PD Dr. Simon Grabowsky

Research Group Leader / Forschungsgruppenleiter
Departement für Chemie, Biochemie und Pharmazie
University of Bern, Switzerland
E-Mail: simon.grabowsky@unibe.ch

Scientific interests

Method Development: X-ray Wavefunction Refinement

Conventional methods for structure determination using single-crystal X-ray diffraction data neglect the deformation of the valence electron density, but only model atoms with spherical electron densities. However, it is exactly those valence deformations into bonding and lone-pair regions that are the heart of chemistry. Therefore methods were developed to determine the total electron density experimentally (multipole model, maximum entropy methods), which are unfortunately only accessible to experts. Our new method X-ray wavefunction refinement (XWR) employs quantum chemistry in order to interpret the diffraction experiment in a simple fashion. Its first step Hirshfeld Atom Refinement (HAR) makes localisation of hydrogen atoms from the X-ray data as precise and accurate as from neutron-diffraction data. The second step X-ray constrained wavefunction (XCW) fitting allows to extract crystal field effects, electron correlation and relativistic effects from the experimental data. We continuously improve XWR and work on corresponding software programs (e.g., NoSpherA2 implemented in Olex2; or lamaGOET).

Relativistic Effects in the Electron Density

In order to extract relativistic effects with our new method XWR from single-crystal X-ray diffraction data, we synthesise and crystallise organo-metallic molecular compounds bearing heavy elements of the 6th period (e.g., Pt, Au, Hg, Tl, Pb, Bi). Crystal quality must be exceedingly good, so that ultra-high resolution data sets can be measured at the synchrotron SPring-8 in Japan at very low temperatures (< 20K). Subsequently, the data are treated with the method IOTC (infinit order two component) during the crystallographic refinement. Moreover, we carry out many theoretical calculations on test molecules in order to separate effects such as electron correlation, polarisation, core deformation and relativistics from each other.

Electron-Density – Property Relationships in Inorganic Chemistry

We synthesise systematic arrays of compounds that only vary in a single substituent in order to correlate geometric with electron-density parameters across the array. This way, reactions or other chemical processes can be simluated through static crystallographic snapshots along a pseudo-coordinate. Each of these snapshots exhibits a complete experimental electron-density study so that deep insights into the electronic nature of the processes can be gained. Currently we work on penta-coordinated silyl naphtalene compounds peri-substituted with amines that represent an attacking group in a nucleophilic substitution reaction with the varying substituent at the silicon atom representing the leaving group. Other compounds of recent interest are

siloxanes where we investigate the change of basicity relative to the Si-O-Si bond angle. The concept can be extended to many other systems and chemical processes.

Academic Positions

- since 08/2019: Research Group Leader and Privatdozent at the Department of Chemistry, Biochemistry and Pharmaceutical Sciences at the University of Bern
- 10/2015 – 07/2019: Extraordinary Professor at the University of Bremen
- 09/2014 – 07/2019: Emmy Noether Research Group Leader at the University of Bremen
- 01/2014 – 08/2014: Assistant Research Professor at the University of Western Australia
- 01/2011 – 01/2014: Australian Postdoctoral Fellow at the University of Western Australia
- 10/2006 – 12/2010: Research assistent at the Free University of Berlin

Education

- 10/2019: Habilitation in Physical Chemistry (venia docendi) at the University of Bern
- 04/2019: Habilitation in Physical Chemistry (venia legendi) at the University of Bremen
- 10/2006 – 12/2010: Doctoral studies and dissertation (Prof Dr Peter Luger): "New Methods in the Analysis of Electron Density and Electron Localizability - Applications to X-O-X Systems (X = C, Si)", Free University of Berlin
- 10/2001 – 09/2006: Studies of chemistry (diploma) at the Free University of Berlin

Societies and Organisations

- Member of the Commission on Quantum Crystallography of the International Union of Crystallography (2023-2026)
- Consultant for Commission on Quantum Crystallography of the International Union of Crystallography (2021-2023)
- Vice President of the Swiss Society for Crystallography
- Treasurer of Bernese Chemical Society
- Member of the European Crystallographic Association
- Member of Swiss Chemical Society
- Member of Gesellschaft Deutscher Chemiker
- Member of Deutsche Gesellschaft für Kristallograhie (DGK)

