investigation of the hypervalency in polyoxoanions via theoretical and experimental charge density studies

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The Lewis picture poses a simple, yet very powerful description of the bonding situation in molecules. It does, however, not come without its limitations: For some molecules containing atoms of the third period or higher, various Lewis formulas that either exceed or follow the octet rule exist. In the former case, the Lewis formula gives a hypervalent description of the molecule. A prominent example for this ambiguity is the sulfate anion for which hypervalent and ionic resonance structures exist [1]. For the perchlorate anion the possible Lewis formulas are depicted in figure 1. The hypervalent formula 1 is the predominant one being taught in schools, undergraduate lectures and even in some textbooks [2], whereas formula 4, which is the only one to follow the octet rule, is considered more unlikely because of a higher charge separation. The theoretical and experimental charge density studies conducted in this project aim to shed light on the bonding situation of the phosphate, sulfate and perchlorate anion, which are isoelectronic polyoxoanions of the third period of the periodic table, for which hypervalent Lewis formulas exist. For a comparison with a polyoxoanion of the second period, the nitrate anion, for which a hypervalent Lewis formula exists, is also investigated by the experimental and theoretical charge density. For the experimental charge density analyses, a multipole modelling [3] as well as an X-ray constrained wavefunction fitting [4] were performed. The results obtained by both the theoretical and experimental charge density studies conclusively validate the non-hypervalent Lewis formula to be of the greatest importance for the phosphate, sulfate and perchlorate anion. Four equivalent polarized single bonds and three lone pairs at each of the four oxygen atoms are suggested by the analysis of the natural bond orbitals [5], the topology of the electron density (Bader analysis) [6], the laplacian of the electron density and the electron localizability indicator [7]. The existence of three oxygen lone pairs of the perchlorate anion can be clearly visualized by considering the laplacian iso-surface shown in figure 2.



Figure 1: Possible Lewis formulas for the perchlorate anion (the resonance in formulas 1,2 and 3 are not considered).



Figure 2: The laplacian iso-surface of the perchlorate anion.

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First X-ray charge density study of a Zundel ion

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The Zundel ion, H_5O_2^+ , occupies a central place in the theory of hydrogen bonding and proton transfer. It is formed as an intermediate during the proton transfer processes in aqueous solutions (and all other protic solutions, too) and biological systems. One can hardly imagine fundamental biological reactions, such as enzyme kinetics, respiration and photosynthesis without transfer of protons and/or electrons. However, it is an ultrafast process, with a timescale of pico- and femtoseconds, which can be directly studied only by the most advanced time-resolved spectroscopic methods (femtosecond laser UV/vis and IR/Raman) and femtosecond X-ray diffraction using an X-ray free-electron lasers (XFEL). Zundel-like states, with dynamic proton disorder, can be 'trapped' in otherwise 'static' crystals, extending their lifetime by a dozen orders of magnitude - from pico- and femtoseconds to days and months. Then it becomes possible to focus on a single hydrogen bond, using a variety of experimental and theoretical methods.[1] An ideal system for study of the proton dynamics in a Zundel ion is nitranilic acid hexahydrate.[1] It is a small molecule which contains only light atoms (C, N, O), eliminating the problem of absorption and allowing accurate location of hydrogen atoms. Moreover, its crystals comprise H_5O_2^+ cations located in the general position, thus artificial centrosymmetry (which is usually the case with Zundel ions in the crystal state) can be avoided.[1] Thus, nitranilic acid hexahydrate is an ideal system for X-ray charge density study of a Zundel ion. We present the first X-ray charge density study of a Zundel ion, which reveals electron density and bond order of its central $\text{O}\cdots\text{H}\cdots\text{O}$ group. To accurately model low electron density on the protons, we have combined X-ray and neutron diffraction (experiment was performed at Laboratoire Léon Brillouin in Saclay, France, with support by prof. Alexandre Bataille): position and anisotropic displacement parameters of the protons used in the refinement of charge density are taken from the structure determined by neutron diffraction.

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Assessment of non-covalent intramolecular interactions within transition metal complexes by high-resolution XRD analysis

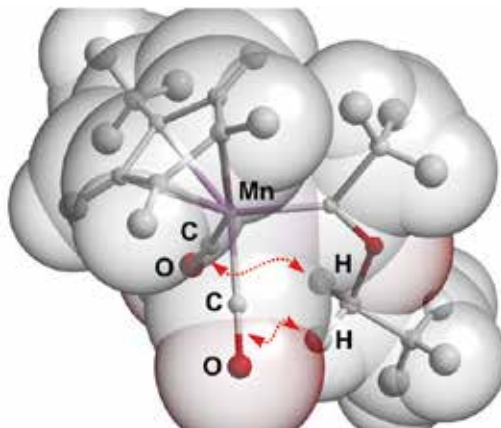
Noël Lugan^a, Rémy Brousses^a, Vincent César^a, Dmitry A. Valyaev^a, Israel Fernández^b, Stéphane Labat^c, Karine Miqueu^c and Jean-Marc Sotiropoulos^c

