Hylleraas

Annual Report 2021

Hylleraas

Hylleraas Centre for Quantum Molecular Sciences
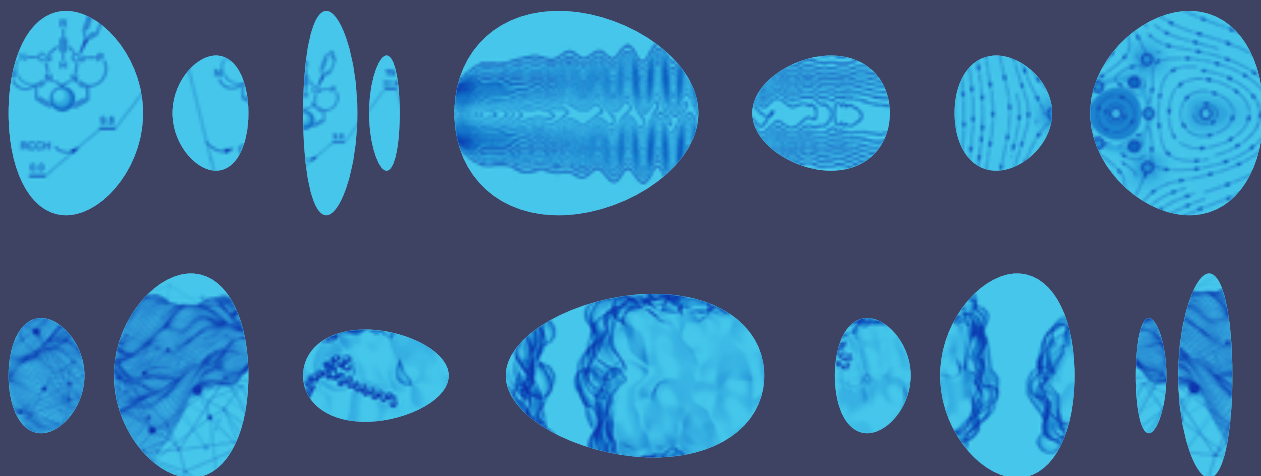
The Hylleraas Centre is a Norwegian Centre of Excellence (CoE) shared equally between the University of Oslo (UiO) and UiT The Arctic University of Norway (UiT), with UiO as project owner. It receives an annual funding of about 15 million NOK from the Research Council of Norway. In addition, it receives substantial financial support from UiO and UiT. The centre was established on October 1st 2017 for a period of six years with the possibility of an extension for a further four years following a midterm evaluation.

The Hylleraas Centre is one of 23 national CoEs in Norway. The goal of the CoE program is to stimulate Norwegian research groups to establish larger units focusing on frontier research at a high international level and to raise the quality of Norwegian research.

The Hylleraas Centre aims to develop and apply computational methods to understand, interpret, and predict new chemistry, physics, and biology of molecules in complex and extreme environments. It has an extensive visitors' program for scientists from around the world, as well as for PhD candidates and postdocs from other research groups who wish to benefit from the expertise at the centre.

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From the Directors

The second year of the pandemic saw many of the same restrictions as the first year. In spite of the difficulties, the Hylleraas Centre was able to meet physically twice — for the Hylleraas Annual Meeting at Hamn in Senja and for the Hylleraas School in Gran. Moreover, both events were organized or co-organized by the representatives of the Young Researcher Parliament.

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Since the Hylleraas Centre works with theory and does not depend on experimental work except through collaboration, we have been able to continue work uninterrupted during the COVID-19 pandemic. Nevertheless, not interacting physically on a day-to-day basis is far from ideal and not conducive to excellent science in the long run. We are therefore grateful that, in the second year of the pandemic, we were able to meet as a centre twice — at the Annual Meeting at Hamn and at the Hylleraas School in Gran. The strong attendance at both events shows clearly how important these events are for the members of the centre. We would like to thank the organizers for the excellent organization — especially the young members Bente Barge and Ryan Wilkins (for organizing the Annual Meeting together with Bjørn Olav Brandsdal) and Karolina Eikås and Audun Skau Hansen (for organizing the Hylleraas School together with David Balcells and Simen Reine).

While the Annual Meeting is a well-established recurring event at the Hylleraas Centre, the Hylleraas School was the first such event, to be repeated on a regular basis. The purpose of the school was to familiarize all members of the centre, senior as well as junior members, with the work in our research themes, in a manner that cannot easily be achieved otherwise. Each day of the school was devoted to one of the six research themes at the centre, with lectures and exercises solved by group work. The technical support was fan-tastic, making it possible to carry out all necessary computing on the personal laptops of the participants. Many thanks to Audun Hansen and Simen Reine for making this possible — we are already looking forward to the next school!

In recent years, the Hylleraas Centre has systematically worked to improve our success in securing external funding by organizing meetings where ideas for proposals are discussed and by performing internal reviews. In part, this work may have contributed to our success in this area — as in 2020, the Hylleraas Centre secured in 2021 substantial funding from national and international agencies: one ERC Starting grant, three FRIPRO grants from the Research Council of Norway (RCN), one Marie Skłodowska-Curie Actions (MSCA) fellowship, and one Peder Sather travel grant. We would especially like to congratulate our young members who secured their own funding: André Laestadius (ERC Starting Grant), Abril Castro (Research Talents Grant), and Michal Repisky (MSCA Grant).

In addition, members of the Hylleraas Centre participate in two interdisciplinary research consortia that were funded in 2021: *Mathematics for Quantum Computation and Manybody Theory* (Large-Scale Interdisciplinary Researcher Project, RCN) with participation of Simen Kvaal and *Hydrogen Storage and Transport Using Ammonia* (EU Horizon 2021 Resilience Call) with participation of David Balcells. These projects illus-

trate the broadness of our research and our active participation in national and international networks.

Five of our PhD candidates defended their PhD theses in 2021: Karen O. H. M. Dundas, Audun Skau Hansen, Lluís Artús Suàrez, Joakim Samuel Jestilä, and Julie Héron. We congratulate all on their degrees and wish them all the best in their future careers.

Several members of the centre received prizes and honours in 2021. At the University of Tromsø, Kenneth Ruud was awarded *Grunnforskningsprisen* (Prize for Fundamental Research) of the Faculty of Science and Technology. At the Department of Chemistry, University of Oslo, PhD candidate Sverre Løyland won the Chemistry Grand Prix presentation competition, Eirill Strand Hauge won the prize for the best master thesis, while Audun Skau Hansen won *Den gyldne spatel* for best teaching and *Miljøskaperprisen* for contributing to an inclusive and good working environment at the department. Several members were elected to academies: Odile Eisenstein (American Academy of Arts & Sciences and US National Academy of Sciences), Trygve Helgaker (Royal Swedish Academy of Sciences) and Bjarte Aarmo Lund (Young Academy of Norway). Congratulations to all!

In 2021, Deputy Director Kenneth Ruud was appointed Director General of the Norwegian Defence Research Establishment (FFI) from January 1, 2022.

Ruud, who will continue in a 20% position at the centre, is replaced as deputy director by Luca Frediani and as a principal investigator by Michal Repisky. In 2022, the Hylleraas Centre will select the next director among the principal investigators in Oslo, to take over from Trygve Helgaker, who retires in August 2023.

In August 2021, Prof. Camilla Brekke became Pro-Rector for Research and Development at UiT The Arctic University of Norway. At the same time, Brekke stepped down as a member of the Hylleraas Board and was replaced in this role by Prof. Annette Bayer, Head of the Department of Chemistry at UiT. We welcome Bayer to the board and would like to thank Brekke for her contributions to the centre.

During 2022, the Hylleraas Centre will prepare for the midterm evaluation of the centre, to be carried out in 2023. As part of this work, we will modify and update our research plans for the last centre period 2023–2027, considering the results that have been achieved in the first centre period, international developments in the field, and changes in staff at the centre.

The scientific production in 2021 was lower than in the previous years, because of changes in staff and probably also the pandemic. With the many new external projects to begin in 2022, we should recover productivity in coming years.

Finally, we would like to thank all members and affiliates of the Hylleraas Centre for their great work in the difficult pandemic year 2021, as documented in this report.

Photo: Ansgar Valbø/NORA

Prof. Trygve Helgaker
Director

Prof. Kenneth Ruud
Deputy Director

From the Board of Directors

The Board of Directors is pleased to note that the Hylleraas Centre continues to produce science at the highest international level. The board notes with satisfaction that the strong track record of securing external funding is continued in 2021, providing an excellent foundation for a continued high level of activity at the centre as activities return to normal in the wake of the pandemic.

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The Hylleraas Centre has been able to come through the COVID-19 pandemic more easily than many other research groups, as it is reliant primarily on computing resources and because it has a long-standing experience with digital seminars across the two nodes. As such, the research activities at the centre have continued at a high level throughout the pandemic. Nevertheless, the board acknowledges that the pandemic has been a difficult period for the staff members, with increased physical isolation. The board appreciates the measures taken to combat such effects through digital social gatherings and outdoor activities but shares the excitement of the staff members of again being able to return to work, travel to international meetings, and restart the international visitors program. The board expects this to further invigorate the scientific activities at the centre.

The Hylleraas Centre has established a collegial system for helping centre members more clearly articulate their scientific ideas in proposals submitted for external funding. This system continues to serve the centre well, as illustrated by the success in securing external funding in 2021: one ERC

Starting Grant awarded to André Laestadius and three FRIPRO projects awarded to David Balcells, Abril Castro, and Luca Frediani. The board congratulates the awardees with their impressive achievements — and the centre with a very successful mentoring scheme.

The board congratulates Deputy Director Prof. Kenneth Ruud with his appointment as Director General of the Norwegian Defence Research Establishment (FFI) from 2022. The board is happy to note that he will remain in a 20% position at the Hylleraas Centre and thus continue to contribute to centre activities, albeit in a less prominent role. The board thanks Ruud for his contributions to the centre as deputy director. We welcome Luca Frediani as the new deputy director and Michal Repisky as the new principal investigator for Research Theme 3, in place of Ruud.

With Ruud stepping down, a new centre director must be found when the current director Trygve Helgaker retires in 2023. The Hylleraas Centre has several candidates with the qualifications and the interest to step up to this important challenge. The board is engaged in the process of finding a new director as part of the planned preparation for

"In short, 2021 has been a successful year for the Hylleraas Centre, which has an excellent foundation to continue its strong track record of producing high-quality scientific results."

the midterm evaluation and in close dialogue with the Research Council of Norway. We are confident that the centre will have a strong leadership also in the future.

The board is concerned about the changes being implemented in the funding of high-performance computing (HPC) in Norway. The expectation of the host institutions that significant parts of the HPC costs are to be contributed by the users themselves may impact the ability of the centre to conduct research at the highest international level – both because less resources may then be available for hiring young research talents and because some of the most innovative projects may have to be set aside due to excessive needs for computer time. The board asks the host institutions to monitor the consequences of these changes closely.

In short, 2021 has been a successful year for the Hylleraas Centre, which has an excellent foundation to continue its strong track record of producing high-quality scientific results. We are confident that the upcoming midterm evaluation will confirm this and at the same time provide guidance for the future development of the centre.

Unni Olsen (chair)
Professor
Dept. Chemistry
UiO

Annette Bayer
Professor
Dept. Chemistry
UiT

Atle Jensen
Professor
Dept. Mathematics
UiO

Nathalie Reuter
Professor
Dept. Bio. Sciences
UiB

Kajsa Ryttberg-Wallgren
Vice President
Vacuum Conveying Division
Piab Group, Sweden

From the Young Researchers

The Young Researcher Parliament (YRP) representatives serve as a voice for the young researchers within the daily running of the Hylleraas Centre. The four elected representatives, consisting of two young researcher representatives from each node, act as a liaison between the Management Team and master's students, PhD candidates, postdoctoral fellows, and other young researchers with temporary positions within the centre.

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Through the YRP, young researchers can express their opinions on how to improve the centre. In the Oslo node, weekly meetings are organized to discuss administrative issues, in which both representatives from Oslo contribute to the decision making. In addition to that, monthly MT meetings are organized between both nodes and all four YRP representatives participate actively in the discussions.

During 2021, the Tromsø node of the YRP was involved in organizing the Annual Hylleraas Meeting. Held over three days at Hamn in Senja, the meeting consisted of a round of Five-Minute Thesis Presentations from the master and PhD students, career development talks by Kenneth Ruud and Trygve Helgaker, and the YRP annual assembly, where both nodes of the YRP met to discuss ways to improve representation and work towards the vision of the centre.

In addition to facilitating professional growth, the YRP also provides a means for young researchers to connect with each other. In the Tromsø node, this was done through a variety of social events, ranging from board-game nights to mini golf and bowling. As for the Oslo node, pizza meetings were organized every month wherein all the members reflected on their experiences as a student and discussed various issues regarding career development. After the pandemic, which had seriously curtailed most physical events for two years, the YRP wishes to strive towards building more opportunities for young researchers to meet and grow togeth-

↑ YRP representatives at Hamn, Senja. From left to right:
Samiran Sen, Bente Barge, Mahika Luthra, and Ryan Wilkins.

er as a scientific community. As part of this agenda, some preliminary ideas have already been exchanged for potential workshops and seminars that can be organized to enhance the scientific knowledge and skill of young researchers, both general and specific to their research fields.

The YRP is headed by two representatives from each node of the Hylleraas Centre, who act as the main communication pathway between the young researchers and the Management Team. Representatives are elected by the young researchers in each node. Early this year, an election was held to replace one representative from each node. Stepping down from their posi-

tions as YRP representatives were Abril Castro (UiO) and Karolina Eikås (UiT). We would like to thank them for their contributions to the Hylleraas Centre. Their replacements are Mahika Luthra (UiO) and Bente Barge (UiT), who together with Samiran Sen (UiO) and Ryan Wilkins (UiT) now represent the young researchers.

Bente Sirin Barge

Mahika Luthra

Samiran Sen

Ryan Scott Wilkins

Elected YRP representatives 2021
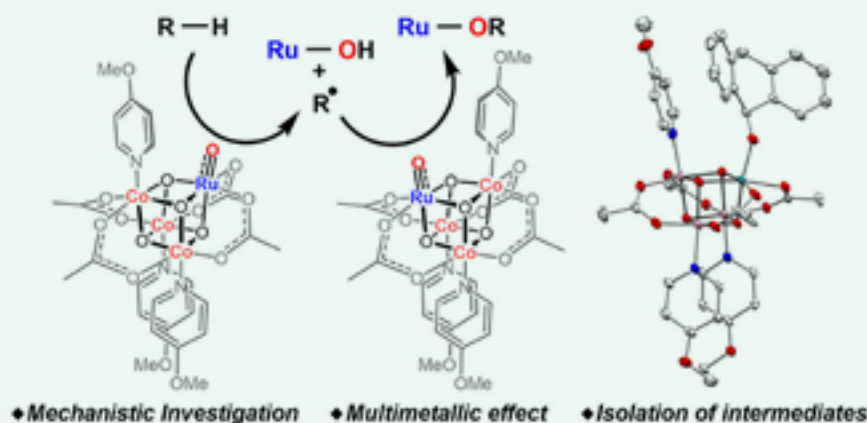
2021
in Brief

* **Mechanistic Investigation**   * **Multimetallic effect**   * **Isolation of intermediates**

Figure 1:

Graphical abstract of the paper *C–H Activation by RuCo$_3$O$_4$ Oxo Cubanes: Effects of Oxyl Radical Character and Metal–Metal Cooperativity*, Reprinted with permission from *J. Am. Chem. Soc.*, 2021, **143**, 12108–12119. Copyright 2021 American Chemical Society.

Publications

Members of the Hylleraas Centre published 41 articles in 2021, bringing our total scientific production to nearly 250. As in previous years, most articles were published in the *Journal of Chemical Theory and Computation*. At the end of 2021, the articles published by the Hylleraas Centre since 2017 have been cited nearly 2000 times (excluding self-citations), with an H-index of 23. About one half of these papers were devoted to theoretical and methodological developments, the other half being computational studies, several in collaboration with experimentalists. The trend towards more complex systems and time-dependent phenomena continues. In early 2021, the total number of papers published by members of the Hylleraas Centre and its predecessor, the Centre for Theoretical and Computational Chemistry (CTCC), exceeded one thousand.

Several of our papers were highlighted by the editors. The article *C–H Activation by RuCo$_3$O$_4$ Oxo Cubanes: Effects of Oxyl Radical Character and Metal–Metal Cooperativity* published in the *Journal of the American Chemical Society* by Hylleraas MSc student Bastian Skjelstad and David Balcells in collaboration with the experimental group of Don Tilley at UC Berkeley was featured in *JACS Spotlights* of August 2021; see Figure 1. The authors demonstrated unprecedented radical chemistry and metal–metal cooperativity effects in oxo cubanes. In addition, two back-to-back articles on molecular dynamics in a magnetic field published in the *Journal of Chemical Physics* were promoted as *Editor's Pick* in July. In these papers, the first *ab initio* molecular dynamics with Lorentz forces were presented.

Meetings and conferences

Because of the pandemic, few meetings were organized in 2021. Nevertheless, the centre convened for the Hylleraas Annual Meeting at Hamn in Senja for two days in October 2021, with as many as 53 participants. As in previous years, the annual meeting was organized by the young members of the centre – this year, by Bente Barge and Ryan Wilkins at UiT.

The 2021 National Meeting of the Division of Quantum Chemistry and Modelling of the Norwegian Chemical Society was organized online by Erik Tellgren, November 29–30 2021, with 80 participants. Tellgren also organized the Young CAS workshop *Global Optimization in Electronic Energy Landscapes: Finding a Needle in a Haystack* at the Hylleraas Centre September 13–17 2021, with the participation of seven young scientists for a full week.

From October 17 to 22, the Hylleraas Centre held its first Hylleraas School at Hotel Hadeland, Gran, with more than 50 participants; see Figure 2. The purpose of the school, where senior

Figure 2:

Participants of the Hylleraas School at Hotel Hadeland October 17–22 2021. *Photo: David Balcells.*

Figure 3:

Cover of *Étonnante Chimie — Découvertes et promesses du XXIe siècle*, for which Odile Eisenstein and Michele Cascella wrote the chapter *La réaction de Grignard, une énigme de XXIe siècle.* With permission from CNRS editions 2021.

Outreach and dissemination

and junior members of the centre participated on an equal footing, was to familiarize our members with ongoing research at the centre, through lectures and exercises. The school, which was organized by Karolina Solheimslid Eikås, Audun Skau Hansen, David Balcells, and Simen Reine, was a great success and will be repeated on a yearly basis (Figure 2).

Two Almlöf–Gropen Symposia were held in 2021, both online. The 2020 Almlöf–Gropen Lecture, *Light and Shadows on the Quantum Simulation of Molecular Electronic Excited States*, was given by Prof. Leticia González, University of Vienna on June 1, while the 2021 Almlöf–Gropen Lecture, *There is No Time for Science as Usual: Materials Acceleration Platforms*, was given by Prof. Alán AspuruGuzik, University of Toronto, on September 10. At both symposiums, two Almlöf–Gropen Young Speakers presented their own work: Abril Castro and Ryan Wilkins at the symposium in June and Tanner Culpitt and Gabriel Gerez in September.

Outreach and dissemination were both reduced because of the pandemic. Still, the members of the centre gave several popular science talks in 2021. Odile Eisenstein gave the virtual talks *L'énigme Grignard une affaire classée... ou pas?* at Le Village de la Chimie Virtual on March 12 and *Le peintre: un chimiste qui s'ignore* at Conférence Abbadia, Hendaye on April 23. Trygve Helgaker talked about the Hylleraas Centre for members of the Norwegian Society of Graduate Technical and Scientific Professionals (Tekna) on September 29 and about *Molecules in a Strong Magnetic Field* at a staff meeting of the Department of Chemistry at the University of Oslo on August 26.

In 2021, members of the Hylleraas Centre wrote two articles for *Kjemi*, the journal of the Norwegian Chemical Society: *Kan en robot tenke som en kjemiker?* (David Balcells, Kjemi nr. 2, 2021) and *Årets Almlöf–Gropen foredrag* (Bente Barge, Kjemi nr. 5, 2021). Odile Eisenstein and Michele Cascella wrote the chapter *La reaction de Grignard, une*

enigme de 120 ans in the popular science book *Étonnante Chimie – Découvertes et promesses du XXIe siècle,* published by CNRS Editions (2021); see Figure 3.

Trygve Helgaker was interviewed about bird navigation by NRK.no in January 2021. In the interview, Helgaker explained the role of quantum mechanics in the theory of magnetoreception proposed by Klaus Schulten in 1978, which is now one step closer to validation by recent findings on cellular autofluorescence. In May 2021, PhD candidate Sverre Løyland was interviewed in *Apollon*, the research magazine of the University of Oslo, explaining his work on sonochemistry, while Helgaker featured in the *Alumni Spotlight* section of the monthly newsletter of the Centre for Advanced Study (CAS) at the Norwegian Academy of Science and Letters, emphasizing the strong connections of the Hylleraas Centre to CAS.

Figure 4:

Dr. André Laestadius, the Hylleraas Centre, University of Oslo
— winner of an ERC Starting Grant in 2021.

Training and career support

A total of 22 Friday Seminars were held in 2021 – among these,17 seminars were given by our young researchers. In addition, four young centre members spoke at the two Almlöf–Gropen Symposia held in 2021.

The Young Researcher Parliament (YRP) organized several events targeted towards the younger members of the Hylleraas Centre in 2021. Bente Barge and Ryan Wilkins organized the Annual Meeting at Hamn, while Karolina Solheimslid Eikås and Audun Skau Hansen organized with David Balcells and Simen Reine the Hylleraas School in Gran. The YRP also continued the Alumni Talks with a contribution from Sangita Sen at IISER Kolkata, India. Four representatives of the YRP participated at the 11 Management Meetings held in 2021.

The *Molecular Response Properties Summer School 2021*, originally scheduled for 2020, was held in Stockholm October 4–8, organized by Prof. Patrick Norman (KTH Royal Institute of Technology, Stockholm), Prof. Trond Saue (Université de Toulouse), and Kenneth Ruud, with 40 participants.

External projects and funding

During the academic year 2021–2022, Thomas Bondo Pedersen and Simen Kvaal lead the CAS project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation (ATTODYN)*, which in addition to the group leaders includes 11 fellows, four of whom worked at CAS in the autumn of 2021.