For a full list of publications, also see:
Researcher ID: H-6014-2012
ORCID: 0000-0002-3377-9474

2023

Yanai, Hikaru; Terajima, Yoshihiko; Kleemiss, Florian; Grabowsky, Simon; Matsumoto, Takashi (2023). *Reversing the Bond Length Alternation Order in Conjugated Polyenes by Substituent Effects.* Chemistry: a European journal, 29(15), e202203538. Wiley 10.1002/chem.202203538

Hupf, Emanuel; Kleemiss, Florian; Borrmann, Tobias; Pal, Rumpa; Krzeszczakowska, Joanna M.; Woińska, Magdalena; Jayatilaka, Dylan; Genoni, Alessandro; Grabowsky, Simon (2023). *The effects of experimentally obtained electron correlation and polarization on electron densities and exchange-correlation potentials.* The Journal of Chemical Physics, 158(12), p. 124103. American Institute of Physics AIP 10.1063/5.0138312

Chulanova, Elena A.; Radiush, Ekaterina A.; Balmohammadi, Yaser; Beckmann, Jens; Grabowsky, Simon; Zibarev, Andrey V. (2023). *New charge-transfer complexes of 1,2,5-chalcogenadiazoles with tetrathiafulvalenes.* CrystEngComm, 25(3), pp. 391-402. Royal Society of Chemistry 10.1039/d2ce01385a

Balmohammadi, Yaser; Grabowsky, Simon (2023). *Arsenic-Involving Intermolecular Interactions in Crystal Structures: The Dualistic Behavior of As(III) as Electron-Pair Donor and Acceptor.* Crystal Growth & Design, 23(2), pp. 1033-1048. American Chemical Society 10.1021/acs.cgd.2c01195

Feige, Felix; Malaspina, Lorraine A.; Kleemiss, Florian; Kögel, Julius F.; Ketkov, Sergey; Hupf, Emanuel; Grabowsky, Simon; Beckmann, Jens (2023). *An investigation into the Brønsted acidity of the perfluorinated alkoxy silanes {(F 3 C) 3 CO} 3 SiH and {(F 6 C 5) 3 CO} 2 Si(Cl)H.* Dalton Transactions, 52(18), pp. 5918-5925. Royal Society of Chemistry 10.1039/D3DT00299C

Malaspina, Lorraine A.; Frerichs, Nils; Adler, Christian; Schmidtmann, Marc; Beckhaus, Rüdiger; Grabowsky, Simon (2023). *Quantum Crystallography and Complementary Bonding Analysis of Agostic Interactions in Titanium Amides.* Helvetica chimica acta, 106(6) Wiley 10.1002/hlca.202300012

2022

Borys, Andryj M; Malaspina, Lorraine A; Grabowsky, Simon; Hevia Freire, Eva (2022). *Towards Hexagonal Planar Nickel: A Dispersion-Stabilised Tri-Lithium Nickelate.* Angewandte Chemie (International ed.), 61(39), e202209797. Wiley-VCH 10.1002/anie.202209797

Pawlędzio, Sylwia; Malinska, Maura; Kleemiss, Florian; Grabowsky, Simon; Woźniak, Krzysztof (2022). *Influence of modelling disorder on Hirshfeld atom refinement results of an organo-gold(I) compound.* IUCrJ, 9(Pt 4), pp. 497-507. International Union of Crystallography 10.1107/S2052252522005309

Grabowsky, Simon; Spackman, Mark A (2022). *Structure correlation and dynamics in crystals - a tribute to Hans-Beat Bürgi.* Acta crystallographica Section B, 78(Pt 3 Pt 1), pp. 281-282. International Union of Crystallography 10.1107/S2052520622005248