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Far beyond geometrical features, high-resolution X-ray diffraction analysis can provide an experimental model of the electron density (ED) of molecules embedded in the condensed phase[1a]. Complemented by a subsequent analysis of the topology of the ED according to Bader's Quantum Theory of Atoms in Molecules[1b], this methodology has emerged as a powerful tool for the experimental assessment of all sort of bonding features, including supramolecular non-covalent interactions[1c]. We have used such an approach for assessing non-covalent intramolecular secondary interactions within chosen transition metal complexes, including piano-stool Mn(I) Fischer carbenes, and Mn(I), Mn(II) and Fe(II) N-Heterocyclic carbene complexes. The topological analysis of the experimental electron density in combination with DFT calculations clearly revealed the occurrence of hitherto unsuspected weak intramolecular C...H or C...C inter ligand interactions, which are likely to play a key role regarding the conformational stability and/or spectroscopic properties of the given complexes[2].

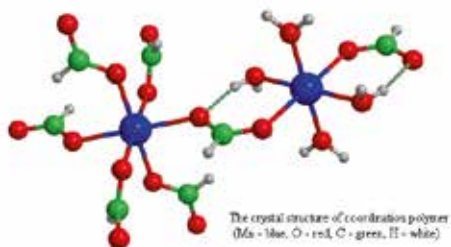


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Electronic structure of coordination polymer $\text{Mn}(\text{HCOO})_2(\text{H}_2\text{O})_2$

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The title manganese (II) coordination polymer compound has been studied using quantum-chemical DFT treatment (hybrid B3LYP functional). The geometric structure used in quantum-chemical calculations is based on X-ray multipole refinement. The QTAIM (Quantum Theory of Atoms-in-Molecule) topological analysis of electron density has been performed on the theoretical electron density and alternatively on X-ray diffraction experimental data. The main aim of this study is to compare the results of theoretical and experimental approaches and to predict the distribution of spin density at metal atoms

of the complex which is unavailable by standard X-ray techniques. Chemical bonds between relevant atoms are described by the properties at bond critical points (such as electron density, its Laplacian and ellipticity). Our results indicate that the coordination bonds between metal and formate oxygen atoms and coordination bonds between metal atom and water oxygen atoms are similar. The coordination bond between manganese and water oxygen atoms is stronger than a similar coordination bond in dimeric copper or chromium acetate dihydrate (see previous study [1]) what indicates different kinds of bonding.

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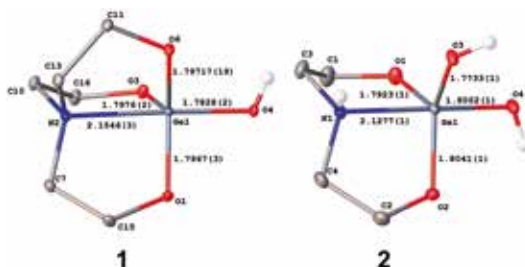
Stereoelectronic interactions in complexes of pentacoordinated germanium. Experimental charge density, IQA and ELI-D study

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Russia

The molecules of 1-hydroxygermatrane (1) and hydroxyl-(2,2'-diethoxyamine-O,O')-germanium (2) contain pentacoordinated germanium atoms surrounded by electron withdrawing oxygen and nitrogen ones. According to literature, several theoretical models were used for description of chemical bonding pattern in compounds of similar type (3c-2e and 3c-4e bonding, sp^3d -hybridization of germanium atom, etc). All of these models predicted the noticeable elongation of the axial Ge1-O4 bond as result of donation of electron pair of nitrogen atom to the region of Ge-O bonds. As it has been shown by high resolution X-ray studies, the Ge1-O4 bonds are equal or even 0.01-0.02 Å shorter relative to equatorial endocyclic Ge-O ones. The reason of such shortening can be related to stereoelectronic effects in coordination environment of germanium atom, i.e. the interactions between lone electron pairs of O atoms and unoccupied orbitals of equatorial Ge-O bonds ($n \rightarrow \sigma^*$ interactions). To account the chemical bonding pattern in 1 and 2 the electron density ($\rho(r)$) study was carried out in the crystal and isolated molecules. Topological analysis of experimental $\rho(r)$ in terms of Bader's QTAIM allowed us to localize the domains of lone electron pair of oxygen atoms and describe the characteristics of covalent and chemical bonds in 1 and 2. It was established, that influence of stereoelectronic interactions on the length of Ge-O bonds is governed by crystal packing. Unfortunately, the accurate description of $n \rightarrow \sigma^*$ interactions in terms of standard QTAIM was impossible. Hence, theoretical approaches combining topological analysis with real space energy and density partitioning (IQA model and ELI-D analysis) were utilized to reveal the characteristics of $n \rightarrow \sigma^*$ interactions. It was demonstrated that strength of $n \rightarrow \sigma^*$ interactions expressed in terms of interacting domains can be compared to strength of covalent Ge-O bonds.