In 2021, the Hylleraas Centre continued its success with securing external funding, winning several grants from national and international funding agencies.

Three FRIPRO grants from the Research Council of Norway (RCN) were awarded to our members in 2021: to David Balcells for *Machine Learning Molecular Legos for Catalyst Discovery within Large Chemical Spaces (catLEGOS)*, to Luca Frediani for *Multiresolution Chemistry: Heavy-Element Compounds at the Complete Basis-set Limit (ReMRCheM)*, and to Abril Castro for her YRT project *Accurate Prediction and Interpretation of NMR Spectra in Transition-Metal Complexes (SpecTraM)*. In addition, Simen Kvaal is a partner in the RCN Large-Scale Interdisciplinary Researcher Project *Mathematics for Quantum Computation and Many-Body Theory (QOMBINE)*, which is part of Fellesløft IV.

Three projects were funded by EU sources in 2021. André Laestadius was awarded an ERC Starting Grant for the project *Regularized Density-Functional Analysis (Regal)* (Figure 4), Michal Répisky won a Marie Sklodowska-Curie COFUND SASPRO2 Grant for the project *EPR and NMR Spectroscopy of Spin–Orbit-Coupled Paramagnetic Solids*, while David Balcells participates in the project *Hydrogen Storage and Transport using Ammonia (HySTrAm)*, granted in the EU Horizon 2021 Resilience call.

Finally, André Laestadius and postdoc Mihály Csirik received a Peder Sather grant *Homotopy Continuation for Unitary Coupled-Cluster Theory*, for collaboration with Ass. Prof. Lin Lin at UC Berkeley.

Figure 5:

Dr. Bjarte Aarmo Lund, elected member of the Young Academy of Norway 2021–2025. *Photo: Anne Lise Norheim / AYF.*

Figure 6:

PhD candidate Sverre Løyland, winner of *Chemistry Grand Prix* 2022 at the University of Oslo. *Photo: Yngve Vogt.*

Personnel

Five members of the Hylleraas Centre defended their PhD theses in 2021: Karen O. H. M. Dundas (UiT), Audun Skau Hansen (UiO), Lluís Artús Suàrez (UiO), Joakim Samuel Jestilä (UiO), and Julie Héron (UiO).

Deputy Director Kenneth Ruud was appointed Director General of the Norwegian Defence Research Establishment (FFI) from January 1, 2022. Odile Eisenstein was elected International Honorary Member of the American Academy of Arts & Sciences and International Member of the US National Academy of Sciences in 2021, while Trygve Helgaker was elected Foreign Member of the Royal Swedish Academy of Sciences. Dr. Bjarte Aarmo Lund was elected to the Young Academy of Norway for a period of four years, as one of 11 new members (Figure 5).

In 2021, PhD candidate Sverre Løyland won *Chemistry Grand Prix*, a presentation competition at the Department of Chemistry in Oslo (Figure 6). MSc Eirill Hauge was awarded the *Master Thesis of the Year Prize* at the same department, for her thesis *Extrapolating the Electric Dipole Moment – Improving the Resolution of Absorption Spectra from Real-Time Time-Dependent Coupled-Cluster Theory* (supervised by Thomas Bondo Pedersen). Dr. Audun Skau Hansen won no less than two prizes in 2021: *Den gyldne spatel* (Golden Spatula) for best teaching and *Miljøskaperprisen* (Environment Creator Award) for contributing to an inclusive and good working environment at the Department of Chemistry in Oslo.

Management

The Management Team met 11 times during 2021 (all months except July), while the Board of Directors met twice (on March 16 and November 2).

Visitors

Because of the pandemic, the number of visitors to the Hylleraas Centre was low in 2021, with only eight visitors to Oslo and three to Tromsø.
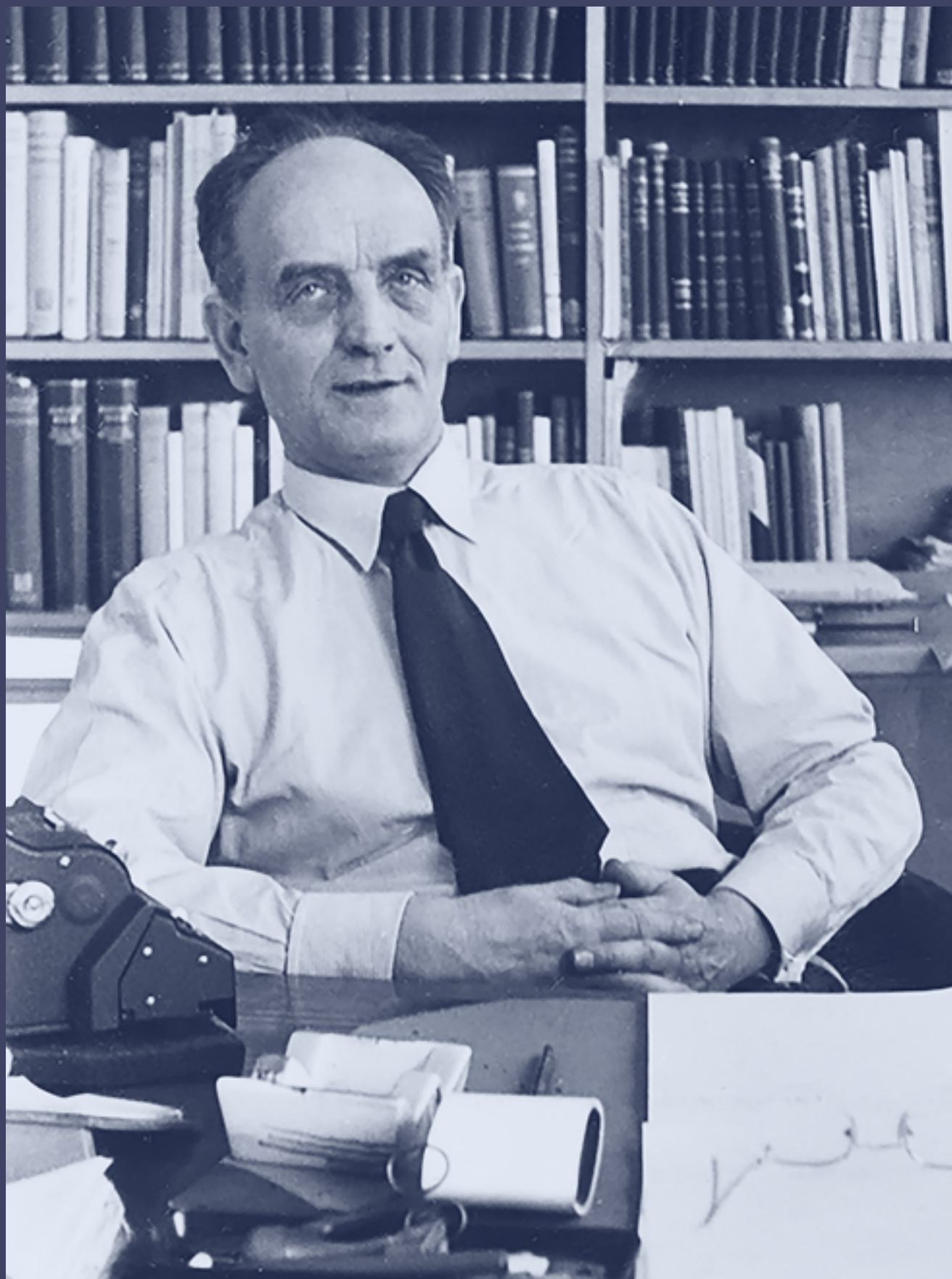
Egil A. Hylleraas

The Norwegian physicist Egil A. Hylleraas (1898–1965) helped usher in the era of scientific computing by carrying out accurate calculations on helium, thereby confirming the validity of quantum mechanics for more than one particle (1929), by predicting the stability of the hydrogen anion, later detected in the Sun's atmosphere (1930), and by performing the first calculation of the cohesive energy of a molecular crystal, LiH (1930). In 1933, he introduced the term "kvantekjemi" into the Norwegian language:

"Idet jeg avslutter den utredning håper jeg at tilhørerne vil ha fått et inntrykk av at der nu foreligger ganske vidtrekkende muligheter for å bygge op en teoretisk kjemi, en kvantekjemi, på samme grunnlag som den fysikalske kvanteteori."

English translation:
"In closing my presentation, I hope to have convinced the audience of the far-reaching opportunities that now exist for establishing a theoretical chemistry, a quantum chemistry, on the same footing as the physical quantum theory."

"Importance of wave mechanics for understanding the chemical bond."
(1933)

CHR. MICHELSENS INSTITUT
for Videnskap og Åndsfrihet
Beretninger III, 3

EGIL A. HYLLERAAS

Bølgemekanikkens betydning for forståelsen av den kjemiske binding

(Foredrag holdt 18. januar 1933)

BERGEN 1933
A/S JOHN GRIEGS BOKTRYKKERI

Research Highlights

The Hylleraas Centre carries out research on a broad range of topics in theoretical chemistry, with relevance not only to chemistry but also to physics, biology, and other related fields of science. Two such research topics are here highlighted, showcasing recent and ongoing work at the centre, including work in fundamental theoretical chemistry, the development of new computational methods and techniques, and the use of computational chemistry to address challenging questions in modern science, often in collaboration with experimentalists.

Exploring the Electronic Structure and Reactivity of Cubanes to Mimic Nature's Oxygen-Evolving Complex

David Balcells

—

The oxygen-evolving complex (OEC) is a polynuclear species catalysing the oxidation of water to oxygen in natural photosynthesis. In several studies combining theory with experiments, we have shown how a series of cubic oxides known as cubanes can be used to mimic the structure and reactivity of the OEC.

—

In natural photosynthesis, carbon dioxide is transformed into carbohydrates using sunlight as energy source. The reducing equivalents needed to drive this reaction are obtained from the oxidation of water to oxygen. Water oxidation is catalysed by the oxygen-evolving complex (OEC), which is one of the main components of photosystem II. The core structure of the OEC consists of a cubic manganese oxide with two intriguing features – namely, the presence of a dangling manganese atom pending outside the cube, and a calcium cation acting as a dopant replacing one of the manganese atoms of the cube.

The structure and reactivity of the OEC remains an active area of research [1]. One of the most promising approaches is the development of synthetic cubic oxides that mimic the properties of the OEC. The interest in this strategy is twofold: first, it sheds light on the fundamental nature of photosynthesis;

second, it can yield catalytic systems with the activity and robustness required in mass-scale technologies for the generation of renewable energies – for example, producing hydrogen and electricity from water and sunlight.

Decorating cubanes with Mn and Co
Cubic cobalt oxides are referred to as cubanes and are one of the most interesting model compounds for the OEC [2]. In chemical processes related to photosynthesis, cubanes can behave as robust catalysts that are both cheap and easy to recycle. The next step towards mimicking the OEC is to introduce dopants and dangling atoms.

In 2017, David Balcells visited for three months the research group of Prof. T. Don Tilley at UC Berkeley (USA). This stay led to a fruitful collaboration with the Hylleraas Centre focused on the electronic structure and reactivity of cubanes. In the first work, we studied
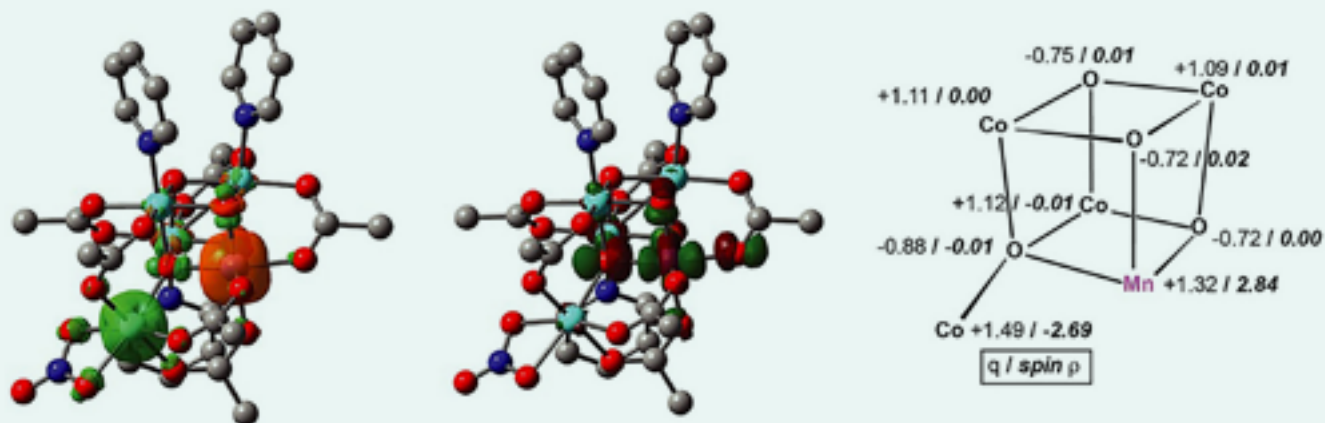
a cobalt cubane doped with manganese and attached to a dangling cobalt cation [3]. Magnetic experiments based on the superconducting quantum-interference device (SQUID) technique revealed that the ground state of this system involves an unusual antiferromagnetic coupling between cobalt and manganese atoms. Besides confirming the spin multiplicity of the ground state, density-functional-theory (DFT) calculations with the TPSSh functional showed that the cobalt atom involved in the spin coupling is the atom dangling from the cubane (Figure 1). An important consequence of this observation is that the dangling cobalt can play an active role in the redox chemistry of the system, in line with voltammetry experiments showing an increased number of electro-chemical events relative to standard cubane.

Trapping the oxyl with the 'Ru trick'
The doping of cubanes with manganese makes them more like the OEC but also makes their characterization difficult under the reaction conditions required for water oxidation. Under these con-ditions, the system yields transient species with oxyl ligands – that is, ter-minal oxo ligands in a highly reactive radical state. An alternative approach is to use metals that form stronger bonds. In this context, we explored the use of ruthenium as dopant metal, which yielded a stable and yet reactive Ru(V)–oxo complex that was charac-terized by X-ray diffraction and DFT calculations [4]. The isolation of this species is remarkable because, in gen-eral, the formation of oxo complexes with late transition metals is encum-bered by metal-ligand electron repul-sion, a phenomenon referred to as the 'oxo wall'. The calculations on this system showed that the ground state is a doublet with radical character on the oxygen bound to ruthenium. This

oxyl state has a Ru–O bond with strong spin polarization, consistent with the π^*(Ru–O) nature of the singly-occupied molecular-orbital (SOMO) radical. Another interesting feature revealed by the calculations is the charge trans-fer from the cobalt–oxo core of the cubane to the Ru–O moiety, demon-strating the electron coupling between these two structural units.

Observing the electron flow
In addition to water, cubanes can also promote the oxidation of other inert substrates including alkanes. In par-ticular, the selective oxidation of meth-ane to methanol is of high interest in systems for energy transformation and transport. For this reaction, we focused on the pristine cubane containing only cobalt and oxygen.

At the reaction-mechanism level, two fundamental questions needed to be addressed: first, which metal ligand assists the reaction; second, what is
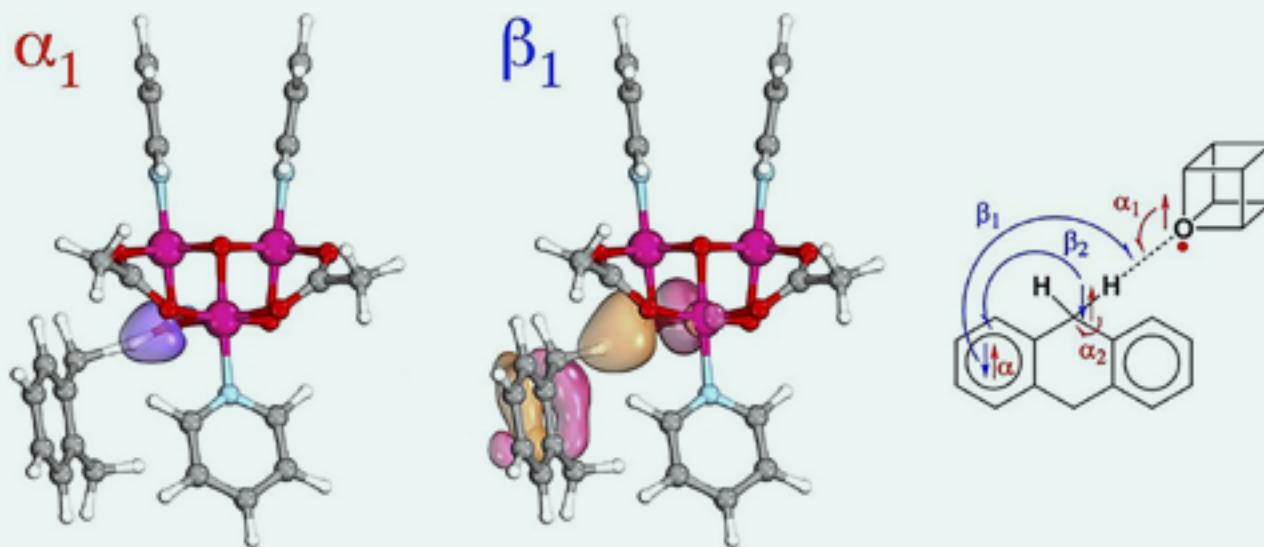
⊙ **Figure 2:** Alpha and beta components of the IBO analysis for the electron flow shown in the diagram. Reprinted with permission from *Inorg. Chem.*, 2020, **59**, 15553-155560. *Copyright 2020 American Chemical Society.*

the nature of the C–H activation step in which this strong bond is cleaved. For the first question, DFT calculations showed that the reaction is initiated by one of the oxo ligands bridging the cobalt vertices of the cubane [5]. This is rather unusual because most systems require a terminal oxo to be active. For the second question, we performed an intrinsic bond orbital (IBO) analysis, showing how the valence alpha and beta electrons rearrange over the system involving not only the reactive oxyl and C–H bond but also one of the aromatic rings of the substrate (Figure 2). This 'electron flow' is consistent with a coupled proton–electron transfer (CPET) mechanism, in agreement with thermodynamic and kinetic experiments.

Escaping the rebound

In general, the C–H activation of alkanes by metal–oxo species yields a carbon radical intermediate and a metal–hydroxo complex in which the OH ligand immediately rebounds to the radical, yielding the C–OH product. The study of this step had been controversial because the generation of radical intermediates should, in principle, generate subproducts that are rarely observed.

To study this reaction, we turned our attention again to the ruthenium-doped cubane [4]. We observed that, when this complex is used in high concentration, the main product is not the C–OH alcohol but a C–O–Ru species, confirming the formation of a C radical. The calculations showed that the system can follow the expected mechanism involving the rebound step, although the latter has an energy barrier significantly higher than that of the coupling between the C and RuO radicals, which is essentially barrierless [6]. Calculations were also combined with experiments to optimize structure-activity

DFT calculations on cobalt cubanes revealed new strategies for trapping reactive intermediates in the catalytic oxidation of water and alkanes.

relationships between the kinetics of the reaction and natural charges and spin densities. This work was featured in the Spotlights of the *Journal of the American Chemical Society*.

In summary, our work showed how to combine computational and experimental techniques to achieve a deeper understanding of cobalt cubanes in oxidation reactions, including dopant and dangling metals. The insight provided by these studies contributed to the development of synthetic systems mimicking the structure and function of the OEC. This project remains active at the Hylleraas Centre, with the perspective of studying dimeric systems with two cubane units and the exploration of complex reaction networks with automated methods.

A significant part of this work was performed by Bastian Skjelstad, who received his MSc degree at the Hylleraas

Centre in 2020. He is now a PhD candidate at the Institute of Chemical Reaction Design and Drug Discovery (ICReDD) at Hokkaido University in Japan, under the supervision of Prof. Satoshi Maeda.

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Reaction Energies Free from Basis-Set Errors
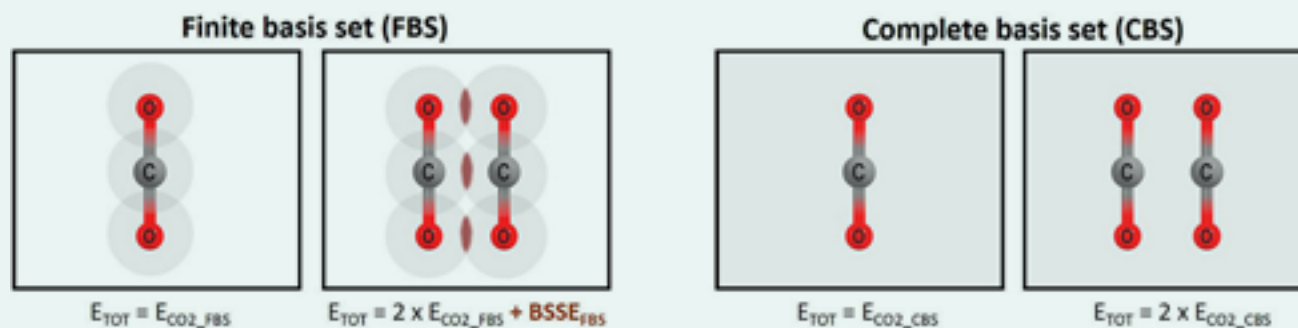
Luca Frediani

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Using multiwavelets, we have, for the first time, calculated reaction energies of nontrivial systems free from basis-set errors and used our results to benchmark standard calculations. In the future, such calculations can become routine, removing a major source of error in quantum-chemical calculations.

—

In standard quantum chemistry, molecular orbitals are expanded in a finite (and therefore incomplete) set of atomic orbitals, thereby introducing an error in the calculations. Such errors can be reduced by increasing the basis sets, but this procedure carries a high cost and does not provide a systematic error control. Employing multiwavelets rather than atomic orbitals, errors can be controlled directly, by means of a simple threshold parameter. Using our multiwavelet code, we have, for the first time, calculated reaction energies of nontrivial systems free from basis-set errors and used our results to benchmark standard calculations. In the future, such calculations can become routine, thereby reducing a major source of error and uncertainties in quantum-chemical calculations.