Pawlędzio, Sylwia; Malinska, Maura; Kleemiss, Florian; Grabowsky, Simon; Woźniak, Krzysztof (2022). *Aurophilic Interactions Studied by Quantum Crystallography.* Inorganic chemistry, 61(10), pp. 4235-4239. American Chemical Society 10.1021/acs.inorgchem.1c03333

Appiarius, Yannik; Gliese, Philipp J; Segler, Stephan A W; Rusch, Pascal; Zhang, Jiangbin; Gates, Paul J; Pal, Rumpa; Malaspina, Lorraine A; Sugimoto, Kunihisa; Neudecker, Tim;

Bigall, Nadja C; Grabowsky, Simon; Bakulin, Artem A; Staubitz, Anne (2022). *BN-Substitution in Dithienylpyrenes Prevents Excimer Formation in Solution and in the Solid State.* Journal of physical chemistry. C, 126(9), pp. 4563-4576. American Chemical Society 10.1021/acs.jpcc.1c08812

Pal, Rumpa; Jelsch, Christian; Momma, Koichi; Grabowsky, Simon (2022). *π-Hole bonding in a new co-crystal hydrate of gallic acid and pyrazine: static and dynamic charge density analysis.* Acta crystallographica Section B, 78(2), pp. 231-246. International Union of Crystallography 10.1107/S2052520622001457

Somerville, Rosie J.; Borys, Andryj M.; Perez-Jimenez, Marina; Nova, Ainara; Balcells, David; Malaspina, Lorraine A.; Grabowsky, Simon; Carmona, Ernesto; Hevia, Eva; Campos, Jesús (2022). *Unmasking the constitution and bonding of the proposed lithium nickelate "Li 3 NiPh 3 (solv) 3 ": revealing the hidden C 6 H 4 ligand.* Chemical Science, 13(18), pp. 5268-5276. The Royal Society of Chemistry 10.1039/d2sc01244h

Davidson, Max L.; Grabowsky, Simon; Jayatilaka, Dylan (2022). *X-ray constrained wavefunctions based on Hirshfeld atoms. I. Method and review.* Acta crystallographica Section B, 78(3), pp. 312-332. International Union of Crystallography 10.1107/S2052520622004097

Davidson, Max L.; Grabowsky, Simon; Jayatilaka, Dylan (2022). *X-ray constrained wavefunctions based on Hirshfeld atoms. II. Reproducibility of electron densities in crystals of α-oxalic acid dihydrate.* Acta crystallographica Section B, 78(3), pp. 397-415. International Union of Crystallography 10.1107/S2052520622004103

Duvinage, Daniel; Puylaert, Pim; Wieduwilt, Erna K.; Malaspina, Lorraine A.; Edwards, Alison J.; Lork, Enno; Mebs, Stefan; Hupf, Emanuel; Grabowsky, Simon; Beckmann, Jens (2022). *Nickel and Palladium Complexes of a PP(O)P Pincer Ligand Based upon a peri -Substituted Acenaphthyl Scaffold and a Secondary Phosphine Oxide.* Inorganic chemistry, 61(22), pp. 8406-8418. American Chemical Society 10.1021/acs.inorgchem.1c03266

Duvinage, Daniel; Malaspina, Lorraine A.; Grabowsky, Simon; Mebs, Stefan; Beckmann, Jens (2022). *Lewis Superacidic Divalent Bis(m -terphenyl)element Cations [(2,6-Mes 2 C 6 H 3) 2 E] + of Group 13 Revisited and Extended (E=B, Al, Ga, In, Tl).* European journal of inorganic chemistry, 26(1) Wiley-VCH 10.1002/ejic.202200482

2021

Feige, Felix; Malaspina, Lorraine A.; Rychagova, Elena; Ketkov, Sergey; Grabowsky, Simon; Hupf, Emanuel; Beckmann, Jens (2021). *Perfluorinated Trialkoxysilanol with Dramatically Increased Brønsted Acidity.* Chemistry - a European journal, 27(64), pp. 15898-15902. Wiley-VCH 10.1002/chem.202103177