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PolaBer - distributed atomic polarizabilities approach

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PolaBer[1] calculates atomic polarizability tensors from electric field perturbations of a partitioned electron density distribution. Among many possible partitioning schemes, PolaBer is currently using the quantum theory of atoms in molecules (QTAIM)[2] and it is interfaced to programs that apply such a partitioning. The calculation of the atomic tensors follows the idea suggested by Keith[3], which enables the removal of the intrinsic origin dependence of the atomic charge contributions to the molecular dipole moment. This scheme allows to export, within chemically equivalent functional groups, properties calculated from atomic dipoles, such as atomic polarizabilities. With the use of PolaBer we can estimate refractive indices of the molecule, calculated with the use of classical Lorentz model, which due to induced electric moments of the molecules in crystalline phase, takes into account the natural increase of atomic polarizabilities. It is also possible to predict sign and the size of optical activity in a crystal structure. When analyzing non-centrosymmetric crystal structures one can detect structural helices (in chiral directions) which would point the directions of the gyration tensor principal axes.[4] Assuming volume polarizability approach to rotatory power [5], such helices could be recognized as built of highly polarizable atoms remaining in close contacts. The electron density concentration at bond critical points may cause slowing down the linear-polarized light travelling within the helix. PolaBer gives a quantitative measure of electron density polarization along a bond which is called bond polarizability.[6] Moreover studies showed very good transferability of the functional group polarizabilities[7], which enables to identify which group mostly contributes to the global dielectric constant. This could be very helpful for the crystal engineering purpose when designing new optically effective materials.

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Verifications of a new simplified charge density model for electrostatic interaction energy estimation

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Classical forcefields with point charges or multipole model are still inaccurate for non-bonded terms. The error for the most dominative contribution within polar compounds - the electrostatic interaction energy (Ees) - can be up to 50%. This is caused by the lack of penetration energy estimation, defined as difference between exact Ees and electrostatic energy from point multipole approximation - E_{mp}. In our approach we combined the promolecule model of an electron density with monopoles fitted to electrostatic potential.[1] That kind of charge density representation enables estimation of electrostatic interaction energy (including E_{pen}) in a straightforward way. It also allows to skip computational-costly integration procedure. The method was verified on S66x8 and S66a8 data sets. These benchmarks provide wide range of molecular geometries and different types of interactions. For reference we used quantum chemical computations at b3lyp/aug-cc-pVTZ theory level. Particular RMDS's are significantly lower when compared to corresponding ones from point charges methods.

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Structural investigation of photoexcited metastable high-spin states

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The phenomenon of spin crossover (SCO) between low-spin (LS) and high-spin (HS) state represents probably one of the most spectacular examples of molecular bistability [1]. The spin state of SCO coordination compounds depends on the external conditions and can be reversibly changed by external triggers like temperature, pressure, magnetic field or light irradiations literature. From the application point of view, the SCO compounds are very attractive materials because change of spin state is accompanied by miscellaneous reversible changes of physical properties on the molecular as well as on the macroscopic level. From the application point of view, the understanding of SCO event activated by light is one of the pivotal challenges of current SCO research. The photoactivated SCO is known from the literature as Light Induced Spin State Trapping (LIESST) and is based on the low temperature irradiation of LS compound at wavelengths coming from the LS d-d electronic transition bands. The mechanism of LS→HS photoswitching is based on the relaxation of electrons from the excited LS states to the ground spin state of HS potential allowed due to the spin-orbital coupling. In the same manner, the reverse effect (reverse LIESST) is possible to happen due to the low temperature irradiation of HS compound at the wavelength coming from the HS d-d bands. At sufficiently low temperature (≈ 10 K), the photoexcited metastable state has infinite stability. The challenge of modern SCO research is to prepare and characterise SCO coordination compounds with wavelength selective photoactivity moved to the room temperature region. With respect to this, in parallel to the structural study of thermally induced SCO, the investigation of structural changes accompanied photoinduced transition are necessary for better understanding of LIESST phenomenon. Charge density studies at low temperature (< 30 K) recorded before and after photoexcitation together with the ab-initio and/or DFT calculations might reveal significant differences in the electronic structure which are responsible for existence and the thermal stability of photoinduced metastable HS states. The preliminary charge density studies at 100 K shows that tetrahedrally coordinated iron atom has two typical coordination bonds (Fe-N1) and two bonds (Fe-N3) in which fully populated orbital interacts with the N3 lone electron pair. In our proposal (GUP-48657) we plan to collect the data at 15 K before and after the excitation.