A chemical reaction is a process where one or more substances combine or split to form other substances. It can be as simple as the formation of a water molecule from hydrogen and oxygen or as complicated as the synthesis of a protein inside your body. The driving force of a reaction is the *reaction energy*: the reaction will proceed spontaneously from reactants to products only if the energy of the products is lower than the energy of the reactants. The process can be viewed as a ball in a hilly landscape: the ball will freely move from a hilltop to a valley, but the opposite process (from the valley to the top) will require that we push the ball. Likewise for a reaction — if the products have lower energy than the reactants, then the reaction will proceed spontaneously, and energy will be released. In the opposite case, we will have to 'push' the reactions by providing the required energy. Knowledge about the reaction energy allows us to predict which reactions happen spontaneously and how

Finite basis set (FBS)

$E_{TOT} = E_{CO2\_FBS}$

$E_{TOT} = 2 \times E_{CO2\_FBS} + \mathbf{BSSE_{FBS}}$

Complete basis set (CBS)

$E_{TOT} = E_{CO2\_CBS}$

$E_{TOT} = 2 \times E_{CO2\_CBS}$

Figure 1: Superposition of basis functions in a CO_2 dimer. Left: in overlapping regions, more basis functions are available and so the description is improved beyond what is expected for each atom. Right: in a complete basis, no such improvement can take place and the basis-set superposition error is therefore zero [1].
Reprinted from Ref. [1], with the permission of AIP Publishing.

to influence the outcome of a reaction to obtain the desired product.

Determining a reaction energy is therefore of paramount importance. At the same time, it is a challenging task. The energy of two molecules is dominated by the energy of the individual atoms, with small contributions that depend on how the atoms are arranged relative to each other in space. When a reaction takes place, it is only this tiny part of the energy that changes. In other words, the reaction energy is a small variation of a tiny part of the total energy. Computing these variations precisely can therefore be challenging. However, although it sounds strange at first, we can obtain quite precise reaction energies even though the total energies themselves have not been computed precisely.

Let us consider the simple example of the formation of a water molecule:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$E = E(H_2O) - E(H_2) - \tfrac{1}{2} E(O_2).$$
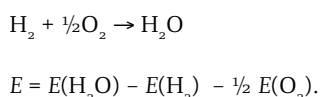
All those energies can be computed, but the computations rely on models that carry an error.

As most of the energy is concentrated in the individual atoms, most of the error is also carried on unchanged from oxygen and hydrogen to the final water molecule. Ideally, if the error is the same for the reactants and the products, then we will obtain a perfect reaction energy. This concept is called *error cancellation* and is the reason why quite precise reaction energies can be computed from rather imprecise total energies. This cancellation is, however,

not perfect and the final reaction energy therefore still carries some error.

Where does the error come from?
This is an important question, which quantum chemists have investigated extensively.

One source of error is the electronic-structure model used. This model cannot be perfect because it would require an infinite amount of computation. The model that is most widely used is called density-functional theory (DFT), where the energy is calculated from the density of the electrons using an exchange–correlation density functional. Many such functionals exist – some of them are quite accurate, but none is perfect. We call the error arising from the functional the *density-functional error*.
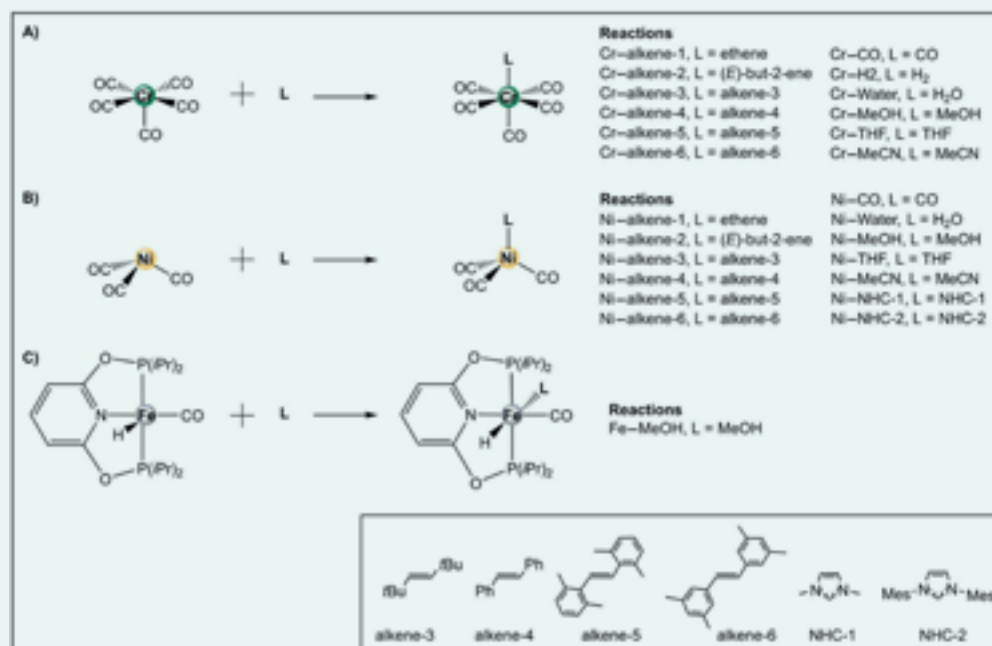
Figure 2: Overview of all 26 transition-metal-ligand association reactions studied.
Reprinted from Ref. [1], with the permission of AIP Publishing.

"Using multiwavelets, we can in fact guarantee that the basis-set error in DFT is below a predefined threshold, giving us complete control over the error."

Another kind of error arises from the description of electrons in terms of molecular orbitals. Each orbital is represented by functions belonging to a *basis set*. Traditionally, the molecular orbitals are expanded linearly in atomic orbitals fixed on the nuclei. To achieve a perfect description, the basis set must be infinitely large, but in practice we must truncate it and use a finite basis set. We call this the *basis-set truncation error*.

Consider now what happens when a reaction takes place. Take, for instance, an oxygen atom. In the reactants, it is bound to another oxygen atom, whereas in the product it is bound to two hydrogen atoms. Its basis set (and those of all other atoms) will therefore see different surroundings. This difference generates the basis-set superposition error — see Figure 1.

How can we avoid errors?
The errors discussed above cannot be eliminated, only reduced. To reduce the functional error, quantum chemists are developing better and better functionals. To reduce the basis-set truncation and superposition errors, we can use larger and more accurate basis sets. Since larger basis sets require more computation time, this strategy has a limitation. To reduce the basis-set superposition error, a *counterpoise correction* may be applied, but this method has its limitations.
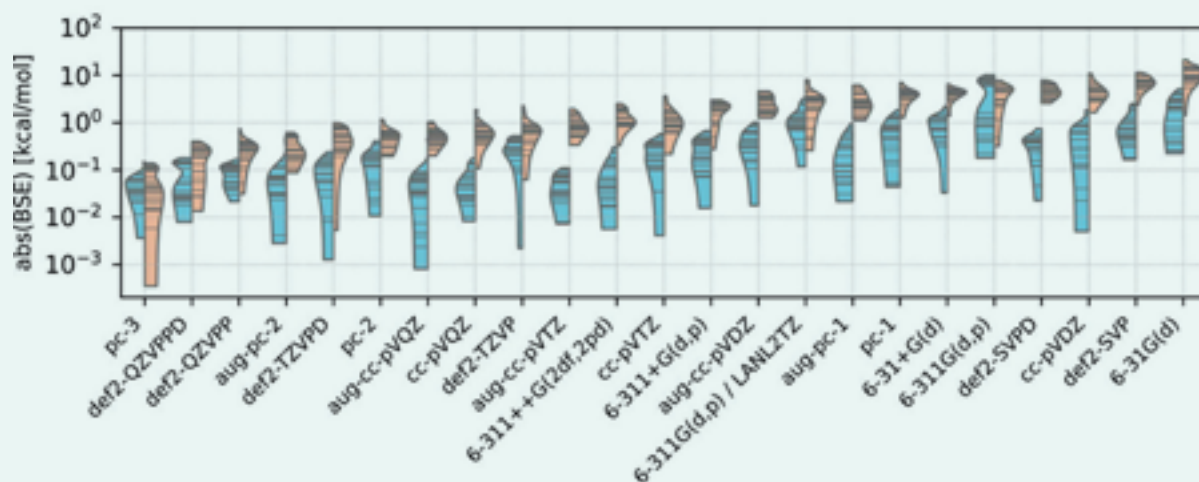
Figure 3: Overview of basis-set errors in reaction energies for 26 transition metal-ligand association reactions, computed with 23 different basis sets [1]. The blue distributions represent counterpoise-corrected errors, while the pink distributions represent uncorrected errors. *Reprinted from Ref. [1], with the permission of AIP Publishing.*

How large are the errors?

Quantifying the errors is difficult. Better density functionals and larger basis sets give better results but how much better? Until recently, it was difficult to answer this question. A significant step towards reducing and quantifying basis-set truncation and superposition errors was recently taken at the Hylleraas Centre, based on the use of *multiwavelets* rather than atomic orbitals. Multiwavelets do not suffer from basis-set superposition error and can quantify the truncation error rigorously. Using multiwavelets, we can in fact *guarantee* that the basis-set error in DFT is below a predefined threshold, giving us complete control over the error.

Basis-set errors quantified

Using multiwavelets, we have computed the reaction energies for 26 reactions [1]; see Figure 2. This gave us very precise reference energies for each reaction, enabling us to quantify precisely the basis-set truncation and superposition errors for 23 standard basis sets.

In Figure 3, we summarize the basis-set errors computed for all 26 reactions and 23 basis sets. Spanning five orders of magnitudes, the errors computed show that the choice of basis set affects the result significantly. Each distribution is split into two halves: the blue half has been corrected for basis-set superposition errors by applying the counterpoise correction, while no such correction has been applied on the red half.

The largest errors are about 10 kcal/mol or more, demonstrating that large basis sets are needed to compute reaction energies reliably. The errors in the counterpoise-corrected reaction energies are generally much smaller than their uncorrected counterparts, showing that much of the total error is a superposition error. The counterpoise correction works better for small to medium-sized bass sets and are less useful for larger (and more accurate) basis sets.

Summary

Thanks to the development of multiwavelet methods at the Hylleraas Centre, it is now possible to give a precise answer to an important question concerning the calculation of reaction energies using DFT: how large are the basis-set errors? We have answered this question precisely for a set of 26 reactions, but the method is applicable to any chemical reaction calculated. In the future, it will be possible to calculate, on a routine basis, DFT reaction energies that are free from basis-set error, although the density-functional error remains.

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Almlöf–Gropen Lecture Series

—

The Almlöf–Gropen Lecture Series was established by the Centre for Theoretical and Computational Chemistry in 2008 to honour the memory of two pioneers of quantum chemistry in Norway: Prof. Jan Almlöf (1945–1996) at the University of Oslo and Prof. Odd Gropen (1941–2005) at the University of Tromsø (now UiT The Arctic University of Norway). Each year, a prominent theoretical chemist is invited to deliver the Almlöf–Gropen lecture at the Hylleraas Centre in Oslo and Tromsø, targeting a broad audience. Since 2020, the Almlöf–Gropen lecturer has been preceded by two Almlöf–Gropen Young Speakers, selected among the young members of the Hylleraas Centre.

Previous Almlöf–Gropen lecturers

2008 **Prof. Bjørn Roos**
University of Lund, Sweden:

Multiconfigurational quantum chemical methods and heavy element chemistry

2009 **Prof. Tom Ziegler**
University of Calgary, Canada:

Analyzing complex electronic structure calculations on large molecules in simple chemical terms

2010 **Prof. Michele Parrinello**
ETH Zürich, Switzerland:

Through mountains and valleys with metadynamics

2011 **Prof. Pekka Pyykkö**
University of Helsinki, Finland:

Relativity and chemistry: some recent results

2012 **Prof. Harry B. Gray**
California Institute of Technology, USA:

The 21st century solar army

2013 **Prof. Henry F. Schaefer**
University of Georgia, Athens, USA:

From donor-acceptor complexes to Gallium Nitride nanorods

2014 **Prof. Leo Radom**
University of Sydney, Australia:

Adventures in free radical chemistry: a computational approach

2015 **Prof. Arieh Warshel**
University of Southern California, USA:

How to model the action of complex biological systems on a molecular level

2016 **Prof. Emily Carter**
Princeton University, USA:

Quantum solutions for a sustainable energy future

2017 **Prof. Jack Simons**
University of Utah, USA:

The wonderful world of molecular anions

2018 **Prof. Walter Thiel**
Max–Planck-Institut für Kohlenforschung, Mühlheim, Germany:

Chemistry with the computer

2019 **Prof. Sharon Hammes-Schiffer**
Yale University, Connecticut, USA:

Proton-Coupled Electron Transfer in Catalysis and Energy Conversion

Almlöf–Gropen Lecturer 2020

Photo: Phillip Lichtenegger / University of Vienna.

↑ Screenshot from the online discussion of Almlöf–Gropen Lecturer Leticia González with members of the Hylleraas Centre on June 1 2021. *Screenshot: Trygve Helgaker.*

Professor Leticia González

Institute of Theoretical Chemistry, University of Vienna, Austria

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Light and Shadows on the Quantum Simulation of Molecular Electronic Excited States

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June 1, 2021, online

Prof. Leticia González obtained her PhD in chemistry from the Autonomous University of Madrid in 1998 and her Habilitation and venia legendi from the Free University Berlin in 2004. She was appointed professor at the Friedrich Schiller University Jena in 2007 and at the University of Vienna in 2011, where she now leads the Institute of Theoretical Chemistry. González received a Heisenberg Fellowship in 2007 and the Dirac Medal in 2011, delivered the Löwdin lecture in 2014, and was awarded an honorary doctorate by the University of Lorraine in 2018. She has authored more than 250 publications and has given more than 180 invited lectures all over the world.

In her Almlöf–Gropen lecture, González asked the question: how do molecules react to light? Light is the driving force behind many reactions in chemistry, biology, and medicine, but understanding how molecules and their properties change upon irradiation is not an easy task. Quantum theory provides the fundamental equations needed to calculate electronically excited states and simulate their time evolution, but application of these equations is difficult.

In her talk, González reviewed recent progress in her research group and discussed the strategies developed to disentangle light-induced processes in systems of varying complexity – in the gas phase, in solution, and embedded in a biological environment.

After the talk, González had lively online discussions with young researchers at the Hylleraas Centre, about her own research and that of the young researchers.

Almlöf–Gropen Young Speakers 2020

Abril Castro

Hylleraas Centre,
University of Oslo

–

Relativity and Dynamics in Computational NMR Spectroscopy

Abril Castro obtained her bachelor's (2010) and master's (2012) degrees in chemistry at the University of Guanajuato in Mexico. After completing her PhD at the University of Girona in Spain in 2017, she returned to Mexico for a postdoctoral position at the University of Guanajuato. In 2019, she joined the Hylleraas Centre as a postdoctoral researcher on a Marie Skłodowska-Curie Individual Fellowship from the European Union. In 2021, Abril Castro received a Young Research Talents Grant for *Accurate Prediction and Interpretation of NMR Spectra in Transition-Metal Complexes* from the Research Council of Norway.

Ryan Wilkins

Hylleraas Centre,
UiT The Arctic University of Norway

–

Evolutionary Principles of Biocatalysis in Extreme Environments

Ryan Wilkins is a PhD candidate at UiT The Arctic University of Norway. He finished his bachelor's degree in physics at Memorial University of Newfoundland, Canada in 2017 and his master's degree in biophysics at the University of Guelph, Canada in 2019. His background is in the development and implementation of statistical-mechanics methodologies in biophysical simulations. For his PhD thesis, he applies such methods to understand the mechanisms by which homologous enzymes can adapt to a wide range of environments.

Almlöf–Gropen Lecturer 2021

Professor
Alán Aspuru-Guzik

University of Toronto,
Canada
–

There is No Time for Science as Usual: Materials Acceleration Platforms

September 10, 2021,
online

Alán Aspuru-Guzik is a professor of Chemistry and Computer Science at the University of Toronto and holds a Canada 150 Research Chair in Theoretical Chemistry and a Google Industrial Research Chair in Quantum Computing. He received his BSc from the National Autonomous University of Mexico in 1999 and his PhD from the University of California, Berkeley, in 2004. Aspuru-Guzik began his independent career at Harvard University in 2006, where he was full professor 2013–2018. He has received the Google Focused Award for Quantum Computing, the Sloan Research Fellowship, and the Camille and Henry Dreyfus Teacher-Scholar Award.

Aspuru-Guzik conducts research at the interface of quantum information theory, machine learning, and chemistry. He is a pioneer in the development of algorithms and experimental implementations of quantum computers and quantum simulators for chemical systems. He has examined the role of quantum coherence in the transfer of excitonic energy in photosynthetic complexes and studied theoretically organic semiconductors, organic batteries, and organic light-emitting diodes.

Currently, Aspuru-Guzik is interested in automation and 'autonomous' chemical laboratories for accelerating scientific discovery, which was the topic of his Almlöf–Gropen lecture. In the lecture, he considered the need to rethink the way science is carried out with emphasis on automation. He discussed progress in developing materials acceleration platforms, or self-driving labs, for this purpose. After his talk, Aspuru-Guzik met young researchers at the Hylleraas Centre for lively online discussions.

Almlöf–Gropen Young Speakers 2021

Tanner Culpitt

Hylleraas Centre,
University of Oslo

–

Electronic Structure and Molecular Dynamics in Magnetic Fields

Tanner Culpitt graduated in 2014 from the University of Wisconsin-La Crosse in USA, with a bachelor's degree in chemistry, 2nd and 3rd majors in physics and applied mathematics. After graduating from the University of Illinois at Urbana-Champaign in 2019 with a PhD in chemistry, he joined the Hylleraas Centre in Oslo as a postdoctoral researcher in 2020, where he works on molecular dynamics in strong magnetic fields.

Gabriel Gerez

Hylleraas Centre,
UiT The Arctic University of Norway

–

Multiwavelets, MRChem, and Solvent

Gabriel Gerez obtained his master's degree in 2019 from UiT The Arctic University of Norway, on a cavity-free real-space formulation of the polarizable continuum model (PCM), which he implemented in the MRChem multiwavelet code. He began his PhD study in 2020, continuing work on the PCM. His project has now moved to excitation energies, which will be extended to solvated systems through the PCM framework.

Meetings and Events

⊕ Banner of the CAS project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation.*
Design: Camilla Kottum Elmar / CAS.

Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation

Simen Kvaal and
Thomas Bondo Pedersen
—
Centre for Advanced Study, Oslo
2021–2022

Beginning in August 2021, several prominent quantum chemists have been working at the Centre for Advanced Study at the Norwegian Academy of Science and Letters, on the project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation* (ATTODYN), led by Simen Kvaal and Thomas Bondo Pedersen.
—

The Centre for Advanced Study (CAS) at the Norwegian Academy of Science and Letters is an independent foundation that furthers fundamental, curiosity-driven research in the fields of humanities, social sciences, and natural sciences, funded by the Norwegian Ministry of Education and Research. Every year, three groups work at CAS, having been selected in an application process two years earlier. The project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation* is led by Thomas Bondo Pedersen and Simen Kvaal during the academic year 2021–2022.

In addition to the group leaders, the ATTODYN team consists of 11 fellows, including chemists, physicists, and mathematicians from three continents:

- **Prof. Caroline Lasser**, Department of Mathematics, Technical University of Munich, Germany
- **Prof. Ludwik Adamowicz**, Department of Chemistry and Biochemistry, University of Arizona, USA
- **Prof. Sonia Coriani**, Department of Chemistry, Technical University of Denmark, Denmark
- **Assoc. Prof. Takeshi Sato**, Department of Nuclear Engineering and Management, University of Tokyo, Japan
- **Prof. Reinhold Schneider**, Department of Mathematics, Technical University of Berlin, Germany

⊛
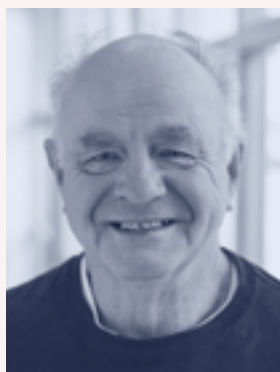
Prof. Ludwik Adamowicz
University of Arizona,
USA

Prof. Caroline Lasser
Technical University of Munich,
Germany

Prof. Sonia Coriani
Technical University
of Denmark

Assoc. Prof. Takeshi Sato
University of Tokyo,
Japan

↑ ATTODYN fellows who visited CAS during fall 2021.
Photos: Camilla Kottum Elmar /CAS.

- **Group Leader Heiko Appel**,
  Center for Free-Electron Laser
  Science, Max Planck Institute
  for the Structure and Dynamics
  of Matter, Hamburg, Germany

- **Assist. Prof. Alicia Palacios**,
  Department of Chemistry, Autono-
  mous University of Madrid, Spain

- **CNRS Researcher Morgane Vacher**,
  Research Institute in Molecular
  Chemistry, University of Nantes,
  France

- **Prof. Trygve Helgaker**,
  Hylleraas Centre, Department
  of Chemistry, University of Oslo,
  Norway

- **Researcher Erik Tellgren**,
  Hylleraas Centre, Department
  of Chemistry, University of Oslo,
  Norway

- **Researcher André Laestadius**,
  Hylleraas Centre, Department
  of Chemistry, University of Oslo,
  Norway

Due to travel restrictions imposed by the COVID-19 pandemic, weekly seminars and status meetings have been organized digitally as video meetings. Lasser and Adamowicz will spend the entire academic year at CAS in Oslo, while Coriani, Sato, Palacios, and Vacher visited during fall 2021. Physical presence is expected to increase during spring 2022 as travel restrictions are loosened.

Several young researchers from the Hylleraas Centre have contributed to the ATTODYN project in 2021: PhD candidates Håkon Kristiansen, Einar Aurbakken, Benedicte Ofstad, and postdoc Mihály Csirik. In addition, Øyvind Schøyen and Jonas Flaten, who are PhD candidates at the Department of Physics but co-supervised by Pedersen at the Hylleraas Centre, contributed to the project.

In the past decade, a rapid development of novel experimental techniques producing laser pulses with a duration on the time scale of the electron — the attosecond (10^{-18} s) time scale — has opened new, exciting opportunities in chemistry. Attosecond laser pulses allow us to create and monitor electronic wave packets within molecules in a controlled fashion. These electronic wave packets radically change the forces driving the motion of the nuclei. Hence, by controlling the wave packets by means of laser-pulse parameters, we may control the motion of the nuclei. In plain words: we can potentially make molecules do what we want them to do by means of attosecond laser pulses, including detailed control of chemical reactions.