Kleemiss, Florian; Dolomanov, Oleg V.; Bodensteiner, Michael; Peyerimhoff, Norbert; Midgley, Laura; Bourhis, Luc J.; Genoni, Alessandro; Malaspina, Lorraine A.; Jayatilaka, Dylan; Spencer, John L.; White, Fraser; Grundkötter-Stock, Bernhard; Steinhauer, Simon; Lentz, Dieter; Puschmann, Horst; Grabowsky, Simon (2021). *Accurate crystal structures and chemical properties from NoSpherA2.* Chemical Science, 12(5), pp. 1675-1692. The Royal Society of Chemistry 10.1039/d0sc05526c

Holsten, Sebastian; Malaspina, Lorraine A.; Kleemiss, Florian; Mebs, Stefan; Hupf, Emanuel; Grabowsky, Simon; Beckmann, Jens (2021). *Different Reactivities of (5-Ph 2 P-Ace-6-) 2 MeSiH toward the Rhodium(I) Chlorides [(C 2 H 4) 2 RhCl] 2 and [(CO) 2 RhCl] 2 . Hirshfeld Atom Refinement of a Rh–H···Si Interaction.* Organometallics, 40(13), pp. 2027-2038. American Chemical Society 10.1021/acs.organomet.0c00804

Fugel, Malte; Dittmer, Anneke; Kleemiss, Florian; Grabowsky, Simon (2021). *On the Role of Hydrogen Bonding in Gas-Phase S N 2 Reactions at Silicon.* Journal of physical chemistry. A, 125(19), pp. 4070-4078. American Chemical Society 10.1021/acs.jpca.1c00601

Schwickert, Kevin; Andrzejewski, Michal; Grabowsky, Simon; Schirmeister, Tanja (2021). *Synthesis, X-ray Structure Determination, and Comprehensive Photochemical Characterization of (Trifluoromethyl)diazirine-Containing TRPML1 Ligands.* The Journal of organic chemistry, 86(9), pp. 6169-6183. American Chemical Society 10.1021/acs.joc.0c02993

Kleemiss, Florian; Wieduwilt, Erna K.; Hupf, Emanuel; Shi, Ming W.; Stewart, Scott G.; Jayatilaka, Dylan; Turner, Michael J.; Sugimoto, Kunihisa; Nishibori, Eiji; Schirmeister, Tanja; Schmidt, Thomas C.; Engels, Bernd; Grabowsky, Simon (2021). *Similarities and differences between crystal and enzyme environmental effects on the electron density of drug molecules.* Chemistry - a European journal, 27(10), pp. 3407-3419. Wiley-VCH 10.1002/chem.202003978

Podhorský, Michal; Bučinský, Lukáš; Jayatilaka, Dylan; Grabowsky, Simon (2021). *HgH 2 meets relativistic quantum crystallography. How to teach relativity to a non-relativistic wavefunction.* Acta Crystallographica Section A Foundations and Advances, 77(1), pp. 54-66. International Union of Crystallography 10.1107/S2053273320014837

Malaspina, Lorraine A.; Genoni, Alessandro; Jayatilaka, Dylan; Turner, Michael J.; Sugimoto, Kunihisa; Nishibori, Eiji; Grabowsky, Simon (2021). *The advanced treatment of hydrogen bonding in quantum crystallography.* Journal of applied crystallography, 54(3), pp. 718-729. Wiley 10.1107/S1600576721001126

Malaspina, Lorraine A.; Genoni, Alessandro; Grabowsky, Simon (2021). *lamaGOET : an interface for quantum crystallography.* Journal of applied crystallography, 54(3), pp. 987-995. Wiley 10.1107/S1600576721002545

Pawlędzio, Sylwia; Malinska, Maura; Woińska, Magdalena; Wojciechowski, Jakub; Malaspina, Lorraine Andrade; Kleemiss, Florian; Grabowsky, Simon; Woźniak, Krzysztof (2021). *Relativistic Hirshfeld atom refinement of an organo-gold(I) compound.* IUCrJ, 8(4), pp. 608-620. International Union of Crystallography 10.1107/S2052252521004541