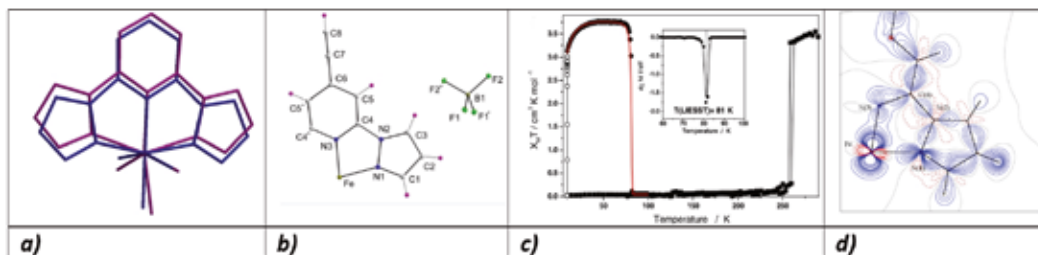


Figure 1 Compound $[\text{Fe}(\text{bpp})_2](\text{BF}_4)_2$ (**bpp** = 2,6-bis(pyrazol-1-yl)pyridine) (**I**) [2,3] **a)** comparison of low temperature structures (30 K) before (blue) and after (purple) photoexcitation with red light (633 nm), atoms of second ligand **bpp** are omitted for the clarity; **b)** independent part of (**I**); **c)** thermal and photoinduced (532 nm) SCO of pure compound (**I**); **d)** charge density at 100 K of (**I**)

Acknowledgments: This study was financially supported by Research and Development Agency of the Slovak Republic under the contracts No. APVV-0202-10 and Scientific Grant Agency of the Slovak Republic (VEGA Projects 1/0871/16).

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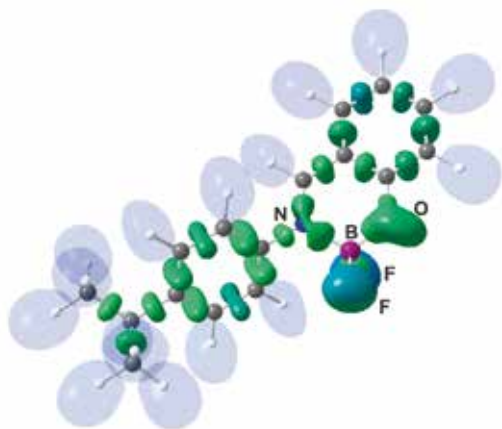
Electronic properties of the dative N-B bond with associated O-B interaction for difluoroborate compounds and models

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Since difluoroborate dyes [1] (see Fig. 1) are compounds that are in the limelight nowadays, the detailed knowledge about their electronic properties is important in the design of new derivatives. Especially, the deeper insight into bonding situation with the emphasis on nature of interactions to boron should help to understand the properties of difluoroborates. In our project, a set of real-space bonding indicators is used to quantify the electronic characteristics of the dative N-B bond with an associated O-B interaction in the R_2N-BF_2-OR environment and the electronic modulations caused by F/H exchange and variations of the nature of the residues R. In order to characterize the nature of B-X ($X=N,O,F$) interactions, the Atoms in Molecules partitioning scheme [2] is com-

plemented by the Electron Localizability Indicator approach [3], both applied to experimental and theoretical electron-density distributions (X-ray wavefunction refinement versus DFT calculations). Fermi orbital analysis [4] for small DFT-models supports and extends the findings for the BF_2 -carrying structures. Figure 1. Experimental ELI-D localization domain representations of salicylidene-4-isopropylaniline difluoroborate (isovalue $Y=1.40$).

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Correlation between electron density and magnetic properties in Cu-pyrazine quantum magnets