The advanced experiments carried out with attosecond laser pulses are, of course, subject to interpretation by means of theoretical models. Therefore, it is of fundamental importance to develop computational models that do not inadvertently lead to misinterpretation or even miss important phenomena. The main objective of the ATTODYN project is to investigate coupled electronic–nuclear dynamics induced by attosecond and few-femtosecond laser pulses. The starting point is the molecular time-dependent Schrödinger equation for both nuclear and electronic

⤴ Deriving equations at the whiteboard at the CAS premises.
Photo: Thomas Bondo Pedersen.
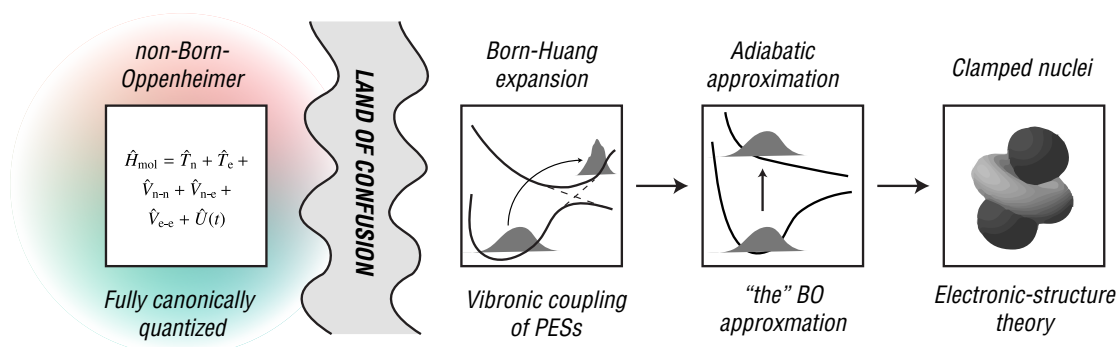
⤴ Non-Born–Oppenheimer theory vs. various
levels of Born–Oppenheimer-based theory.
Illustration: Simen Kvaal.

degrees of freedom, which we seek to solve numerically without assuming the Born–Oppenheimer approximation.

Imposing the concept of molecular structure on the quantum theory of matter, the Born–Oppenheimer approximation is omnipresent in theoretical chemistry and solid-state physics. Developing computational models without it, we face fundamental conceptual difficulties. Our initial efforts aim at a simplified computational non-Born–Oppenheimer model that can correctly predict laser-induced molecular alignment, including the post-pulse periodic revival structure arising from quantum interference, which is a key phenomenon routinely exploited in attosecond experiments.

The short duration of attosecond laser pulses implies a broad energy distribution which, almost invariably, leads to nonvanishing one- and many-electron ionization probabilities and, in turn, a nonzero probability of molecular dissociation and fragmentation. Consequently, another research line pursued in the ATTODYN project is the mathematical representation of ionization and dissociation continua using computationally efficient, fully flexible complex Gaussians as basis functions. The key challenge is the development of numerically stable integrators with the required adaptivity in both space and time.

Participants of the 2021 Young CAS Workshop (left to right); André Laestadius, Tanner Culpitt, Michael Herbst (Aachen University), Erik Tellgren, Markus Penz (University of Innsbruck), and Mihály Csirik.

Young CAS Workshop:
Global Optimization in Electronic Energy Landscapes:

Finding a Needle in a Haystack

Hylleraas Centre, Oslo
September 13–17, 2021
—

Young CAS Fellow and Hylleraas member Dr. Erik Tellgren organized September 13–17 2021 the first workshop in his Young CAS project *Global Optimization in Electronic Energy Landscapes: Finding a Needle in a Haystack.*

—

In computer simulations of electrons in a molecule or in a material, it is common to adopt a simplified mean-field picture wherein some of the detailed pairwise interactions are replaced by averaged interactions. This approach makes calculations much easier, but an overlooked aspect is that the model also becomes more nonlinear and the true ground state (the global energy minimum) may be 'hidden' in a landscape with extremely many false candidates (local minima, saddle points, and local maxima).

During the workshop, eight young researchers met at the Hylleraas Centre for presentations and discussions related to different aspects of this problem, ranging from pure mathematical considerations to practical numerical experiments. The mathematical justification for the Aufbau principle, which serves as a bridge between the mean-field picture and the full picture and is believed to characterize local minima, sparked several discussions and ideas.

↑ Group photo from the Annual Meeting at Hamn September 20–22, 2021.

↑ Overview over Hamn and Bergs-fjorden, with Skaland in the far distance. *Photo: Trygve Helgaker.*

Hylleraas Annual Meeting 2021

Hamn, Senja
September 20–22, 2021
—

→ Dr. Tilmann Bodenstein presenting the Hylleraas Software Platform at the Hamn meeting. *Photo: Trygve Helgaker.*

For our second Annual Meeting during the COVID-19 pandemic, the Hylleraas Centre convened for two days at Hamn in Senja, with a record attendance of 53 centre members.
—

The 2021 Annual Meeting of the Hylleraas Centre was held September 20–22 at Hamn in Senja. With 53 members in attendance, it was the largest annual meeting to date. Activities at the meeting were a mixture of discussions of matters related to the centre (including the upcoming Hylleraas School and the Hylleraas Software Platform) and presentations on transferable skills (including data handling, sharing practices, and web-app development). Master students and PhD candidates participated in a Five-Minute Thesis Competition, which was won by Jhonnatan Carvalho.

Since the Hylleraas Centre consists of two nodes separated by more than 1100 km, an important element of the annual meetings is the opportunity to socialize. At the Hamn meeting, the attendees were invited to participate in a hike to Sukkertoppen, overlooking Hamn. A pub quiz was also held, covering topics from chemistry and other sciences. The weather was excellent, with opportunities for viewing the Northen Lights at full moon.

The annual meetings are organized by young researchers at the Hylleraas Centre, supported by a senior member. The Hamn meeting was chaired by Bente Barge and Ryan Wilkins at UiT, supported by Bjørn Olav Brandsdal and Stig Eide.

↑ Thomas Bondo Pedersen getting ready for the introductory lecture at the Hylleraas School. *Photo: Trygve Helgaker.*

Hylleraas School 2021

Hotel Hadeland, Gran
October 17–22, 2021
—

In October 2021, all members of the Hylleraas Centre convened for six days of quantum-molecular sciences, consisting of lectures and exercises, with one day devoted to each research theme of the centre. The school was held at Hotel Hadeland in Gran, located about 60 km from Oslo and 50 km from Gardermoen Airport.

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The main purpose of the six-day school was to teach all PhD candidates, post-docs, researchers, and PIs at the centre the core scientific concepts of our six research themes (RTs), thereby promoting new inter-RT collaborations and reinforcing those already in place. The schedule included lectures in the morning and tutorials with hands-on exercises in the afternoon. The tutorial groups were set by mixing gender and career stages, as well as Oslo and Tromsø affiliations to promote inter-node collaborations.

The topics covered in the school included: DFT and multiwavelets, with tutorials on the MRChem and VAMPyR programs (RT1); statistical mechanics, molecular dynamics, and multiscale modelling, including coarse graining (RT2); molecular properties, response theory, and relativistic effects in the solid state, with Dalton and ReSpect tutorials (RT3); strong magnetic fields, including molecular dynamics, with tutorials using the LONDON program (RT4); organometallic chemistry, including orbital theory and reaction mechanisms for transition-metal complexes, with pen-and-paper exercises (RT5); and free-energy simulations and conformational sampling, with tutorials on data analysis and visualization using the Q, PyMOL, and VMD programs (RT6).

The school's program also contained social activities, including a hike to Sølvsberget hilltop and a quiz with pictures from the childhood of the PIs.

↑ View towards the east from Hotel Hadeland, with Jaren lake to the left and Gran village to the right. *Photo: Trygve Helgaker.*

At the end of the Hylleraas School, all participants were asked to fill an evaluation form, which provided the organizers with valuable feedback, including new ideas for the organization of the next school in the winter of 2022/23. In general, participants were highly satisfied with the first school.

The Hylleraas School was organized by Karolina Solheimslid Eikås, Audun Skau Hansen, David Balcells, and Simen Reine.

→ David Balcells teaching RT5 contents at the Hylleraas School. *Photo: Trygve Helgaker.*

Sunset in Oslo at 2:25 am on November 29, as seen from the Hylleraas Centre during a break at the 2021 NKS online meeting. *Photo: Trygve Helgaker.*

- Tromsø
- Trondheim
- Bergen
- Oslo
- Kjeller
- Copenhagen
- Hamburg, Germany
- Erlangen (Germany), formerly Stavanger

41.3%

7.5%

27.5%

18.8%
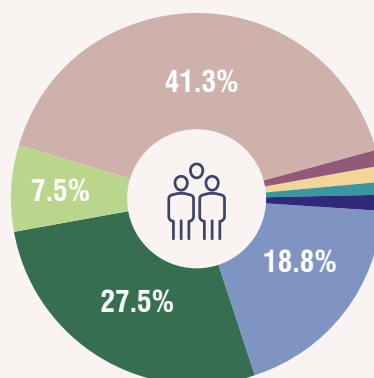
Geographical distribution of the 80 online meeting attendees. *Illustration: Erik Tellgren.*

2021 National Meeting of the NKS Division of Quantum Chemistry and Modelling

Online from the University of Oslo
November 29–30, 2021
—

The 2021 National Meeting of the Division of Quantum Chemistry and Modelling of the Norwegian Chemical Society (NKS) was held online November 29–30, chaired by Erik Tellgren at the Hylleraas Centre in Oslo.

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The NKS meeting of the Division of Quantum Chemistry and Modelling is organized annually by the theory group at one of the four universities in Norway where theoretical chemistry is present: Norwegian University of Science and Technology, University of Bergen, University of Oslo, and UiT The Arctic University of Norway. In 2021, the meeting was chaired by Erik Tellgren at the Hylleraas Centre in Oslo.

Because of uncertainties related to the COVID-19 pandemic, the 2021 NKS meeting was held online. A total of 16 scientific talks were given by mostly young researchers representing the major academic computational-chemistry research institutions in Norway. The topics spanned a good range, from calculations of the effects of quantum electrodynamics on molecular electronic structure to simulations of bacterial membranes.

Two longer plenary lectures were given to introduce the new professor II members of the Hylleraas Centre: Prof. Thereza Soares (University of São Paulo, Brazil) and Dr. Stella Stopkowicz (University of Mainz, Germany). Additionally, the annual Members' Assembly of the Division took place at the NKS meeting.

Despite the limitations of the online format, the meeting was successful in giving everyone an update on theoretical-chemistry research in Norway. A total of 80 participants attended the meeting, including three from locations outside of Norway.

→ Ass. Prof. Sangita Sen,
IISER Kolkata, India.
Photo: Sangita Sen.

Alumni Talk: Ass. Prof. Sangita Sen

Indian Institute
of Science Education
and Research Kolkata,
India
—
Online seminar
December 17, 2021

To inspire and help the young researchers at the Hylleraas Centre in planning their future career, the Young Researcher Parliament (YRP) of the centre invites previous members and collaborators to give a short seminar about their career choices and the position they hold today, whether in academia or in industry. In 2021, the YRP organized an alumni talk by Ass. Prof. Sangita Sen from the Indian Institute of Science Education and Research Kolkata (IISERK), on December 17.

Sangita Sen received her PhD in chemistry from the Indian Association for the Cultivation of Science (IACS) in Kolkata in 2015, under the supervision of Prof. Debashis Mukherjee. She then travelled to Oslo, where she worked with Dr. Erik Tellgren, first at the Centre for Theoretical and Computational Chemistry (CTCC) and then at the Hylleraas Centre, financed by a Marie Skłodowska-Curie Individual Fellowship.

PhD Defences

Candidate
Karen O. H. M. Dundas
—

University:	UiT The Arctic University of Norway
Date:	February 23, 2021
Thesis:	*Vibrational Spectroscopy Beyond the Harmonic Approximation*
Trial Lecture:	*Intermolecular Interactions: Computational Modeling and Benchmarking*
Supervisors:	Prof. Kenneth Ruud, UiT The Arctic University of Norway
	Dr. Maarten T. P. Beerepoot, UiT The Arctic University of Norway
	Dr. Magnus Ringholm, UiT The Arctic University of Norway
	Prof. J. Magnus H. Olsen, Technical University of Denmark
Committee:	Dr. Filippo Lipparini, University of Pisa, Italy
	Prof. Sandra Luber, University of Zürich, Switzerland
	Prof. Luca Frediani, UiT The Arctic University of Norway
Chair:	Prof. Camilla Brekke, UiT The Arctic University of Norway
Format:	hybrid

Candidate
Audun Skau Hansen
—

University:	University of Oslo
Date:	April 8, 2021
Thesis:	*Local Correlation Methods for Infinite Systems*
Trial Lecture:	*Machine Learning in Electronic-Structure Theory*
Supervisors:	Prof. Thomas Bondo Pedersen, University of Oslo
	Dr. Simen Kvaal, University of Oslo
	Prof. Trygve Helgaker, University of Oslo
Committee:	Dr. Denis Usvyat, Humboldt–Universität zu Berlin, Germany
	Assoc. Prof. Ida-Marie Høyvik,
	Norwegian University of Science and Technology, Trondheim
	Prof. Stian Svelle, University of Oslo
Chair:	Steven Ray Wilson, University of Oslo
Format:	online

Candidate
Lluís Artús Suàrez
—

University:	University of Oslo
Date:	May 19, 2021
Thesis:	*Computational Study of the Deaminative Hydrogenation of Amides Catalyzed by Base Metal Complexes*
Trial Lecture:	*Machine Learning in Computational Chemistry*
Supervisors:	Dr. Ainara Nova, University of Oslo
	Prof. Mats Tilset, University of Oslo
	Dr. David Balcells, University of Oslo
Committee:	Prof. Stuart Alan MacGregor, Heriot–Watt University, Edinburgh, UK
	Dr. Maria Besora, Universitat Rovira i Virgili, Tarragona, Spain
	Dr. Erik Tellgren, University of Oslo, Norway
Chair:	Prof. Harald Walderaug, University of Oslo
Format:	hybrid

Candidate
Joakim Samuel Jestilä
—

University: University of Oslo
Date: September 16, 2021
Thesis: *Reductive Gas-Phase Ion Chemistry of Simple Oxocarbons*
                     in the Presence of Alkali and Alakaline Earth Metals
Trial Lecture: *The Role of CO_2 in Space as a Building Block for Complex Organic Molecules (COMs)*
Supervisors: Prof. Einar Uggerud, University of Oslo
                     Prof. Trygve Helgaker, University of Oslo
Committee: Prof. Peter R. Schreiner, Justus-Liebig-Universität Giessen, Germany
                     Ass. Prof. Héloïse Dossmann, Sorbonne Université, Paris, France
                     Prof. Armin Wisthaler, University of Oslo
Chair: Prof. Harald Walderhaug, University of Oslo
Format: physical

Candidate
Julie Héron
—

University: University of Oslo
Date: November 18, 2021
Thesis: *C–H Activation and CuAAC Reactions with 1,8-Naphthyridine*
                     Based Dicopper Complexes from a Computational Perspective
Trial Lecture: *Methods for Modeling First Row Transition Metal Complexes*
Supervisors: Dr. David Balcells, University of Oslo
                     Dr. Ainara Nova, University of Oslo
                     Prof. Mats Tilset, University of Oslo
Committee: Assoc. Prof. Xavier Solans-Monfort, Autonomous University of Barcelona, Spain
                     Dr. Amalia Poblador Bahamonde, University of Geneva, Switzerland
                     Assoc. Prof. Jonathan Smith, Temple University, USA, and University of Oslo
                     Ass. Prof. Mohamed Amedjkouh, University of Oslo
Chair: Prof. Harald Walderhaug, University of Oslo
Format: physical

PhD defence of Karen O. H. M. Dundas at UiT on February 23, 2021. From left to right: Prof. Camilla Brekke, Prof. Luca Frediani, and Dr. Karen O. H. M. Dundas.

Dr. Lluís Artús Suàrez with Hylleraas Director Trygve Helgaker after the defence on May 19 2021.

Trial lecture of Julie Héron on November 18, 2021. From left to right first row: Amalia Poblador Bahamonde, Xavier Solans-Monfort, and Jonathan Smith. From left to right second row: Mats Tilset, Ainara Nova, David Balcells, and Julie Héron (standing). *Photo: Trygve Helgaker.*
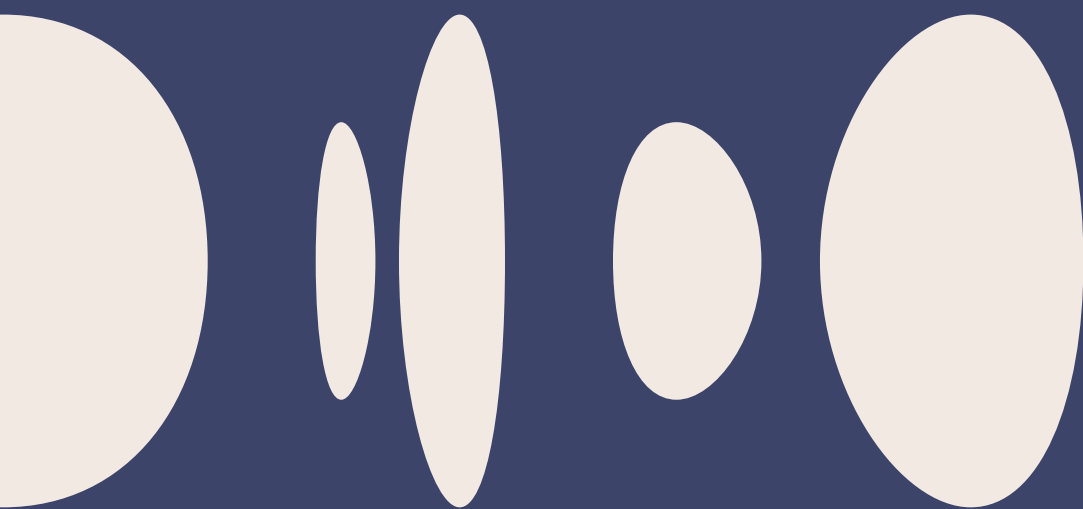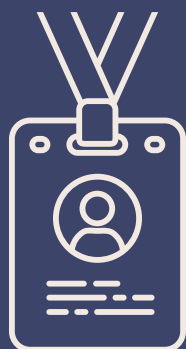
Visits
and Mobility

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Interview with visiting researcher:

Ludwik Adamowicz

Dr. Ludwik Adamowicz is a professor at the Department of Chemistry and Biochemistry and the Department of Physics, University of Arizona in Tucson, Arizona, USA.

Ludwik Adamowicz received his PhD in 1977 from the Institute of Physical Chemistry of the Polish Academy of Sciences, under the supervision of Andrzej Sadlej. In 1980, he moved to the US, where he worked with E. A. McCullough at Utah State University (1980–1983) and Rodney J. Bartlett at the University of Florida (1983–1987). Ludwik Adamowicz joined the Chemistry Faculty at the University of Arizona in 1987. He was promoted to Associate Professor in 1993 and Full Professor in 1998. Since 2003, he has also been a Professor of Physics at the University of Arizona. He has been visiting professor at University of Lund, Université Paul Sabatier in Toulouse, Nagoya University, and University of Pisa.

—

During his career, Ludwik Adamowicz has worked on projects involving the development of new quantum-mechanical methods for very accurate calculations of spectra and other prop-

erties of atoms and molecules and for modeling energy and charge transport in molecular systems — in addition, he has worked on application projects related to spectroscopy of biomolecules, carbon clusters, and molecular anions.

Adamowicz visited the Centre for Theoretical and Computational Chemistry (CTCC) and the Hylleraas Centre for several weeks every summer 2010–2019, working with Erik Tellgren and Trygve Helgaker on molecules in strong magnetic fields. Since September 2021, he has been a fellow of the Centre for Advanced Studies (CAS) at the Norwegian Academy of Science and Letters, working on the project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation (ATTODYN)* led by Thomas Bondo Pedersen and Simen Kvaal.

Why did you choose to visit the Hylleraas Centre and how did you learn about the Hylleraas Centre and its visitor program?

The theoretical-chemistry group at the University of Oslo has been one of the leading research centres for theoretical-

chemistry studies in Europe. I first visited Oslo in 1994 when I was on sabbatical in Lund, Sweden. At that time, I was very impressed with the breadth and scope of the theoretical research performed at the Chemistry Department in Oslo. In particular, the efforts of the Oslo group in the development of new quantum-mechanical methods for electronic-structure calculations of molecules were very close to the research interest of my group at the University of Arizona, which focused on the development of advanced single- and multi-reference coupled-cluster methods, as well as on methods utilizing explicitly correlated Gaussian functions for performing such calculations.

At some point in the early 2010s, I became interested in extending our studies of molecular spectra to include the effect that an external magnetic field has on the positions and intensities of the spectral lines. That interest led me to renew my contact with Trygve Helgaker and with other members of the Oslo group. From then on, I started to visit Oslo every year for two or more weeks in the summer, to pursue col-

→ Prof. Ludwik Adamowicz, Department of Chemistry and Biochemistry and the Department of Physics, University of Arizona, Tucson, Arizona, USA. *Photo: Camilla Kottum Elmar / CAS.*

laboration concerning the interaction of an external magnetic field with isolated atoms and molecules.

Our goal has been to employ methods involving multi-particle explicitly correlated Gaussian functions in molecular calculations that include a magnetic field, performed without assuming the Born–Oppenheimer approximation. Such calculations can potentially reveal the effects that the magnetic field has on the coupled motions of the electrons and the nuclei, which are treated on an equal footing in non-Born–Oppenheimer calculations. This work was performed in collaboration with Drs. Trygve Helgaker and Erik Tellgren. Initially, our approach involved using one-particle orbitals to expand the non-Born–Oppenheimer wave functions, but at the next stage, all-particle explicitly correlated Gaussians were implemented in the calculations. The computer program written included both paramagnetic and diamagnetic effects. The molecular models we studied included immobilization of a molecule in a magnetic trap.

At present, the non-Born–Oppenheimer approach for describing the interaction of a magnetic field with a molecular system is being extended to systems with an arbitrary number of nuclei and electrons. This extension requires implementation of analytical derivatives of the matrix elements representing the interaction of the magnetic field with the particles forming the molecule with respect to the nonlinear parameters of the correlated Gaussians.