Kleemiss, Florian; Puylaert, Pim; Duvinage, Daniel; Fugel, Malte; Sugimoto, Kunihisa; Beckmann, Jens; Grabowsky, Simon (2021). *Ibuprofen and sila-ibuprofen: polarization effects in the crystal and enzyme environments.* Acta crystallographica Section B, 77(6), pp. 892-905. International Union of Crystallography 10.1107/S2052520621009379

Novelli, Giulia; McMonagle, Charles J.; Kleemiss, Florian; Probert, Michael; Puschmann, Horst; Grabowsky, Simon; Maynard-Casely, Helen E.; McIntyre, Garry J.; Parsons, Simon (2021). *Accurate H-atom parameters for the two polymorphs of L -histidine at 5, 105 and 295*

K. Acta crystallographica Section B, 77(5), pp. 785-800. International Union of Crystallography 10.1107/S205252062100740X

Midgley, Laura; Bourhis, Luc J.; Dolomanov, Oleg V.; Grabowsky, Simon; Kleemiss, Florian; Puschmann, Horst; Peyerimhoff, Norbert (2021). *Vanishing of the atomic form factor derivatives in non-spherical structural refinement – a key approximation scrutinized in the case of Hirshfeld atom refinement.* Acta Crystallographica Section A Foundations and Advances, 77(6), pp. 519-533. International Union of Crystallography 10.1107/S2053273321009086

2020

Meyer, Fabio; Hupf, Emanuel; Lork, Enno; Grabowsky, Simon; Mebs, Stefan; Beckmann, Jens (2020). *Bis(6-diphenylphosphino-acenaphth-5-yl)sulfoxide. A New Ligand for Late Transition Metal Complexes.* European journal of inorganic chemistry, 2020(40), pp. 3829-3836. Wiley-VCH 10.1002/ejic.202000610

Kleemiss, Florian; Justies, Aileen; Duvinage, Daniel; Watermann, Patrick; Ehrke, Eric; Sugimoto, Kunihisa; Fugel, Malte; Malaspina, Lorraine A.; Dittmer, Anneke; Kleemiss, Torsten; Puylaert, Pim; King, Nelly R.; Staubitz, Anne; Tzschentke, Thomas M.; Dringen, Ralf; Grabowsky, Simon; Beckmann, Jens (2020). *Sila-Ibuprofen.* Journal of medicinal chemistry, 63(21), pp. 12614-12622. American Chemical Society 10.1021/acs.jmedchem.0c00813

Damgaard-Møller, Emil; Krause, Lennard; Lassen, Helene; Malaspina, Lorraine A.; Grabowsky, Simon; Bamberger, Heiko; McGuire, Jake; Miras, Haralampos N.; Sproules, Stephen; Overgaard, Jacob (2020). *Investigating Complex Magnetic Anisotropy in a Co(II) Molecular Compound: A Charge Density and Correlated Ab Initio Electronic Structure Study.* Inorganic chemistry, 59(18), pp. 13190-13200. American Chemical Society 10.1021/acs.inorgchem.0c01489

Sanjuan-Szklarz, W. Fabiola; Woińska, Magdalena; Domagała, Sławomir; Dominiak, Paulina M.; Grabowsky, Simon; Jayatilaka, Dylan; Gutmann, Matthias; Woźniak, Krzysztof (2020). *On the accuracy and precision of X-ray and neutron diffraction results as a function of resolution and the electron density model.* IUCrJ, 7(5), pp. 920-933. International Union of Crystallography 10.1107/S2052252520010441

Rohdenburg, Markus; Yang, Zheng; Su, Pei; Bernhardt, Eduard; Yuan, Qinqin; Apra, Edoardo; Grabowsky, Simon; Laskin, Julia; Jenne, Carsten; Wang, Xue-Bin; Warneke, Jonas (2020). *Properties of gaseous closo -[B 6 X 6] 2− dianions (X = Cl, Br, I).* Physical Chemistry Chemical Physics, 22(31), pp. 17713-17724. Royal Society of Chemistry 10.1039/d0cp02581j