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We have investigated the correlation between the accurate electron density (ED) distribution and the magnetic properties of metal-organic polymeric quantum magnets, $\{[\text{Cu}(\text{pyz})_2\text{X}]\text{Y}\}_n$ (pyz = pyrazine; X=Cl, Br, NO₃; Y = BF₄, NO₃). These materials have attracted interest for the role played by pyrazine in the magnetic coupling and the potential role of weak inter-chain interactions. We determined ED through high resolution single crystal X-ray diffraction and density functional theory (DFT) calculations. DFT calculations are carried out both in the whole crystal and on selected fragments of the framework. Topological Analysis based on Quantum Theory of Atoms in Molecules (QTAIM) has been applied to characterize the possible magnetic exchange paths. Molecular orbital and spin density analysis have been used to identify the atomic and group contributions to the magnetic coupling. The experimentally observed antiferromagnetic coupling can be explained by the copper-copper super-exchange coupling mediated by the pyrazine ligands. However, in $\{[\text{Cu}(\text{pyz})_2\text{Cl}]\text{BF}_4\}_n$ our results suggest a non-negligible coupling through the chlorine, although the electron density shows a much weaker interaction than the one observed along pyrazine. To further investigate the exchange mechanism, we measured $\{[\text{Cu}(\text{pyz})_2\text{X}]\text{BF}_4\}_n$ species under pressure. Periodic DFT simulations were used to estimate the pressure induced changes of structural and electronic features. Moreover, models using restricted multipoles were refined against the high pressure X-ray diffraction data. The species shows a remarkable stability of the magnetic network up to quite high pressure (above 10 GPa). From this study, it is clear that systematic electron density analysis on transition metal compounds could lead to a better understanding of the super exchange mechanism with a topological description of the involved interactions.

Chemical bonding in ternary intermetallic borides and the $[\text{As@Ni}_{12}\text{@As}_{20}]^{3-}$ triple-shell cluster

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Position space chemical bonding analysis in transition metal diborides TB_2 with the simple AlB_2 type of crystal structure has revealed a rather complex bonding scenario of polar 3-center bonds B-B-T related to deltahedral B clusters.[1] Proceeding from the hexagonal graphene like B layers with interconnecting T atoms to intermetallic framework structures like in AlNi_9B_8 , where the B partial structure can be considered as the third layer of interconnected triple-shell clusters with a filled Al@Ni_{12} icosahedral core [2], necessitates the analysis of certain prototype molecular clusters like $[\text{As@Ni}_{12}\text{@As}_{20}]^{3-}$ [3]. In the latter, the conceptual framework for electron counting is yet under debate, touching both the cluster Wade-Mingos model and the “superatom” jellium model. A comparative position space bonding analysis for the intermetallic phase and the intermetalloid cluster is presented based on the QTAİM approach, ELI-D analysis, and 2- and 3-center delocalization indices.

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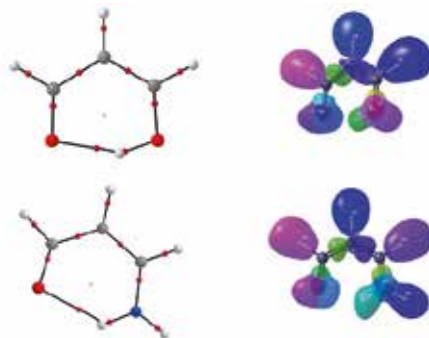
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Theoretical charge density study, the case of intramolecular hydrogen bond

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Seven theoretical molecules containing five- and six-membered rings are reported with special focus on intramolecular hydrogen bonds (O/N-H ... O/N). Geometry of theoretical moieties were optimized with using 7 various database functions. The geometrical and topological parameters based on QTAIM theory[1] were analyzed. Additionally, electron localizability indicator (ELI)[2] and delocalization index[3] was calculated. In some cases the analysis confirmed the O/N-H...O/N, interactions to be resonance assisted. For five – membered ring the intramolecular hydrogen interaction is not so evident even if different substituents in ring were analyzed.

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Investigation of geometric properties of nucleobases crystals in Cambridge Structural Database

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Nucleobases (adenine, cytosine, guanine, thymine and uracil) are molecules of biological importance high enough, that it doesn't need to be proofed. No wonder many scientists all over the world are studying them from various perspectives – including me. Cambridge Structural Database (CSD) is a repository containing results of X-ray and neutron diffraction data of organic small molecules or metal-organic crystal structures. It enables easy search through many different structures with combined queries, taking into account search terms as molecule parts, names, elements or name of author that deposited the data. It is a part of the Cambridge Crystallographic Data Centre (CCDC), dedicated to development of crystallographic knowledge all over the world. Molecules can interact differently in living organisms and in vial, and as most previous surveys were done from more 'biological' or theoretical point of view, I tried to check how nucleobases interact in more 'chemical' environment – inside a crystal. To have some insight into those interactions, I went through Cambridge Structural Database searching for occurrences of various possible homodimers of nucleobases, resembling those appearing in nucleic acids. That means two identical nucleobases interacting through multiple hydrogen bonds formed in plane. I tried to include every possible interaction in my survey, therefore not only Watson-Crick edge can be involved in interaction, but Hoogsteen and Sugar Edge as well. Even if searched interaction was rather unlikely to occur (like those involving hydrogen bonds with C as donor), I still included it in my survey. In my work I wish to explain and draw conclusions from obtained data about frequencies of occurrences of particular interactions.