A system that we are currently investigating is the BH molecule, in which an interesting interplay between the lowest electronic states occurs.

Since early September 2021, I have been a member of the ATTODYN team at CAS. Together with Drs. Caroline Lasser, Thomas Pedersen, and Simen Kvaal, and also other international members of the CAS team, we have been working on creating a quantum-mechanical

"My visits to the CTCC and the Hylleraas Centre and my current stay at CAS have established productive collaborations leading to exciting new research. The work on the interaction of molecules with a strong magnetic field involving explicitly correlated Gaussians without assuming the Born–Oppenheimer approximation and the work on the theoretical description of attosecond spectroscopy are particularly inspiring."

model for describing attosecond spectroscopy experiments. The approach involves various developments concerning the interaction of molecular systems with ultrashort, oscillating laser pulses. The expertise of my research group at the University of Arizona in the calculation of bound states of atoms and molecules without assuming the Born–Oppenheimer approximation and in employing various forms of all-particle explicitly correlated Gaussian functions is being utilized in the ATTODYN project.

In what way are visits to Oslo important for your scientific activities?

My visits to the CTCC and the Hylleraas Centre and my current stay at CAS have established productive collaborations leading to exciting new research. The work on the interaction of molecules with a strong magnetic field involving explicitly correlated Gaussians without assuming the Born–Oppenheimer approximation and the work on the theoretical description of attosecond

spectroscopy are particularly inspiring. The former topic is closely related to the interest of my research group in very accurate calculations of spectra of atomic and molecular systems relevant to astrochemistry. The addition of a magnetic field to the computational model allows us to predict spectra that can be measured of interstellar atomic and molecular systems exposed to a strong magnetic field such as those existing around white dwarfs and neutron stars.

Due to the diversity of the research carried out at the Hylleraas Centre and at CAS, I have learned new techniques and theoretical tools for the toolbox that my research group at the University of Arizona uses in our studies. As for my work at CAS, the topic of describing the time evolution of a molecular system in intense laser pulses represents an exciting extension of my research. The international ATTODYN team is multidisciplinary, including experts in the fields of applied mathematics, physics, and chemistry. Such an environment is very conducive to

fruitful discussions and collaborations. I am very pleased to be a member of the ATTODYN team and I am confident that our work here will result in important advances in the quantum-mechanical characterization of attosecond experiments.

I would like to add that I have felt very welcome at both the Hylleraas Centre and CAS, by the researchers as well as the staff. The atmosphere at frequent social gatherings has been fantastic, leading to many genuine friendships. I am very much looking forward to continuing my collaboration with the Hylleraas and CAS members, after the ATTODYN project ends in 2022.

How did you find Norway in general and Oslo in particular?

Through my visits to Oslo, I have become very fond of Norway and the Norwegian people. Oslo is a thriving, modern city with an international flavour. People are very friendly and open to foreigners. I have spent many hours walking and biking in Oslo and the neighboring areas. I have hiked the hills and forests around Oslo, as well as the shoreline. These excursions have contributed to me feeling at home here. Through my conversations with people at work and outside work, I have found Norwegians to project a strong sense of professional and personal ethics and a strong sense of community. The atmosphere at work is relaxed but people work hard, and the focus is on achieving things. I like that style.

During my visits to Norway, I have traveled to the north and to the south of the country. I found the beautiful and unique scenery very inspiring. I have been immensely impressed with the Norwegian landscape and with the resilience and optimism of the Norwegian people. I am very thankful for the CTCC, Hylleraas, and CAS funding to allow me to be a part of exciting research and to get acquainted with Norway and, in particular, with Oslo.

8

There were in total 8 visitors to the Hylleraas Centre in 2021.

Incoming Visits

Visitors to Oslo

Dr. Raquel Jimenez Rama	University of Sevilla, Spain	October 2 2020 – April 1 2021
Dr. Markus Penz	University of Innsbruck, Austria	September 13–17
Dr. Michael Herbst	RWTH Aachen University, Germany	September 13–17
PhD candidate Asier Urriolabeitia Rodrigo	University of Zaragoza, Spain	September 13 – December 13
Prof. Ludwik Adamowicz	University of Arizona, USA	September 20–22
Ass. Prof. Agus Sevink	Leiden University, the Netherlands	September 28 – October 2
Prof. Trond Saue	Université Toulouse III – Paul Sabatier, France	October 10–15

Visitors to Tromsø

Dr. Stanislav Komorovsky	Slovak Academy of Sciences, Slovakia	August 23–29
Dr. Florian Lemken	Aaachen University, Germany	August 23–29
Debora Pastvova	Slovak Academy of Sciences, Slovakia	August 23–29

Externally Funded Projects

The financial support the Hylleraas Centre receives as a Centre of Excellence from the Research Council of Norway and from its host institutions constitutes a long-term secure funding allowing us to develop and pursue research projects that require a sustained effort over years. However, to reach the ambitious goals of the centre, additional funding is needed—to focus on particular research challenges and to pursue promising new research directions that may arise in the course of the work at the centre. In the following, we present the external research grant proposals that have been approved for funding in 2021. Progress in these projects will in the future be reported as part of the activities of the research themes.

Accurate Prediction and Interpretation of NMR Spectra in Transition-Metal Complexes (SpecTraM)

Abril C. Castro (UiO)
—
RCN Young Research Talents (YRT) Grant, RCN
2022–2025
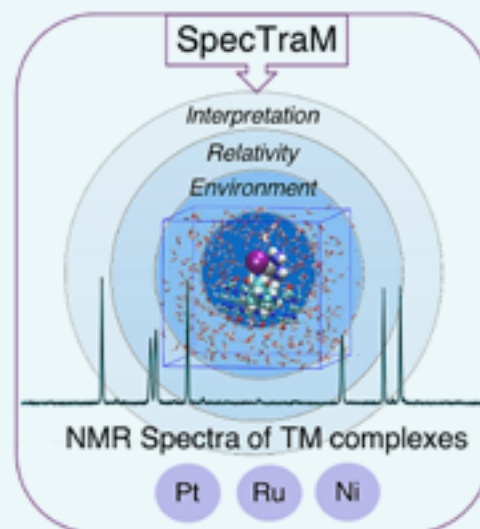
The YRT SpecTraM grant enables Abril Castro to establish her own, independent research group at the Hylleraas Centre, contributing to computational advances in nuclear-magnetic-resonance (NMR) spectroscopy.

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Abril Castro has received funding of 7.9 MNOK from the Research Council of Norway for the project *Accurate Prediction and Interpretation of NMR Spectra in Transition-Metal Complexes (SpecTraM)*. This project aims to provide a broader modelling of NMR properties in heavy transition-metal compounds, combining robust and nonconventional quantum-chemistry methods capable of accurately representing the interactions of a molecule within the environment and of the NMR parameters of interest.

A nucleus with a nonzero nuclear spin is an extremely sensitive probe of the local electron distribution in a molecule. Because of this high sensitivity, NMR spectroscopy is among the most important spectroscopic techniques in chemistry today. An NMR spectrum provides a fingerprint of the molecule, giving valuable information about its physical and chemical environment.

On the computational side, this same sensitivity poses considerable challenges to theoreticians, and most studies up to now have focused on applications to small compounds containing light nuclei.

The computational challenges increase in heavy-nuclei or paramagnetic molecules because of their extreme sensitivity to relativistic and environmental effects. Indeed, such effects may affect the chemical shifts to such an extent that they appear outside the normal chemical-shift range. The use and validation of more realistic models to simulate the experimental conditions is therefore urgently needed in the modelling of NMR properties. The SpecTraM project will contribute to this development by employing elaborate computational models such as fully four-component relativistic methods combined with *ab initio* molecular

dynamics simulations to accurately determine NMR parameters.

Considering the widespread use of NMR spectroscopy in many areas such as chemistry, biology, and materials science, the SpecTraM project will focus on demanding heavy-nuclei and paramagnetic molecules with specific bonding situations, unravelling challenging problems for synthesis and catalysis in which a reliable approach with predictive power is required. It is of interest to explore platinum, ruthenium, and nickel–fluoride complexes, with important potential applications, ranging from optimization of hydrocarbons in petrochemical feedstock to drug design in the pharmaceutical sector.

The SpecTraM project will be carried out at the Hylleraas Centre in close collaboration with Prof. Mats Tilset and Prof. Odile Eisenstein, as well as with international researchers including Prof. Robin Perutz (University of York, UK). It will be operational from 2022 to 2025 and will fund one PhD candidate for a three-year period.

Machine Learning Molecular Legos for Catalyst Discovery within Large Chemical Spaces (catLEGOS)

David Balcells (UiO)
—

FRIPRO Research Project, RCN
2022–2025

The catLEGOS project aims at filling a knowledge gap in the application of machine learning (ML) to homogeneous catalysis. The project focuses on the three key elements of the ML pipeline — namely, data, representations, and models. With a budget of 11.9 MNOK, the project supports the hiring of one PhD candidate and two postdocs. The project will be led by David Balcells and involves an interdisciplinary team of partners.

—

Today, ML is revolutionizing many fields of science and technology — in chemistry, it is at the core of new methods that advance the state of the art in drug discovery and the development of new materials. However, despite the exponential growth of ML in chemistry in the last ten years, there are areas that, because of their complexity, remain largely unexplored – catalysis and, in particular, homogeneous catalysis is one of them. The catLEGOS project aims at filling this knowledge gap by generating new data, representations, and models that enable catalyst discovery in large chemical spaces.

One of the main difficulties in the development of ML for homogeneous catalysis is the scarcity of data. Experimental data is difficult to obtain — especially at the scale required by the most efficient ML methods, which is on the order of 10^3 data points and more. Building on preliminary work by Balcells and Skjelstad (*J. Chem. Inf.*

Model., 2020, **60**, 6135), the catLEGOS project will explore the alternative approach of computing the data by first-principles methods. The resulting data sets will be used to optimize ML models for predicting properties that are relevant in catalysis. The generation of these data sets will be based on protocols that automate both generation and curation of the data.

Once the data is available, it must be transformed into a representation that can be processed by an ML algorithm. A representation is a set of features describing each data point — for example, chemical descriptors. One of the most powerful representations for ML are molecular graphs. In general, these graphs are easily built from skeletal formulas although, unlike for organic compounds, these formulas are difficult to define for catalysts containing transition metals due to high valence and multicentre bonding. The catLEGOS project will develop new graph
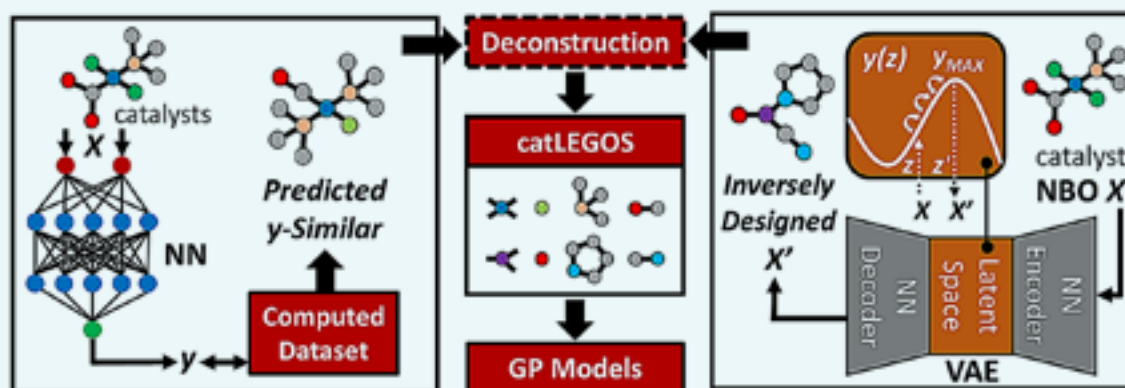
⊕ ML methods used in the generation and exploitation of molecular fragments for catalyst discovery in the catLEGOS project. *Illustration: David Balcells*

representations based on electronic-structure theory, including natural bond orbitals (NBO). This computational data will be used to define the geometry of the graphs and to inform their nodes and edges with features.

The last step in the ML pipeline is the optimization of the predictive models. Building on preliminary work (Friederich, Gomes, De Bin, Aspuru-Guzik, and Balcells, *Chem. Sci.*, 2020, **11**, 4584), the catLEGOS project will explore the combination of different ML methods including neural networks (NNs), variational autoencoders (VAEs), Gaussian processes (GPs), and gradient-boosted regression trees (GBRTs). The NNs and VAEs will be used as recommender and generation systems, yielding metal complexes that are predicted to be active in catalysis. These potential catalysts will be deconstructed in metal and ligand fragments for building chemical spaces containing other complexes. GPs will be used to explore these

spaces with the aim of finding new catalysts. Finally, GBRTs will enable explainability by computing the relevance of the representation features in the predictions made by the models.

The catLEGOS project will be led by Hylleraas PI Dr. David Balcells. The project has a budget of 12 MNOK to support the hiring of one PhD candidate and two postdocs. Following its strong interdisciplinary character, the project involves a diverse team of partners with expertise in AI- and robot-driven labs (Prof. Aspuru-Guzik, University of Toronto, Canada), ensemble learning and graph theory (Assoc. Profs. Riccardo de Bin and Johan Pensar, Department of Mathematics, UiO), and theoretical and computational chemistry (Simen Reine and Thomas Bondo Pedersen). In this way, the project will reinforce the international network of the Hylleraas Centre as well as inter-RT collaborations.

Relativistic MultiResolution Chemistry: Heavy-Element Compounds at the Complete Basis Set Limit (ReMRChem)

Luca Fredianti (UiT)

—

FRIPRO Research Project, RCN
2021–2026

In the ReMRChem project, a team led by Luca Frediani will develop methods for relativistic calculations on compounds containing heavy elements, using multiwavelets for rigorous error control and guaranteed precision. The project extends over a period of five years with a budget of 12.0 MNOK supporting two postdoctoral fellows and one part-time researcher.

—

Heavy elements are important. Their properties, strongly affected by relativity, are exploited in many technological applications: solar panels, high-capacity batteries, light-emitting diodes (LEDs), and solid-state drives all benefit from such properties. Computational modeling gives valuable insight into the properties of heavy-element compounds – insight that often cannot be obtained by experimental investigations alone. At the same time, heavy elements expose the challenges and limitations of traditional methods based on the expansion of molecular orbitals in a finite basis of atomic orbitals.

By avoiding atomic orbitals, the ReMRChem project will instead make use of multiwavelets to perform precise calculations of energy and properties of heavy-element compounds. Multiwavelets are special mathematical functions that not only allow for rigorous error control, but also provide a simple framework for translating the

theory into a program running on supercomputers.

With the ReMRChem project, it will be possible to generate highly precise results for energy and properties of heavy-element compounds, including relativistic effects, which in turn will impact materials science and the energy sector.

The goals of the project will be achieved through three work packages (WPs):

- In WP1, relativistic methods using multiwavelets will be developed and implemented, considering the full range of relativistic methods – from simple scalar relativistic methods to rigorous four-component methods.

- In WP2, we will consider the calculation of molecular properties to arbitrary order in the perturbation, at the relativistic level of theory, within the multiwavelet framework.

- In WP3, we combine the results of WP1 and WP2 into a software capable of computing energetics and properties of molecules containing heavy elements, focusing on benchmarks and applications.

For the project, we will hire two postdoctoral fellows to work in WP1 and WP2, respectively. Dr. Stig Rune Jensen and Dr. Peter Wind will oversee code development. Luca Frediani will supervise the two postdoctoral fellows and work actively in all WPs, especially regarding the theoretical developments and the design of benchmark and applications.

The ReMRChem team will benefit from the expertise at the Hylleraas Centre and the Department of Chemistry at UiT, concerning relativistic methods (Dr. Michal Repisky, Kenneth Ruud), molecular properties (Dr. Magnus Ringholm, Kenneth Ruud), and applications (Prof. Kathrin Hopmann, Prof. II Laura Ratcliff). Several external collaborators are involved in the project, including Prof. Trond Saue (University of Toulouse), Prof. Stefan Goedecker (University of Basel), and Prof. Volker Blum (Durham University).

During the project, we plan to hold two small workshops focused on the development of relativistic methods and a larger conference for a wider audience.

Hydrogen Storage and Transport using Ammonia (HySTrAm)

David Balcells (UiO)
—

EU Horizon 2021 Resilience Project
2022–2024

The HySTrAm project aims at building a demonstration plant for the industrial synthesis of ammonia using renewable energy. The project involves a large consortium of academic and industrial partners in twelve European countries. The project supports the hiring of one postdoc at the Hylleraas Centre, under the supervision of David Balcells. The focus of this postdoc will be on the use of high-throughput virtual screening and machine learning for the discovery of metal–organic frameworks with high capacity in the storage of green hydrogen.
—

In response to the climate emergency, Norway has defined a national 'green shift' policy, aiming at transforming society and the economy towards a model that minimizes emissions. A key ingredient of this policy is a transformation of the industrial sector, replacing current energy sources by renewables. In this context, the goal of the HySTrAm project is to build a demonstration plant using green hydrogen for the industrial production of ammonia with the Haber–Bosch process. Once transformed into ammonia, hydrogen is much more easily stored and transformed.

The project has an overall budget of 6 million euros, supporting a large consortium with multiple partners from academia and industry in twelve European countries. In Oslo, HySTrAm supports the hiring of one postdoc at the Hylleraas Centre under the supervision of Balcells. The work of this postdoc will focus on the development of new metal–organic frameworks (MOFs) for hydrogen storage. In the demonstration plant, hydrogen will be generated by electrolysing water using solar energy. A major difficulty with this approach is the intermittency of the energy source, which hampers the constant feeding of hydrogen needed in the reactor. The project will tackle this problem by developing a hydrogen storage system based on a MOF acting as a high-capacity nanoporous material.

In collaboration with the Norwegian ProfMOF company, we will use first-principles calculations to generate data sets containing the quantum properties of many functionalized MOFs. By combining high-throughput virtual screening (HTVS) and machine learning, we aim at discovering MOFs that are suitable for a Haber–Bosch process using green hydrogen.

The HySTrAm project has a strong multidisciplinary character, including expertise in the diverse fields of catalysis, materials science, chemical engineering, electrochemistry, and computational and data sciences. From this perspective, the Hylleraas Centre will benefit from the secondments plan supported by the project, including exchanges between the different institutions that participate in the consortium. In particular, the project may contribute to expanding the network of the Hylleraas Centre towards the industry.

EPR and NMR Spectroscopy of Spin–Orbit-Coupled Paramagnetic Solids

Michal Repisky (UiT)

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Marie Skłodowska–Curie COFUND Action SASPRO2
2022–2025

Dr. Michal Repisky at the Hylleraas Centre in Tromsø received a funding of 2 MNOK for the project *EPR and NMR Spectroscopy of Spin–Orbit-Coupled Paramagnetic Solids* from the Slovak Academic and Scientific Programme (SASPRO), co-funded by the European Commission under the Horizon 2020 Marie Skłodowska-Curie Actions and led by three top research institutions in the Slovak Republic. The project will be operational during 2022–2025.

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Unpaired electrons are at the heart of many important processes in physics, chemistry, and biology, such as electron transport, conductivity, and reactivity. Our ability to probe and describe the topology of unpaired electrons in paramagnetic systems is therefore essential if we are to understand electronic structure in these systems and establish a connection between their structure and properties.

Electron paramagnetic resonance (EPR) and paramagnetic nuclear magnetic resonance (pNMR) spectroscopies, the interpretation of which is often impossible without computational aid, enable us to relate experimental spectra of paramagnetic solids to details of their electronic structure, thereby facilitating the design of new materials. However, whereas the theoretical description of these magnetic resonance phenomena is well established for closed-shell molecules in the gas, liquid and solid phases, there is at present no relativistic all-electron methodology available for paramagnetic solids, leaving a large gap in our ability to understand structure–property relationships in these systems.

The project aims to fill this gap by developing a modern all-electron two-component relativistic solid-state approach based on density-functional theory for modeling EPR and pNMR spectra in solids. The project builds on our recently developed atomic mean-field X2C Hamiltonian (amfX2C) for molecules and solids and its implementation in our in-house program ReSpect to make a major step forward in the modeling of magnetic materials. This will allow us to advance the use of EPR and pNMR to the study of paramagnetic solids, while the inclusion of relativity will allow us to reliably describe the topology of unpaired electrons in paramagnetic solids involving elements across the periodic table. On the application side, we will study battery materials based on lithium or sodium transition-metal oxides.

Homotopy Continuation for Unitary Coupled-Cluster Theory

André Laestadius (UiO) and
Mihály A. Csirik (UiO)

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Peder Sather Grant Program
2021-2023

The goal of the project *Homotopy Continuation for Unitary Coupled-Cluster Theory* is to analyse unitary coupled-cluster theory, an advanced method of quantum chemistry popular in the quantum-computing community, using the tools of algebraic geometry and topological degree theory.

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A key feature of unitary coupled-cluster theory, setting it apart from traditional coupled-cluster theory, is its Hermitian formulation. However, the mathematical foundation of unitary coupled-cluster theory is not clear at all, which is what we are attempting to clarify within this project. One example is the representation problem: it has not yet been proved that every normalized wave function can be written as a unitary coupled-cluster wave function.

The principal investigators of the project are Drs. André Laestadius and Mihály A. Csirik at the Hylleraas Cen-tre in Oslo and Ass. Prof. Lin Lin at the Department of Mathematics, University of California (UC), Berkeley. A key collaborator is Dr. Fabian M. Faulstich, a previous PhD candidate at the Hylleraas Centre, now at Berkeley. The lifespan of the project is 2021–2023.

The grant was received in autumn 2021 and has since initiated work on the mathematical aspects of the unitary coupled-cluster method together with Lin and Faulstich. A research visit at UC Berkeley is planned for Csirik and Laestadius to take place in early 2022. Later in the same year, Faulstich plans to visit the Hylleraas Centre in Oslo.

⊕ Collaborators of the Peder Sather Grant *Homotopy continuation for unitary coupled-cluster theory*. From left to right: Lin Lin (UCB), André Laestadius (UiO), Fabian Faulstich (UCB, former UiO), and Mihály Csirik (UiO).