Duvinage, Daniel; Lork, Enno; Grabowsky, Simon; Mebs, Stefan; Beckmann, Jens (2020). *Synthesis, Structure and Bonding Analysis of the Zwitterionic PPP-Pincer Complex (6-Ph2P-Ace-5-)2P(O)AuCl2.* Crystals, 10(7), p. 564. Molecular Diversity Preservation International MDPI 10.3390/cryst10070564

Pal, Rumpa; Jelsch, Christian; Malaspina, Lorraine A.; Edwards, Alison J.; Murshed, M. Mangir; Grabowsky, Simon (2020). *Syn and anti polymorphs of 2,6-dimethoxy benzoic acid*

and its molecular and ionic cocrystals: Structural analysis and energetic perspective. Journal of Molecular Structure, 1221, p. 128721. Elsevier 10.1016/j.molstruc.2020.128721

Malaspina, Lorraine A.; Hoser, Anna A.; Edwards, Alison J.; Woińska, Magdalena; Turner, Michael J.; Price, Jason R.; Sugimoto, Kunihisa; Nishibori, Eiji; Bürgi, Hans-Beat; Jayatilaka, Dylan; Grabowsky, Simon (2020). *Hydrogen atoms in bridging positions from quantum crystallographic refinements: influence of hydrogen atom displacement parameters on geometry and electron density.* CrystEngComm, 22(28), pp. 4778-4789. Royal Society of Chemistry 10.1039/d0ce00378f

Mayer, Martin; Rohdenburg, Markus; van Lessen, Valentin; Nierstenhöfer, Marc C.; Aprà, Edoardo; Grabowsky, Simon; Asmis, Knut R.; Jenne, Carsten; Warneke, Jonas (2020). *First steps towards a stable neon compound: observation and bonding analysis of [B 12 (CN) 11 Ne] −.* Chemical communications, 56(33), pp. 4591-4594. Royal Society of Chemistry 10.1039/d0cc01423k

Schlüter, Dirk; Kleemiss, Florian; Fugel, Malte; Lork, Enno; Sugimoto, Kunihisa; Grabowsky, Simon; Harmer, Jeffrey R.; Vogt, Matthias (2020). *Non-Oxido-Vanadium(IV) Metalloradical Complexes with Bidentate 1,2-Dithienylethene Ligands – Observation of Reversible Cyclization of the Ligand Scaffold in Solution.* Chemistry - a European journal, 26(6), pp. 1335-1343. Wiley-VCH 10.1002/chem.201904103

Grabowsky, Simon; White, Allan H.; Healy, Peter C.; Lapere, Kim M.; Ng, Seik Weng; Skelton, Brian W.; Wild, Duncan A.; Bowmaker, Graham A.; Hanna, John V. (2020). *Solid-State NMR, X-Ray Diffraction, and Theoretical Studies of Neutral Mononuclear Molecular Bis(triphenylphosphine)silver(i) Mono-Carboxylate and -Nitrate Systems.* Australian journal of chemistry, 73(6), p. 556. CSIRO Publishing 10.1071/CH19616

Wieduwilt, Erna K.; Macetti, Giovanni; Malaspina, Lorraine A.; Jayatilaka, Dylan; Grabowsky, Simon; Genoni, Alessandro (2020). *Post-Hartree-Fock methods for Hirshfeld atom refinement: are they necessary? Investigation of a strongly hydrogen-bonded molecular crystal.* Journal of Molecular Structure, 1209, p. 127934. Elsevier 10.1016/j.molstruc.2020.127934

Grabowsky, Simon; Genoni, Alessandro; Thomas, Sajesh P.; Jayatilaka, Dylan (2020). *The Advent of Quantum Crystallography: Form and Structure Factors from Quantum Mechanics for Advanced Structure Refinement and Wavefunction Fitting.* In: Mingos, D. Michael P.; Raithby, Paul R. (eds.) 21st Century Challenges in Chemical Crystallography II: Structural Correlations and Data Interpretation. Structure and Bonding: Vol. 186 (pp. 65-144). Cham: Springer International Publishing 10.1007/430_2020_62