Crystal engineering and charge density studies of smart materials for nonlinear optics

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Rapid evolution of materials science requires effective solutions in crystal engineering. Smart materials for linear and/or nonlinear optics have to fulfill several criteria concerning symmetry (necessary condition), electron properties of the building blocks, show mechanical and optical stability. Properties like optical activity (OA) or second harmonic generation (SHG) can be observed only in noncentrosymmetric crystals [1]. Obtained crystal phases are thus bound by symmetry restrictions: structural polarity and/or chirality. Additionally, for an outstanding bulk effect molecular or ionic building blocks should possess large values of polarizability and/or hyperpolarizability. Crystal engineering of such materials is still challenging. There are many ways to overcome centrosymmetry barrier: usage of chiral molecules or chiral solvents for crystallization and co-crystallization, utilization of co-crystal formers that promote the formation of noncentrosymmetric crystal structures and many others. In our research we combine quantitative crystal engineering techniques together with prediction and measurements of optical properties [2,3,4]. The evaluation of intermolecular interactions through experimental and theoretical charge density studies gives the means for understanding molecular assembly and thus design materials with improved performance. The goal is to build 3D polar/chiral material from the known starting components ensuring large bulk properties of a crystal. In particular we utilize favorable donor/acceptor spatial distribution and synthon formation flexibility of Active Pharmaceutical Ingredients (APIs) and combine them with NLO chromophores [5] to obtain material with enhanced optical properties. Here we present comparative charge density analysis for two new crystal phases showing non-linear optical properties, both based on the same API molecule. The properties of two new materials were examined both experimentally (measurements of optical properties: refractive indices, linear and non-linear optical properties including second harmonic generation) and by means of theoretical calculations.

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High pressure crystallography - X-ray analysis of crystal structures of toluene derivatives

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Many substances can crystallize in different structures depending on external conditions. Such ability is known as polymorphism. According to Dunitz, polymorphs are different in crystal structures, but melt giving identical liquids [1]. In our research we examined halogen derivatives of toluene in high pressure to determine how those compounds differ in their crystal structures and intermolecular interactions from structures at low temperature. For our experiments we used Diamond Anvil Cell (DAC) as a tool to obtain high pressures. Typical procedure of loading DAC involves putting sample and a chip of ruby inside a small hole in a gasket. Then the sample is compressed by culets of two diamond anvils that are then pushed towards by screws that control the pressure. Chip of ruby that is loaded with a sample is a fluorescent pressure sensor. When illuminated by a laser, ruby fluoresces giving two R-line peaks. Shift of those peaks depends on the pressure inside the cell. Compressing liquid sample results in polycrystallization of the substance. The next step is to raise the temperature up to the melting point so that there is only one crystallite left. Cooling the sample from that point allows to grow a single crystal inside DAC. To notify if any unwanted crystallites appear during cooling sample should be placed between polarizer and analyzer. During our research we examined p-fluorotoluene, p-chlorotoluene, p-bromotoluene and p-iodotoluene under high pressure. We determined structures they form in different pressures ranging up to few GPa. Although in our research three of those compounds did not exhibit polymorphism, we managed to crystallize the last one in two different structures. We would like to show our results, discuss them and compare high pressure structures with those that had already been achieved by low-temperature crystallization.

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Experimental and theoretical charge density assessments for the 4-perfluoropyridyl- and 4-perfluorophenyl-1,2,3,5-dithiadiazolyl radicals

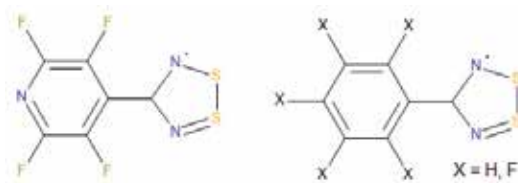
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The results of an experimental density analysis of 4-perfluoropyridyl-1,2,3,5-dithiadiazolyl (NF-radical) are presented and compared with the previously reported analysis of the related 4-perfluorophenyl-1,2,3,5-dithiadiazolyl (F-radical) (Figure). Both NF-radical and F-radical form dimers in their crystal lattice. The strong interaction between sulphur atoms in the dimers is confirmed by the high values of the electron density at the bond critical points. Some additional bond paths relating to weaker interactions are also observed in the dimers, notably between carbon atoms and between F and N atoms. For both radicals, the spin density is almost entirely located on the nitrogen and sulphur atoms of the dithiadiazolyl ring. However, the values of the spin density are higher in the case of the NF-radical, which may result in stronger interactions between sulphur atoms in the dimers. The electron density derived properties from the experimental and theoretical multipolar models are in fairly good agreement.