Regularized Density Functional Analysis (REGAL)

André Laestadius (UiO)
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ERC Starting Grant
2022–2027
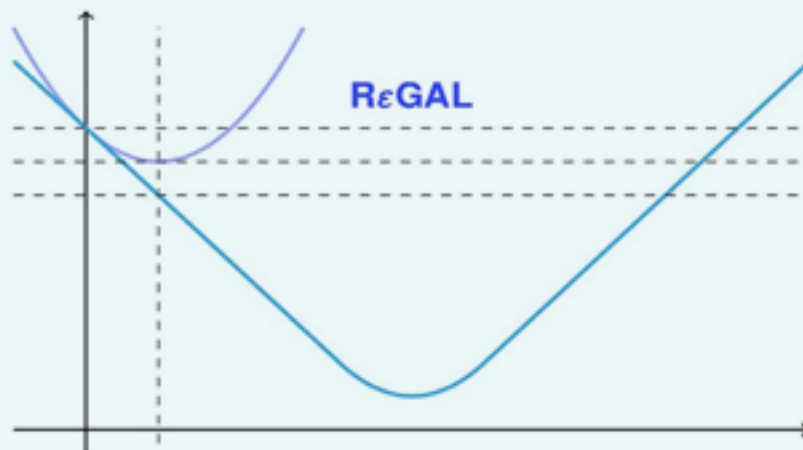
A core problem in density-functional theory (DFT) is that its central object, the universal density functional, is a highly irregular and not explicitly known functional of the electron density. Development of approximate functionals is therefore important. The project *Regularized Density-Functional Analysis (REGAL)* seeks to gain a better understanding of the density functional and to offer better approximations to it by means of Moreau–Yosida regularization, a regularization technique of convex analysis.

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The Kohn–Sham scheme of DFT is the most widely used method in quantum chemistry for electronic-structure calculations and can hardly be over-estimated as a practical tool. However, since the central object of the theory – the density functional – is nondifferentiable, the standard derivation of the scheme is unfounded. Nevertheless, extensive work has been done to establish exact conditions for the density functional, constituting one of the cornerstones of functional development.

Specifically, André Laestadius will in the REGAL project explore Moreau–Yosida regularization as a tool to create a more well-behaved formulation of Kohn–Sham DFT, more amenable to approximations. Moreau–Yosida regularization of DFT was originally proposed by members of the Hylleraas Centre in 2014 (Kvaal, Ekström, Teale, and Helgaker, *J. Chem. Phys.*, 2014, **140**, 18A518). Although several papers have since been published on the subject, REGAL is the first concerted attempt at leveraging Moreau–Yosida regularization into a transformative tool in DFT, with emphasis on the development of approximate exchange–correlation functionals and Kohn–Sham self-consistent-field iterations with robust convergence properties.

The project runs for five years, beginning on September 1, 2022, with a total budget of 1.5 million euros. In addition to funding two PhD candidates and two postdocs, the project will include a workshop during the later stage of the project.

The REGAL grant is the fifth ERC grant awarded to members of the Hylleraas Centre: Trygve Helgaker (Advanced Grant 2010), Kenneth Ruud (Starting Grant 2011), Simen Kvaal (Starting Grant 2014), Andrew Teale (Consolidator Grant 2017), and André Laestadius (Starting Grant 2021). Three of these grants (those of Helgaker, Teale, and Laestadius) concern the fundamentals of DFT.

Mathematics for Quantum Computation and Many-Body Theory (QOMBINE)

Simen Kvaal (UiO)

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Consortium led by Prof. Nadia S. Larsen, Department of Mathematics, UiO

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Large-Scale Interdisciplinary Researcher Project, Fellesløft IV, RCN and UiO 2022–2024
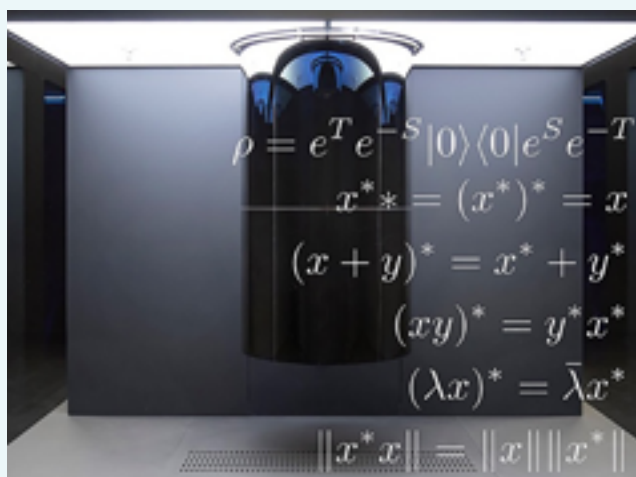
⬆ IBM's Q System One commercial quantum computer and the defining equations of coupled-cluster theory and C*-algebra. *Illustration: Simen Kvaal; photo by IBM Quantum System One, Ehningen, Germany.*

The interdisciplinary project *Mathematics for Quantum Computation and Many-Body Theory (QOMBINE)* **aims to develop new mathematical methods for central problems of quantum technology, including a new framework for coupled-cluster theory. The QOMBINE project will be carried out by a consortium of mathematicians, physicist, and chemists at the University of Oslo, including Hylleraas researcher Simen Kvaal.**

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Late in 2021, a consortium led by Prof. Nadia S. Larsen at the Department of Mathematics and with Hylleraas researcher Simen Kvaal as one of the participants was awarded the large-scale interdisciplinary researcher project QOMBINE through the Fellesløft IV program of the Research Council of Norway (RCN). The QOMBINE project addresses several cutting-edge research topics at the interface of mathematics, physics, and chemistry related to quantum technology such as quantum computers and cryptography. One of the most important applications of near-future quantum computers where one can gain a 'quantum advantage' over classical computers is the solution of the many-electron Schrödinger equation.

The Faculty of Mathematics and Natural Sciences and RCN have each provided 12.5 MNOK for the QOMBINE project, allowing an exciting and broad range of research problems to be addressed. In addition to Simen Kvaal, the consortium comprises Eric Bedos, Sergiy Neshveyev, Alexander Müller-Hermes and Makoto Yamashita at the Department of Mathematics as well as Franz Georg Fuchs and Joakim Bergli at the Department of Physics.

The QOMBINE project seeks to develop new mathematical methods for central problems of quantum technology. Among the topics to be developed is a new mathematical framework for coupled-cluster theory, one of the most popular quantum-chemical computational methods. Even if coupled-cluster theory in its standard formulation for molecular systems is relatively well understood from a mathematical viewpoint, Kvaal, Neshveyev, and Larsen will together with two PhD candidates use C^*-algebra to unify the theory for electrons, protons, and other elementary particles, in addition to more exotic particle-like phenomena such as anyons and Majorana fermions. The latter are important building blocks in the development of topological quantum computers. On the other hand, a version of coupled-cluster theory called unitary coupled-cluster theory is classically intractable, but very fast on a quantum computer. Thus, the chemistry arm of QOMBINE aims not only at a better understanding of coupled-cluster calculations to be run on quantum computers, but also at a better understanding of how to build future quantum technologies. The QOMBINE project introduces an exciting new research direction and interdisciplinary collaboration for the Hylleraas Centre, involving several departments and the industry sector.
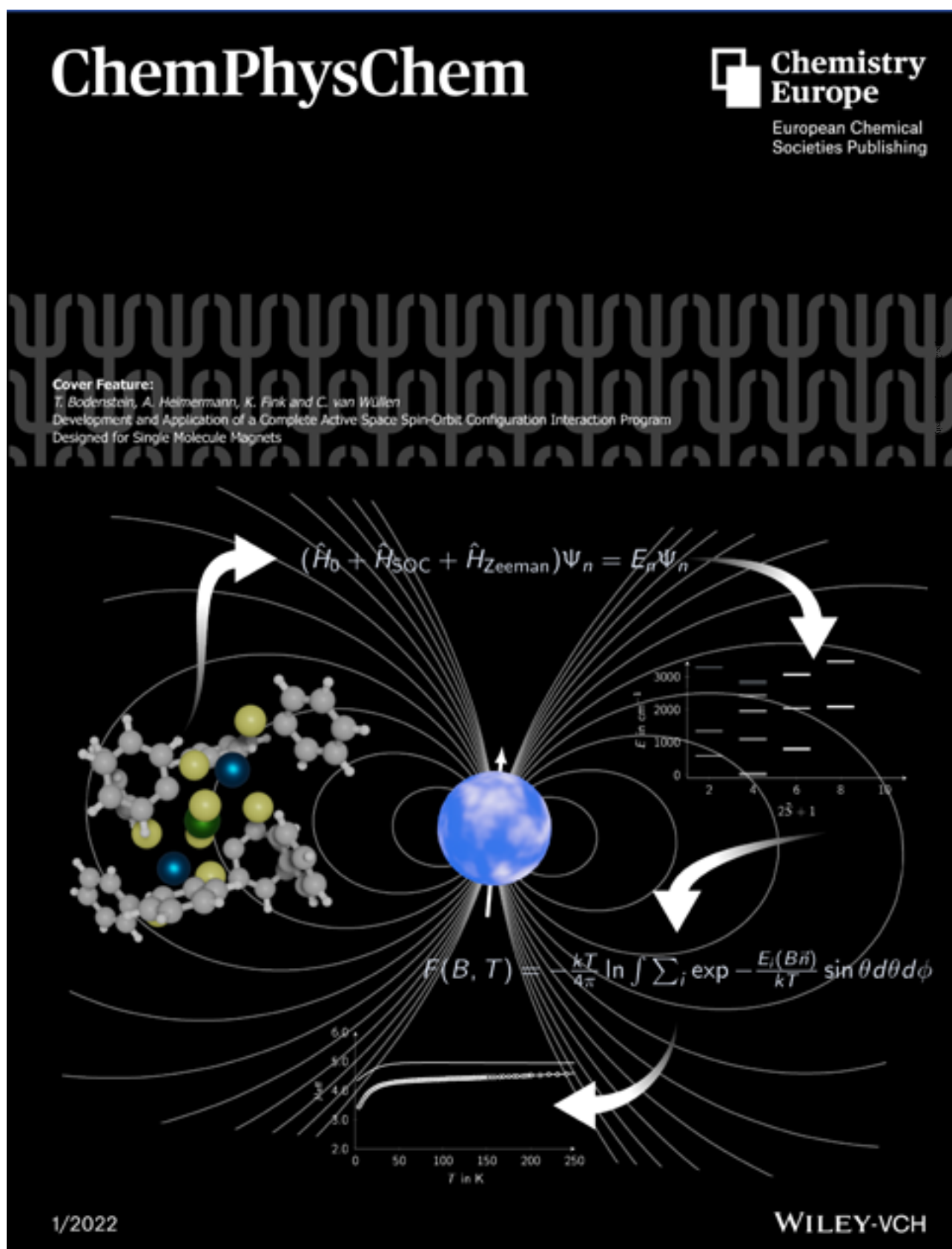
↑ Cover picture of *ChemPhysChem* 1/2022, highlighting the work *Development and Application of a Complete Active Space Spin-Orbit Configuration Interaction Program Designed for Single Molecule Magnets* (T. Bodenstein, A. Heimermann, K. Fink and C. van Wüllen, *ChemPhysChem*, 2021, **23**, e202100648). The article was published online September 10, 2021. *Reproduced with permission from John Wiley.*

Research Theme Activity Reports

At the Hylleraas Centre, we develop and apply computational methods to understand, interpret, and predict new chemistry, physics, and biology of molecules in complex and extreme environments. Our work is organized into six research themes (RTs):

- Electronic Structure (RT1)
- Multiscale Modelling (RT2)
- Spectroscopic Processes (RT3)
- Extreme Environments (RT4)
- Chemical Transformations (RT5)
- Multiphase Systems (RT6)

Each RT has its own deliverables, directed towards the common goal of the centre. The first two themes, RT1 on electronic structure and RT2 on multiscale modelling, describe matter in isolation, providing the backbone for our work. The next two themes, RT3 and RT4, introduce fields and photons. They are at the heart of the centre, dealing with spectroscopic processes and extreme environments. The tools developed in these four RTs will enable our application themes to address problems that are today beyond the reach of computation. The focus is on chemical transformations in RT5 and on multiphase systems in RT6 — areas that, among many other things, aim to secure clean energy and to combat antimicrobial drug resistance.

In the following, the 2021 report is provided for each RT.

⬆ Hylleraas Research Themes
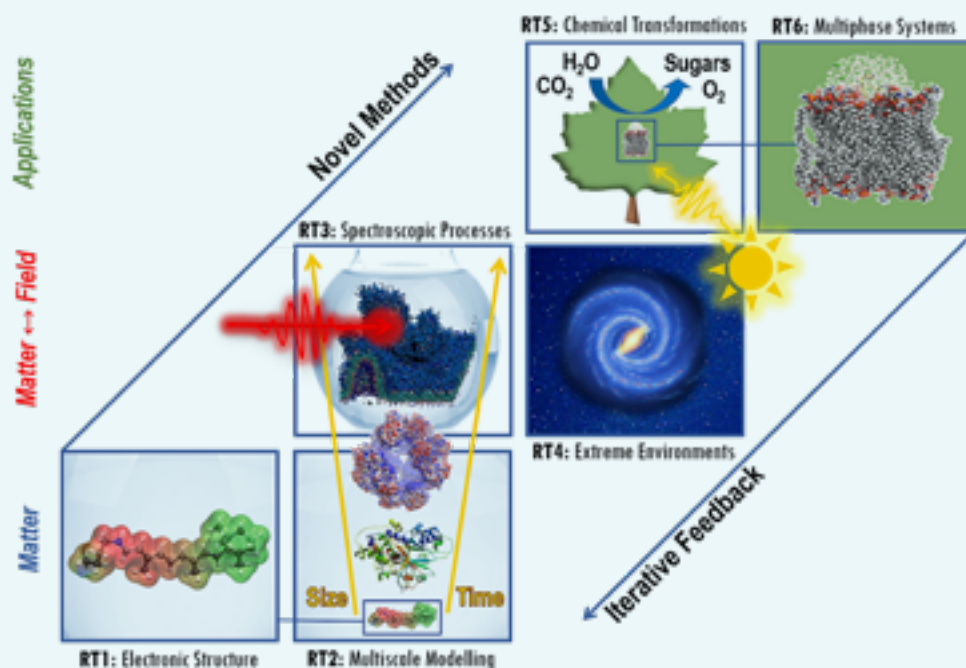
RT1

Electronic-Structure Theory

Principal investigators:
Thomas Bondo Pedersen and Luca Frediani
—
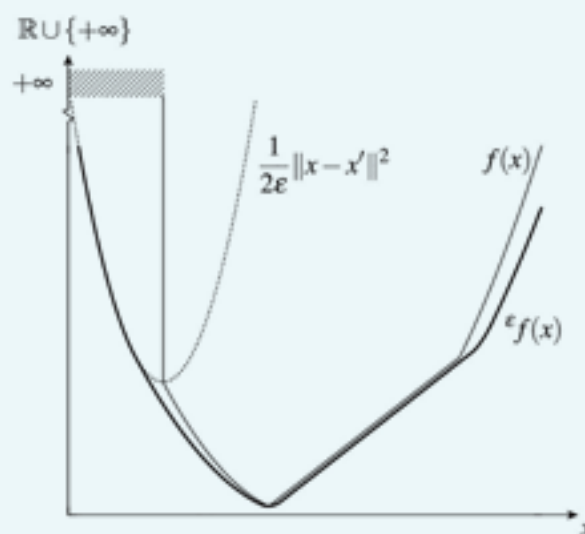
⊙ **Figure 1:** Illustration of the Moreau–Yosida regularization of a simple one-dimensional convex function. The original function *f(x)* is regularized by 'sweeping' a parabolic function along the graph, tracing out the graph of the regularized function (thick line). *Reproduced from Kvaal, Ekström, Teale, and Helgaker, J. Chem. Phys., 2014,* **140**, *18A518, with the permission of AIP Publishing.*

In spite of the COVID-19 pandemic, RT1 research activity has in 2021 been broad and marked by several significant achievements: a long-standing problem in current-density functional theory has been solved, a deep mathematical analysis of coupled-cluster theory has been made, and an ERC Starting Grant has been awarded to a young researcher in RT1.

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Density-functional theory
Density-functional theory (DFT) is the workhorse of electronic-structure theory in chemistry and materials science. In DFT, a many-electron system is described in terms of its spatial density, thereby avoiding the construction of the many-body wave function. Despite this enormous simplification, DFT is an exact theory, meaning that the ground-state energy of each system can, in principle at least, be calculated exactly from a universal density functional (the same for all systems). Unfortunately, this universal functional is not explicitly known. Developing good approximations to the universal density functional is therefore an important task.

At the Hylleraas Centre, much of the work on DFT revolves around the topic of Moreau–Yosida regularized DFT (MYDFT), and current DFT (CDFT). DFT for electronic systems is mathematically described using convex analysis, and Moreau–Yosida (MY) regularization is an important analytical tool in this mathematical framework; see Figure 1. Hylleraas researchers pioneered MYDFT

in 2014, with several deep and surprising results [1]. For example, the notorious *v*-representability problem disappears in MYDFT, and the all-important Kohn–Sham scheme of DFT has its only mathematically rigorous derivation using MY regularization. In 2021, Simen Kvaal collected the findings so far, together with a self-contained introduction to MY regularization in DFT, in a book chapter to be published in a volume on mathematical DFT by Springer.

While MYDFT is a powerful reformulation of exact DFT, it has so far not led to practical realizations in the shape of new density-functional approximations. However, in 2021, André Laestadius was awarded an ERC Starting Grant for his project REGAL, whose aim is precisely to develop density-functional
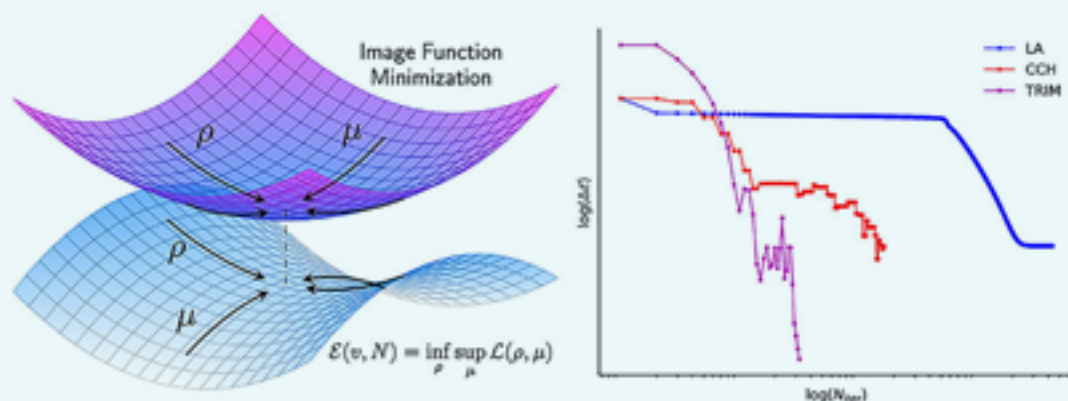
approximations using Moreau–Yosida regularization; see elsewhere in this report.

Molecular systems in an external static magnetic field require a theory beyond DFT: CDFT, where the electronic current density is introduced alongside the electronic charge density as a basic variable. Hylleraas members have been at the forefront of CDFT research since 2012 [2]. It is remarkable that, since its introduction in the 1980s, a mathematically rigorous formulation of CDFT was not found until Hylleraas researchers in 2021 demonstrated convex lower semi-continuity of the constrained-search universal functional in CDFT [3]. Another point of contention is what type of current density is proper to use in CDFT: the physical gauge-invariant current, or the paramagnetic current

[2]. This question was in 2021 further addressed using a modern perspective by André Laestadius and Erik Tellgren in collaboration with Dr. Markus Penz (Max Planck Institute, Hamburg, Germany) [4].

In 2021, Trygve Helgaker and Assoc. Prof. II Andrew Teale published the article *Robust All-Electron Optimization in Orbital-Free Density-Functional Theory Using the Trust-Region Image Method* [5]. This paper represents a breakthrough in orbital-free DFT in that, for the first time, the ground-state energy can be reliably and efficiently optimized for atomic systems. Our method combines the trust-region image method (TRIM) of Helgaker [6] with a convex–concave representation of the ground-state energy as a function of the density and

of the chemical potential, respectively; see Figure 2.

Coupled-cluster theory

Coupled-cluster (CC) theory comprises a class of computational methods for the electronic-structure problem that are based on an exponential ansatz for the many-electron wave function. Unlike DFT, CC theory can be systematically improved, achieving near-exact results that compare directly with experimental results for small and medium-sized systems. Thus, while DFT is the workhorse of quantum chemistry, being able to describe much larger molecules than wave-function-based methods, there is still a need for more accurate calculations for the smaller molecules that the CC model can tackle. At the Hylleraas Centre, we do state-of-the-art research into both theoretical
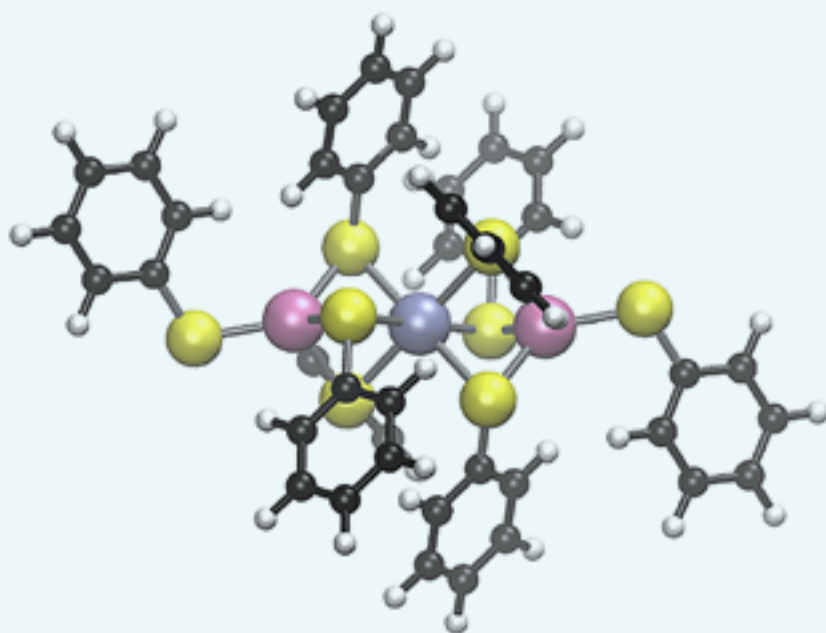
Figure 3: Trinuclear CoIIVIICoII single-molecule magnet studied by Bodenstein and coworkers with their CASOCI program [9]. Co: magenta, V: blue, S: yellow, C: black, H: white. *Reproduced from Ref. [8] with permission from John Wiley and Sons.*

and practical aspects of CC theory and other wave-function-based schemes.