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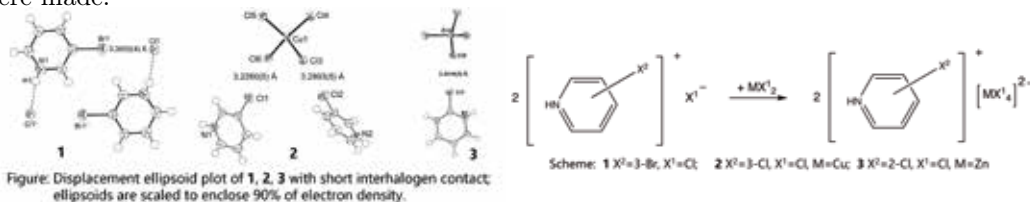


Short interhalogen contacts in pyridinium salts: experimental results

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Crystal Engineering deals with the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties [1]. Next to hydrogen bonds, halogen bonds count among the most relevant directional interactions. A "halogen bond" denotes a short contact between an electron density donor D and a (heavy) halogen atom X as the electrophile [2,3]. For the pyridinium salts compiled in the scheme below, 1 [4], 2 [5] and 3, crystals of high quality were obtained. The figure shows displacement ellipsoid plots based on high resolution (better than 0.5 Å) diffraction data collected at 100 K. Multipole refinement [6,7] and analysis of the resulting electron density according to Bader's AIM theory [8] were carried out. Comparisons to the established standard model for the halogen bond were made.



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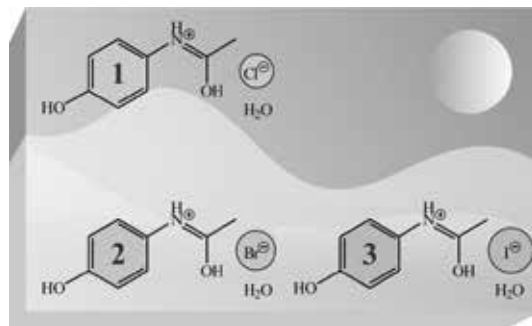
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Solid-state analysis of monohydrated halide salts of paracetamol

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Three monohydrated halide salts of paracetamol: hydrochloride, hydrobromide, and hydroiodide were obtained and crystallized in order to compare their structures in the solid state including the role of intermolecular interactions. Experimental (X-ray diffraction measurements, melting point determination) and theoretical (lattice and interaction energy calculations) investigations were performed. All three compounds create layered structures in the crystal lattice. Correlation between anion size, melting point, lattice energy, and separation of layers in the crystal structure has been found [1].

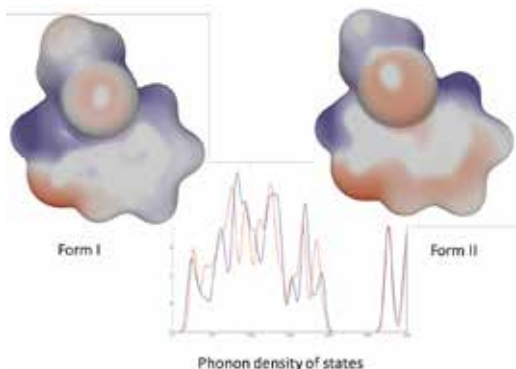


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Aspirin polymorphs revisited

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Since 2005, when the second polymorphic form of aspirin (form II) has been discovered, many studies were devoted to rank its stability in comparison to the first polymorph (form I) [1]. This is especially important as both forms are often observed to form intergrown crystals, and the issue remains experimentally demanding. Quite recently Reilly & Tkatchenko[2] showed that an advanced first principles calculations predict the form I of aspirin to be more thermodynamically stable than form II. They show that the lattice vibrations (i.e., phonons) have a significant contribution to the free energy of this system, in addition to the lattice energy alone, and thus influence the relative stability of poly-

morphic forms. To study this aspect we decided to apply our new method of the normal mode refinement (NoMoRe) [3] to aspirin polymorphs. In NoMoRe, we refine the frequencies of the low frequency modes obtained from periodic DFT calculations against the X-ray diffraction data. Our findings allow to conclude that these (refined) low frequency modes differentiate both polymorphic forms considerably, and are indeed important factor contributing to the relative stability of forms I and II. Moreover, in this contribution we present, for the first time the results of experimental charge density studies for second polymorphic structure of aspirin - form II, and we are comparing results with results obtained by us for form I and with those reported earlier for form I in literature [4].