Since 2014, the team of Simen Kvaal's ERC Starting Grant *Bivariational Approximations in Quantum Mechanics and Applications to Quantum Chemistry (BIVAQUM)* has worked on the bivariational principle to formulate CC methods in an unconventional manner. The ERC project ended in 2021, but several research topics from BIVAQUM are still being explored. Ongoing work includes Dr. Tilmann Bodenstein's development of state-universal multireference CC methods and a study of the time-dependent bivariational principle and response theory by Kvaal.

The CC research by the former BI-VAQUM team has close ties with RT3; see elsewhere in this report.

The RCN Young Research Talents (YRT) project *Error Estimates for Coupled-Cluster Methods, Ground States and Excited States (CCerror)* began in December 2019. In the first project year, 2020, post-doctoral fellow Dr. Mihály Andras Csirik joined project leader Dr. André Laes-

tadius to work on the mathematical description of CC theory. In the second project year, 2021, Csirik and Laestadius finished the work *Coupled-Cluster Theory Revisited* [7], analysing the non-linear equations of single-reference CC theory using topological degree theory. This paper generalizes previous work based on (local) strong monotonicity, which is limited to the nondegenerate ground-state case. Existence results were established and qualitative information about the solutions of these equations, which also sheds light on some numerically observed behaviour, was obtained. To investigate typical truncation schemes employed in practical CC calculations, the Kowalski–Piecuch homotopy was utilized. In this setting, an energy error bound for approximate eigenstates of the Schrödinger equation for ground and excited states was derived.

In summer 2021, Laestadius visited Dr. Michael Ruggenthaler at the Max Planck Institute in Hamburg, funded by a Kristine-Bonnevie travel grant; he was joined by Csirik for a second visit later in 2021. Ruggenthaler, who is an expert

on light–matter interactions, has been a close collaborator of the Hylleraas Centre since 2018.

The workshop *Tensor Product Methods for Strongly Correlated Molecular Systems,* which had been postponed because of the pandemic, was held as an online event (rather than physically at the Max Planck Institute in Dresden) in March 2021. Laestadius gave the contributed talk *Analysis of Size-Extensive Alternative Coupled-Cluster Models Based on Arponen's Extended Theory,* presenting a mathematical study of alternative formulations of extended CC theory carried out in collaboration with Kvaal and Bodenstein. In November, Laestadius visited Dr. Martin Rahm and his group at Chalmers University of Techology in Gothenburg and gave the talk *Coupled-cluster theory revisited.*

The Peder Sather Grant *Homotopy Continuation for Unitary Coupled-Cluster Theory,* with principal investigators Laestadius and Csirik at the Hylleraas Centre and Ass. Prof. Lin Lin at University of California, Berkeley, is described elsewhere.

Complete-active-space spin–orbit configuration-interaction (CASOCI) method

In 2021, Tilmann Bodenstein together with his German colleagues Andreas Heimermann and Christoph van Wüllen (Technical University of Kaiserslautern) and Karen Fink (Karlsruhe Institute of Technology) published the CASOCI method together with a highly efficient parallel implementation of it [8]. The method is particularly well suited to the description of the magnetic properties of polynuclear transition-metal complexes. These multireference molecules, which often form single-molecule magnets, are particularly challenging for electronic-structure theory and beyond the reach of DFT. The power of the CASOCI method was illustrated by a study of a trinuclear $Co^{II}V^{II}Co^{II}$ complex; see Figure 3.

Electronic-structure theory at the basis-set limit with multiwavelets

A large part of the RT1 activity in Tromsø focuses on developing multiwavelet methods for electronic-structure calculations. Multiwavelets are a relatively new mathematical tool that makes it possible to represent functions (orbitals, electronic density, potentials) with a predefined, guaranteed precision. This feature makes multiwavelets an ideal tool to completely remove one of the main errors in electronic-structure calculations − namely, the basis-set truncation error. With multiwavelets, such errors are rigorously controlled and kept below an arbitrary, predefined threshold. In combination with DFT, for example, the only remaining source of error arises in the density-functional approximation. Another strength of the multiwavelet framework is that its implementation closely resembles the theoretical development, often with a one-to-one correspondence between equations on paper and lines of code, allowing for a rapid code development.

After many years of development, our multiwavelet code MRChem has reached a degree of maturity where it can be applied to a wide range of interesting systems and phenomena. Capitalizing on the strength of multiwavelets, Anders Brakestad and Stig Rune Jensen have recently implemented the zeroth-order relativistic approximation (ZORA) and begun benchmarking ZORA energies against energies calculated using traditional Gaussian-type orbitals. Gabriel Gerez and Roberto Di Remigio have finalized the development of the generalized Poisson equation to include solvent effects and have conducted a large benchmark study, comparing with the polarizable continuum model. Magnar Bjørgve and Stig Rune Jensen have worked on the extension of MRChem to periodic boundary conditions and have released a new version of the VAMPyR code for fast prototyping. Peter Wind and Stig Rune Jensen have extended the parallel implementation of MRChem to the challenging Hartree–Fock exchange contribution. Roberto Di Remigio has begun work on a tensor-train implementation to be used in higher dimensions, which will eventually enable CC calculations within the MRChem code. As part of the RCN FRIPRO project ReMRChem described elsewhere, Luca Frediani has used the VAMPyR library to develop a prototype four-component relativistic implementation within MRChem.

Precise evaluation of special functions

Fast integral evaluation is essential for high-performance electronic-structure calculations. Researcher Bin Gao has developed new algorithms for the accurate evaluation of mathematical special functions needed for core-potential integrals. The new algorithms are designed with rigorous floating-point error control and have been implemented into the library tIntegral using the C++ programming language. Their GPU versions are under development.

Funding and personnel

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RT2

Multiscale Modelling

Principal investigators:
Michele Cascella and Bjørn Olav Brandsdal
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RT2 is devoted to the development of multiresolution methods, bridging quantum-chemical methods for small systems with mesoscale methods for large systems. In 2021, we focused on the development of embedding protocols for *ab initio* molecular-dynamics (AIMD) and quantum-mechanics/molecular-mechanics (QM/MM) simulations, as well as on the development of coarse-grained (CG) methods that couple particle resolution to density-functional-based potentials.
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The year 2021 has been a year of seeding for multiscale-modelling research at the Hylleraas Centre. A special effort has been put into long-term software development, both as plug-ins for existing packages and as new initiatives, aimed at providing significant contributions to the Hylleraas Software Platform.

AIMD with wave-function-based methods

For efficiency reasons, AIMD and QM/MM methods have been dominated by density-functional theory (DFT). Nonetheless, there is a need to establish protocols that enable advanced conformational sampling of the hierarchy of more accurate, wave-function-based methods, including coupled-cluster (CC) theory. Following efforts presented in the past reports, 2021 has seen the finalization of our work aimed at interfacing the quantum-mechanical package CFOUR to the AIMD and QM/MM platform MiMiC [1]. Thanks to this new tool, it is now possible to run AIMD and QM/MM simulations at any high level of theory available in CFOUR, including Møller–Plesset perturbation theory, complete-active-space theory, and CC theory. The higher computational costs

of these methods compared with DFT can at least partially be alleviated by using multiple time-step algorithms that propagate the equations of motion along a fast-evolving potential-energy at the DFT level, while adding a slow-evolving correction obtained by the higher-level method.

This work has been the main topic of the PhD thesis of Till Kirsch (University of Mainz). It involved visiting periods at the Hylleraas Centre, in a collaboration with the group of Prof. Jürgen Gauss (University of Mainz) within the framework of the DFG TRR-146 in Mainz and Darmstadt, where Michele Cascella is an international PI in the period 2018–2022. This work also involves Hylleraas adjunct Jógván M. H. Olsen, who overlooked the implementation in the MiMiC code.

Hamiltonian-hPF model

In a 2020 paper [2], former Hylleraas PhD candidate Dr. Sigbjørn Bore together with Cascella rederived and
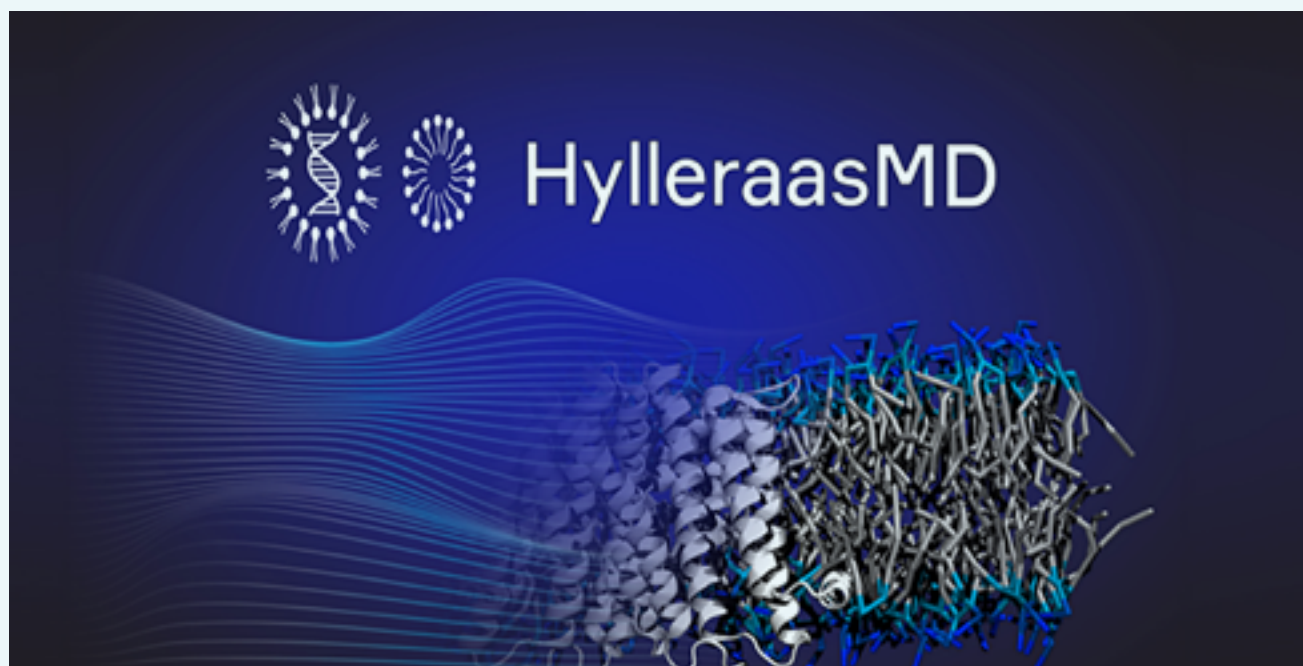
Figure 1: Logo of the Hylleraas-MD software
and its algorithmic structure.

reformulated the hybrid particle–field (hPF) model, showing how it obeys purely mechanical principles and does not require statistical mean-field considerations. In their paper, Bore and Cascella introduced filtered densities into the hPF model, defining in a rigorous manner the amount of density spread associated with each particle in the system:

$$\varphi_i(\mathbf{r}) \rightarrow \overline{\varphi_i}(\mathbf{r}) = \int \varphi_i(\mathbf{x}) H(\mathbf{r} - \mathbf{x}) d\mathbf{x}$$

The appearance of a convolution product between the fine-grained density and a filter H indicates that, within this new *Hamiltonian-hPF (HhPF)* formalism, there is an intrinsic advantage in moving all real-space operations to the Fourier space, where each convolution integral simplifies into a simple product,

$$\overline{\varphi_i}(\mathbf{r}) \rightarrow \widehat{\overline{\varphi_i}}(\mathbf{k}) = \hat{\varphi}_i(\mathbf{k}) \hat{H}(\mathbf{k})$$

Here the hat indicates the Fourier transform of the original function. Results from Ref. [2] indicate that, in a simple monoatomic fluid at least, the HhPF
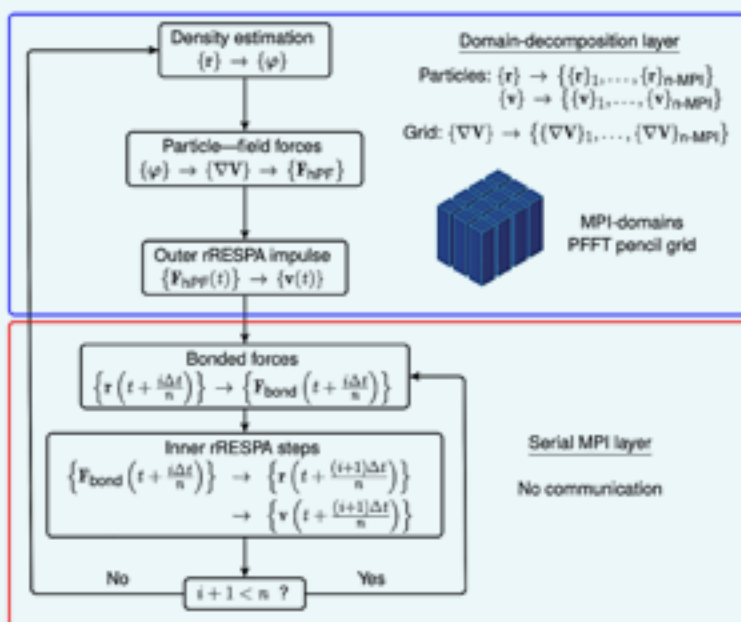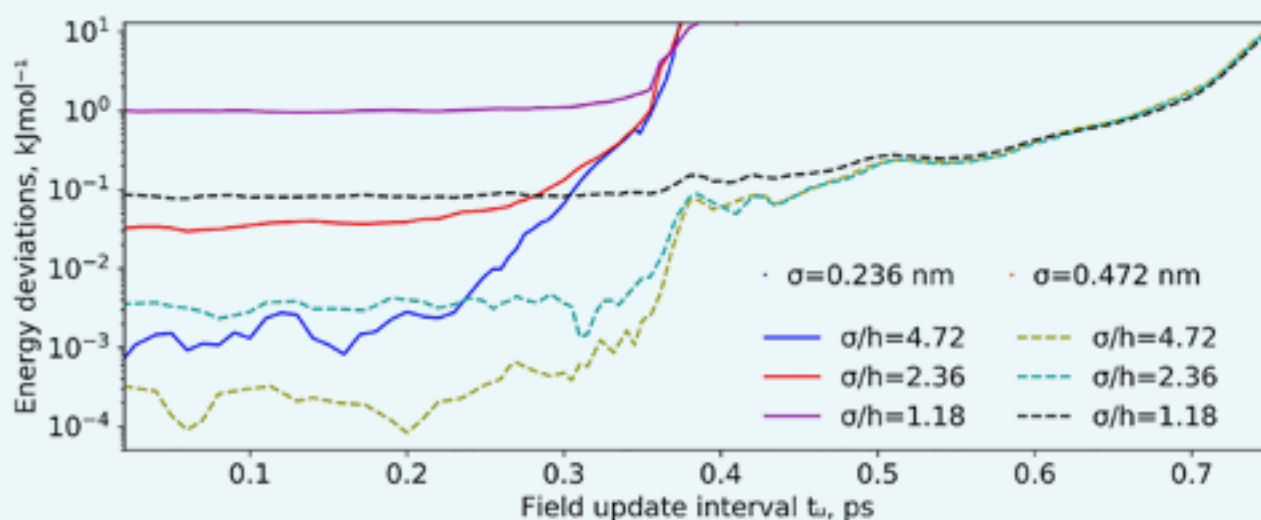
⊕ **Figure 2:** Conservation of the energy as a function of the multiple time-step interval t_u, the grid spacing h, and the spread σ.

formulation outperforms the original formulation of the hPF model with respect to energy conservation and, more generally, in the control of numerical errors leading to known aliases in the hPF model.

HyMD software

Most of our efforts in RT2 in 2021 were dedicated to the establishment of a software for HhPF simulations of molecular systems called Hylleraas-MD (HyMD) [3]; see Figure 1. The coding of the HyMD software was mostly done by PhD candidate Morten Ledum, with valuable contributions from postdoc Xinmeng Li, from PhD candidates Manuel Carrer and Samiran Sen, and from Bore, who is now postdoc at University of California San Diego (UCSD).

The need for a new software was motivated by the differences between the HhPF and original hPF formalisms, which call for different implementation strategies. First, all operations in the HyMD code are carried out in Fourier space, with no need for adopting and adjusting reciprocal particle-mesh routines. Second, in the HyMD code, we opted for a multiple-timestep reversible reference system propagation algorithm (r-RESPA) to treat the time propagation of the particles over fast-changing intramolecular and slow-changing intermolecular forces. The decision to abandon the traditional quasi-static approximation used in standard hPF implementations was again motivated by Ref. [2], where it is shown how the conservation of energy suffers from a systematic drift in the quasi-static approximation. Third, the HyMD code does not use shared memory, opting instead for a domain-decomposition parallelization strategy; see Figure 1.

The HyMD code is written in Python, with a few numerically intensive routines in Fortran. The first version of the HyMD code was released in December 2021 under a Lesser GPL v3.0 license, making it the first free open-source software for hPF simulations available to the community [3].

A manuscript recently submitted for publication describes the features and performance of the code [4]. There, we show how it is possible to simulate realistic molecular systems in the multi-phase while respecting rigorous mechanical laws – in particular, that it is possible to run HhPF simulations for molecular systems in a microcanonical ensemble. The conservation of energy is respected (within standard error-propagation in molecular-dynamics integrators), depending on a judicious choice of numerical grid spacing and intrinsic particle-density spread; see Figure 2.

A rigorous sampling of a canonical ensemble is obtained by coupling the
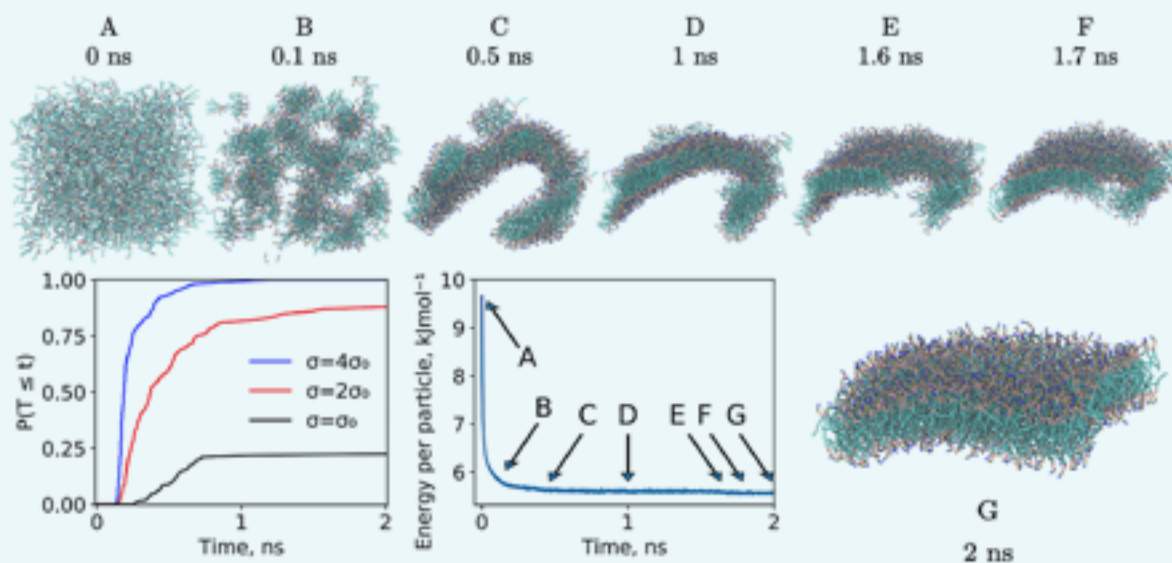
⊕ **Figure 3:** Top: self-aggregation of a DPPC bilayer.
Bottom: self-aggregation of a Lipid A vesicle.

correct NVE dynamics to a canonical-sampling velocity-rescaling (CSVR) thermostat. In this way, we can observe the expected ultrafast dynamics for these models, resulting in the capability of self-assembling lipid bilayers on the nanosecond scale (Figure 3, top). Importantly, we were able to self-assemble charged moieties like Lipid A vesicles (Figure 3, bottom) and charged surfactant micelles, which can be difficult also for standard CG models based on the Martini force field.

The current version of the HyMD code enables HhPF simulations in both NVE and NVT ensembles, incorporating an explicit treatment of electrostatics in a constant dielectric medium. The use of symbolic differentiation makes the code 'agnostic' with respect to the shape of the filter and to the form of the interaction-energy functional. As such, the code can easily be extended to any model that one may wish to implement.

The protocol for automated Bayesian optimization of hPF parameters for any molecular moiety [5] is provided as a utility tool.

Ongoing work involves performance optimization and the implementation of pressure coupling and electrostatics with variable dielectrics. The release of an updated version of the HyMD software is planned for 2022.

Funding / Personnel
In 2021, the RT2 group at UiO employed Dr. Henrique Musseli Cezar as postdoc to work on further development of the Hylleraas MD. The intention is to extend the code to diverse methodologies for multi-scale modelling − in particular, to Monte Carlo approaches.