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On aspherical charge density and ionic radii in fluorite

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Electron density of fluorine in CaF₂ was found to be compressed by neighbouring calcium ions and extended towards other fluorides and empty regions of the unit cell. The article written by Kurki-Suonio and Meisalo in 1966 ends with a sentence: “For more accurate information of these problems the experimental data ought to be extended to higher values of κ ” where κ stands for resolution and is equal to $\sin\theta/\lambda$. In this work we present such high resolution data collected up to 1.63 Å⁻¹. The excellent quality of data presented here permits a very good deconvolution of the thermal motion and refinement of the aspherical model of ED in fluorite. On the basis of a multipole refinement (Hansen and Coppens (1978)), of high resolution low temperature (90K) X-ray diffraction data (silver source), a quantitative experimental charge density distribution has been accomplished for fluorite. An Atoms-In-Molecules integrated experimental charges (Bader 1994) at Ca and F ions are +1.70e and -0.85e, respectively. Established maximum electron density paths, interaction lines, and bond critical points (BCPs) along the Ca...F and also F...F contacts confirmed the closed shell character of the interactions. The position of BCP divides the length of a given interatomic contact into two parts: from a given atom/ion to BCP and from BCP to the other atom/ion participating in this contact. These distances can be used as “ionic radii” based on Bader’s partition of electron density into atomic/ionic contributions. The ionic radius in the direction of the bond axis of the Ca cation obtained by applying this method is 1.21 Å, and the ionic radius in the bond direction of F is 1.15 Å. A comparison of such radii with the Shannon ionic radii leads to the conclusion that in some cases Shannon’s approach overestimates the anionic radius with regard to the cationic. Moreover, an aspherical shape of ions and their volumes should be considered during analysis.

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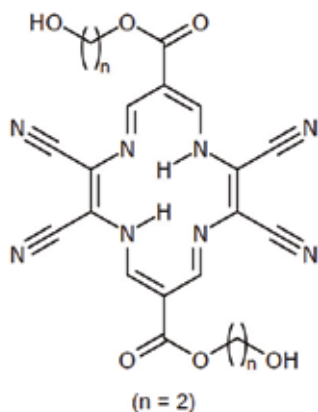
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Experimental charge density study of a model tetraaza[14]annulene

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Scheme of our studied compound: bis(2-hydroxyethyl) (2Z,4E,6E,9Z,11E,13E)-2,3,9,10-tetracyano-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaene-6,13-dicarboxylate

For many years cyclidenes have been used as building units to construct a range of macrocycles, including catenanes, oligomacrocycles and rotaxanes. Some of these compounds present interesting applications: as molecular switches, others are able to recognize small aromatic systems and recently some examples of DNA intercalators have been presented [1,2,3]. In the search for similar, planar and even more electron-rich π systems, ester derivatives of 1,8-dihydro-1,4,8,11-tetraaza[14]annulene have been synthesized. Such compounds are expected to have very interesting physicochemical properties, including an increase of their π -acceptor capacity, due to the presence of nitrile groups, in comparison to similar cyclidene systems. In this work, high resolution X-ray diffraction data were collected for the monocrystal of bis(2-hydroxyethyl)(2Z,4E,6E,9Z,11E,13E)-2,3,9,10-tetracyano-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaene-6,13-dicarboxylate (see figure) at 100K. The experimental modelling of the total electron density was performed using the Hansen and Coppens formalism [4]. The nature of chemical bonding and interactions in the crystal lattice has been studied by the topological analysis using the Bader's quantum theory of atoms in molecules (QTAIM). The deformation density maps and electrostatic potential isosurfaces are also presented. We hope this analysis will be useful as a reference for further studies of metal-complexes derivatives of 1,8-dihydro-1,4,8,11-tetraaza[14]annulene.

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Experimental spin and charge densities on a pure organic radical: comparison with ab initio and DFT calculations

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Alessandro Genoni^b, Marco Marazzi^b, Zeyin Yan^c, Jean Michel Gillet^c
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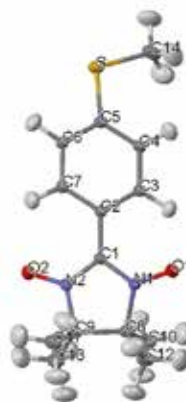
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We have recently developed a method for jointly refine X-ray diffraction (XRD) and polarized neutron diffraction (PND) data. Implemented in the Mollynx program, this approach allows modelling of spin resolved experimental electron densities. This method was applied to magnetic coordination compounds^{1,2} to explore precisely the magnetic exchange pathways in crystals. In our study we will discuss the molecular or collective origins of the magnetic properties of a purely organic radical: 2-(4-thiomethylphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide commonly known as Nit(SMe)Ph (figure). This molecule presents a delocalised electron on the nitronyl-nitroxide function (O-N-C-N-O). In our work, we combine X-ray and polarized neutron diffraction data in a purely experimental model that was confronted to theoretical calculations (DFT and CASSCF). Thorough comparison between the joint experimental model and the theoretical calculations will be presented. Density maps will also be discussed to demonstrate the importance of testing several theoretical methods and confront them to experimental results, especially for exploring weak effects.



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