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RT3

Spectroscopic Processes

Principal investigators:
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Thomas Bondo Pedersen
—
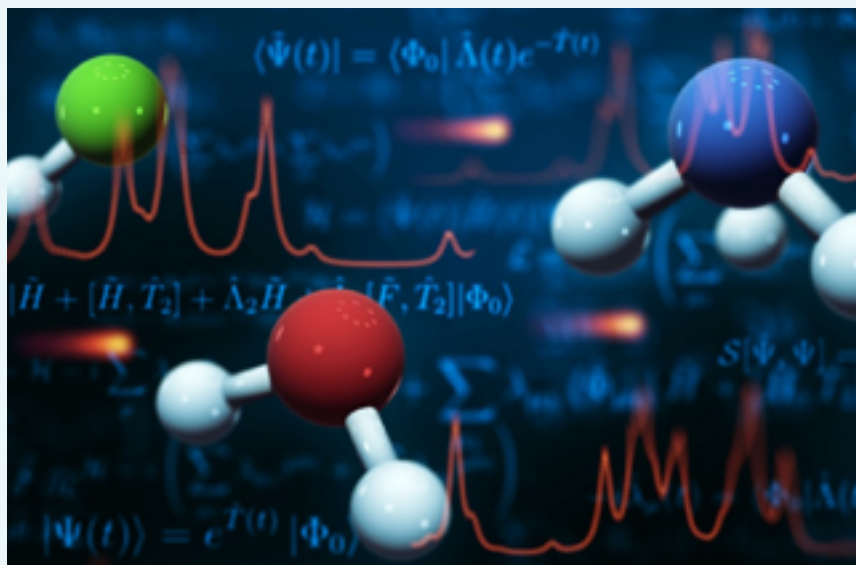
⊕ *Illustration by Sindre Bjøringsøy Johnsen and Håkon Emil Kristiansen.*

The goal of RT3 is to model the interactions between complex systems and electromagnetic fields in a wide frequency range. During 2021, we made significant progress in this area, with emphasis on two main developments: the study of real-time dynamics of electrons and nuclei induced by laser pulses with or without the Born–Oppenheimer approximation, and the study of spectroscopic processes of molecular systems using advanced relativistic methods. —

Laser-driven many-electron dynamics
Laser-driven many-electron dynamics has in 2021 remained a major topic in RT3, where we have developed time-dependent coupled-cluster (TDCC) models in a project led by Thomas Bondo Pedersen and Simen Kvaal. Besides Pedersen and Kvaal, project participants in 2021 were master student Eirill Hauge and PhD candidates Håkon Emil

Kristiansen, Benedicte Ofstad, Einar Aurbakken, Øyvind Sigmundson Schøyen, and Jonas Boym Flaten. The latter two are PhD candidates at the Department of Physics, UiO, co-supervised by Pedersen. Hauge, who graduated in December 2021, was awarded the prize for best master thesis at the Department of Chemistry at the University of Oslo, for her dissertation

Extrapolating the Electric Dipole Moment – Improving the Resolution of Absorption Spectra from Real-Time Time-Dependent Coupled-Cluster Theory, while Kristiansen will defend his PhD thesis in May 2022.

In RT3, we work with several flavours of TDCC theory. In addition to conventional TDCC theory based on time-independent Hartree–Fock orbitals, we work with time-dependent orbital-optimized CC (TDOCC) theory based on time-dependent orthonormal orbitals [1], and time-dependent nonorthogonal orbital-optimized CC (TDNOCC) [2] and orbital-adaptive time-dependent CC (OATDCC) [3] theories based on time-dependent biorthonormal orbitals. There are several advantages of using time-dependent orbitals such as improved numerical stability for simulations of many-electron dynamics driven by high-intensity lasers [4]
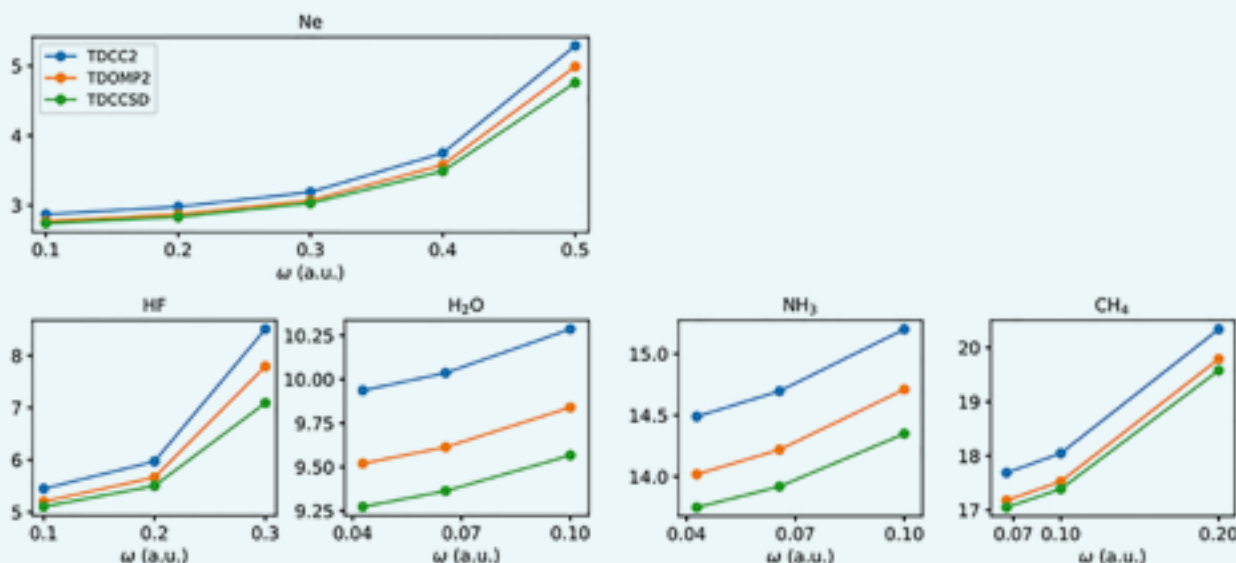
⊕ **Figure 1:** Isotropic electric-dipole polarizabilities from CC simulations.
Illustration: Thomas Bondo Pedersen and Håkon Emil Kristiansen.

and the preservation of gauge invariance [1–3,5]. More importantly, time-dependent orbitals pave the way for simulations of strong-field phenomena such as ionization and high-harmonic generation.

The cluster operators are in all cases truncated after single and double excitations to yield the TDCCSD, TDOCCD, and TDNOCCD models. Although accurate, simulations performed with these models are computationally demanding, scaling as $O(N^6)$ where N is a measure of system size. Rather than aiming for even higher accuracy at significantly increased computational cost by including triple excitations, we have in 2021 derived and implemented working equations for the TDCC2 and TDOMP2 models, which are second-order approximations to the TDCCSD and TDOCCD models, respectively. The TDCC2 [6] and TDOMP2 [7] models

show a more benign $O(N^5)$ scaling, which enables simulations of larger molecules. Furthermore, their relative simplicity makes them excellent candidates for a 10 to 100-fold acceleration by commonly used techniques in quantum chemistry – in particular, by integral-factorization algorithms previously developed and used with great success by several researchers at the Hylleraas Centre for time-independent methods. In the future, we plan to exploit such techniques to significantly increase the size of molecules that can be routinely treated at the TDCC level of theory.

In 2021, we have validated the TDCCSD, TDCC2, and TDOMP2 implementations for a series of 10-electron molecules by computing valence- and core-excitation spectra, dynamic electric-dipole polarizabilities, and the diagonal components of dynamic hyperpolarizabilities char-

acterizing the nonlinear optical processes of second harmonic generation and optical rectification. The results were compared with those obtained from conventional frequency-dependent CC2 and CCSD response theory. Our investigations revealed that, in the transparent spectral regions, the full orbital relaxation of TDOMP2 theory generally yields polarizabilities and hyperpolarizabilities in closer agreement with TDCCSD theory than does TDCC2 theory (Figure 1). The TDOMP2 spectra, on the other hand, are virtually identical to the TDCC2 spectra [8].

In collaboration with Assoc. Prof. II Stella Stopkowicz and Assoc. Prof. II Andrew Teale, we have investigated laser-driven many-electron dynamics in the presence of static, uniform magnetic fields, which are treated nonperturbatively using Teale's QUEST software to generate the prerequisite
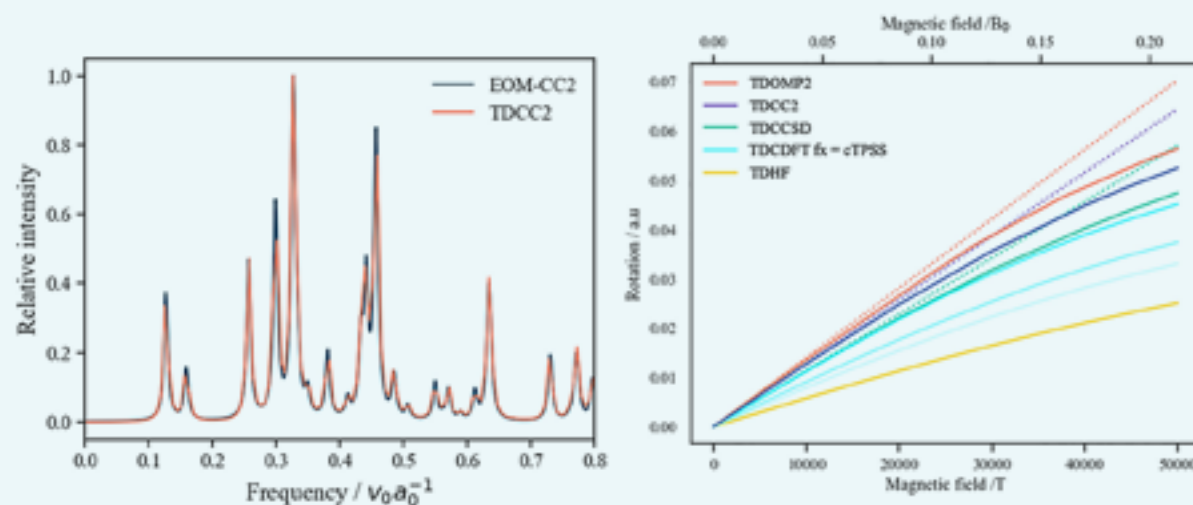
⊕ **Figure 2:** Left: Absorption spectra from equation-of-motion CC2 (EOM-CC2) theory and from TDCC2 simulations of LiH with the aug-cc-pVTZ basis set in a magnetic field of strength $B = 0.2B_0$ parallel to the bond axis. Right: Magnetic optical rotation of HF as a function of magnetic-field strength from time-dependent wave-function theories and from TDCDFT with the aug-cc-pVDZ basis set. The dotted lines show Verdet's linear approximation. *Illustration: Benedicte Ofstad.*

Hamiltonian integrals in a basis of complex London orbitals. In this case, too, we have validated our implementation by comparing valence spectra obtained from TDCC2 and TDCCSD simulations with those obtained from equation-of-motion CC theory by Stopkowicz.

The main purpose of the project, however, is to exploit the nonperturbative treatment of magnetic fields to investigate the range of validity of Verdet's description of the Faraday effect, which is exploited to measure magnetic field strengths in the interstellar medium and to design devices used for high-power laser systems. According to Verdet, the optical rotation angle depends linearly on the magnetic field strength, which translates into a quantum-mechanical first-order perturbation treatment. Completely avoiding the

perturbation expansion, we can compute the Faraday rotation angle by extracting electric-dipole polarizabilities from simulations in the presence of static, uniform magnetic fields of strengths up to one atomic unit ($B_0 \sim$ 235 000 Tesla) and, hence, determine the magnetic field strength at which Verdet's linear formulation breaks down.

In addition to the TDCCSD, TDCC2, and TDOMP2 methods, we use time-dependent current density-functional theory (TDCDFT) methods recently developed by Teale and co-workers, thus providing benchmark results for the latter. Examples are shown in Figure 2.

The simulated valence- and core-excitation spectra are generated by applying a weak electric-field impulse

to the electronic system in its ground state, followed by recording the induced dipole moment over time to reveal the oscillation frequencies (excitation energies of the electronic system) and their amplitudes (spectral intensities) by means of a Fourier transformation. This procedure requires very long simulation times to produce sufficient spectral resolution, and the project of MSc Eirill Hauge was aimed at reducing the simulation time through extrapolation of the induced dipole moment. The proposed extrapolation algorithm, which is based on a combination of Fourier–Padé approximants, unsupervised machine learning, and sinusoidal curve fitting, yields up to 10-fold reduction of simulation times for simple test cases with the TDCCSD method.

In collaboration with Dr. Michal Repisky, Dr. Marius Kadek, and Dr. Lukas
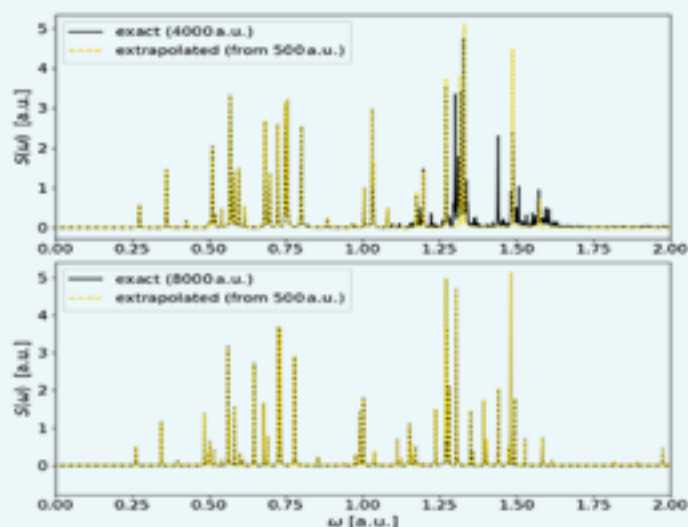
Figure 3: TDCCSD (top) and TDDFT (bottom) absorption spectra of the water molecule from full simulations and from dipole extrapolation. *Illustration: Eirill Hauge.*
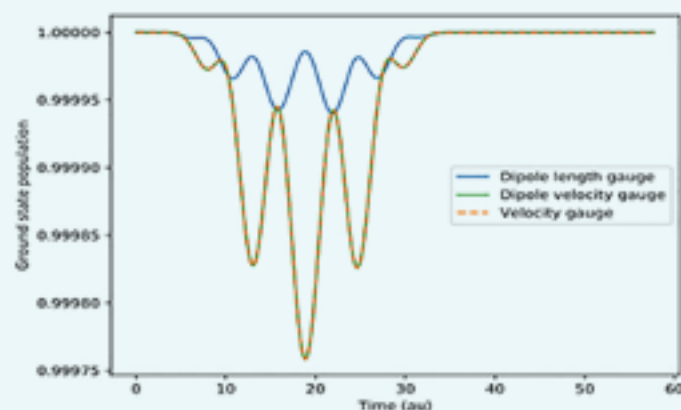
Figure 4: Gauge-dependence of the TDCCSD/aug-cc-pVDZ ground-state population of the He atom during interaction with a laser pulse. *Illustration: Einar Aurbakken.*

Konecny at UiT, a manuscript is in preparation where the extrapolation technique is used in conjunction with time-dependent density-functional theory (TDDFT), which is the workhorse of real-time time-dependent electronic-structure theory, as well as TDCCSD, TDCC2, and TDOMP2 theories. An example is shown in Figure 3 for the water molecule in the aug-cc-pVDZ basis.

In these studies, the interaction between the electrons and the external electromagnetic field has been described within the electric-dipole approximation in the length gauge. There is, however, no computational penalty associated with using the exact (*i.e.*, not multipole-expanded) semiclassical interaction between the electrons and laser fields in explicitly time-dependent simulations. Therefore, we have in 2021 collaborated with Prof. Roland Lindh,

Uppsala University, Sweden, on establishing a new interface between our TDCC code and the OpenMolcas software package, which provides the integrals for the exact semiclassical interaction. Use of the exact interaction in simulations implies that the effects of the nonuniform electric and magnetic components of laser fields are fully included, allowing electric-dipole forbidden states to participate in the dynamics.

Our initial investigations of exact semiclassical many-electron dynamics have been hampered by issues related to gauge invariance. In particular, the calculation of stationary-state populations cannot be done as proposed in Ref. [9] during exact interaction with laser pulses due to gauge dependence; see Figure 4 for the TDCCSD ground-state population of the He atom exposed

to a laser pulse described in the dipole approximation in the length and velocity gauges and with the exact semiclassical interaction (labelled velocity gauge in the figure). Also, the simulation of transient pump-probe spectra based on a frequency analysis of the energy transfer between lasers and electrons requires a gauge-invariant time-dependent energy operator consistent with the electrodynamical work done by the fields on the electrons. In contrast to formulations in the recent literature, this energy operator is not equal to the Hamiltonian. With these issues resolved, we are currently simulating transient pump-probe X-ray absorption spectroscopy using the exact semiclassical interaction. Our findings will be submitted for publication in 2022.
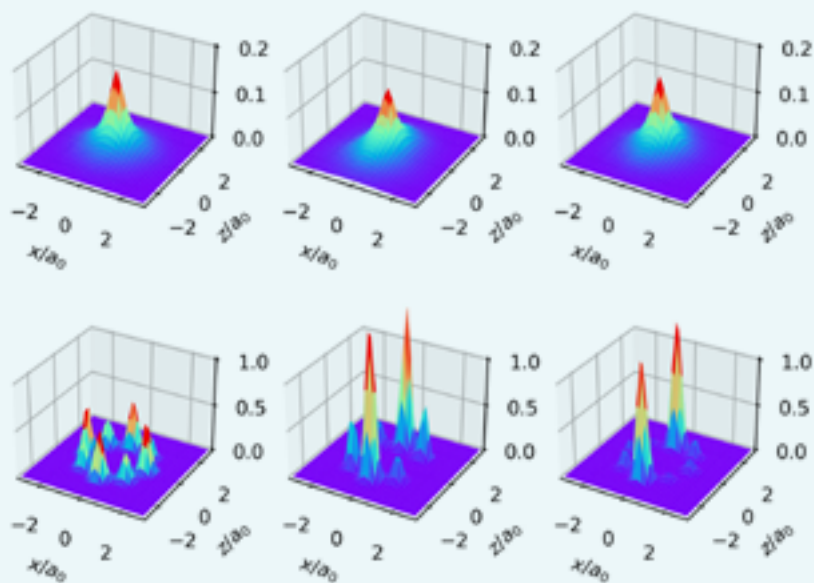
Figure 5: Non-Born–Oppenheimer pseudo-electron (top) and pseudo-proton (bottom) densities of HD plotted in the *xz*-plane with deuterium at the origin of the internal coordinate system: initial ground-state densities to the left, at peak laser intensity in the middle, and after the laser pulse to the right. The final state is oriented with the pseudo-proton probability almost exclusively located close to the *z*-axis, which is defined as the polarization direction of the laser pulse. *Illustration: Thomas Bondo Pedersen.*

CAS project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation*

The 2021/2022 CAS project *Attosecond Quantum Dynamics Beyond the Born–Oppenheimer Approximation (ATTODYN)*, led by Kvaal and Pedersen, has been a central component of RT3 in the second half of 2021, where the core CAS fellows were Prof. Ludwik Adamowicz, University of Arizona, USA, and Prof. Caroline Lasser, Technische Universität München, Germany. In the ATTODYN project we treat electronic and nuclear degrees of freedom on the same quantum-mechanical footing without Born–Oppenheimer separation using explicitly correlated Gaussian (ECG) basis functions. In a proof-of-principle study to be submitted for publication in 2022, we have used Adamowicz' code for time-independent calculations to optimize a polarized minimal basis set of 990 ECGs distributed on a coarse spherical grid for the HD molecule. This basis was used to expand the time-dependent wave function, which was propagated according to the full molecular Schrödinger equation in the presence of an external laser field. The interaction of the fully correlated rovibronic internal motion with a 100-cycle laser pulse with carrier wavelength 94.4 nm and peak intensity 3.51 TW/cm² leads to an effective orientation of the HD molecule along the polarization direction (*z*-axis) of the laser. Figure 5 shows snapshots of the simulation in which the HD molecule is initially in its ground state and the final oriented state is a superposition of 48 rovibronic stationary states. The total simulation time is 34 fs.

The only significant approximation in this study of the orientation of the HD molecule by a laser field is the choice of basis. While 990 basis functions may seem large, the basis set is too small to yield quantitative results. Accurate simulations would require either much larger basis sets or a much more flexible parameterization, where the nonlinear basis parameters (complex width matrices, positions, and momenta) are propagated along with the linear expansion parameters. We have opted for the latter, generalizing the ECG parameterization based on Gaussian wave packets (GWPs). The GWPs are often used for semiclassical nuclear quantum dynamics, most often in the frozen formulation, where the width is kept fixed for numerical stability. Initially, we have experimented with fully flexible GWPs as basis functions for expansion of the wave function of a single electron in a model potential mimicking the hydrogen atom. Exposed to an extreme-
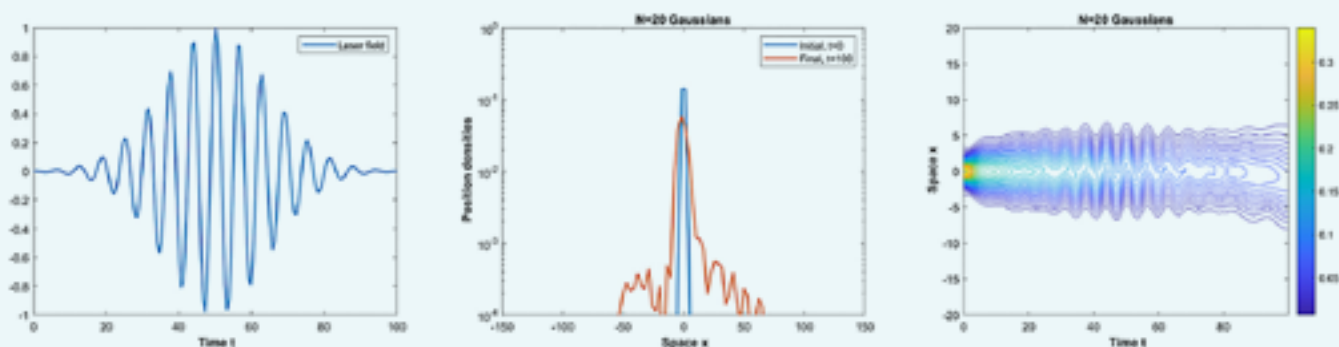
Figure 6: Simulation of a single electron in a model potential exposed to the laser field plotted in the left-hand panel. The middle panel shows the initial (ground state, blue) and final (red) densities on a logarithmic scale. The right-hand panel shows density contours as a function of time. The time-dependent wave function is expanded in a basis of 20 time-dependent GWPs. *Illustration: Caroline Lasser.*

ly intense, nonresonant laser pulse, strong-field phenomena such as ionization and high harmonic generation is induced and the wave function rapidly changes from being localized within the model potential to being significantly spread over wide ranges, up to several hundred bohrs. An example is shown in Figure 6. As might be anticipated, the integration of the time-dependent Schrödinger equation poses significant numerical challenges for such processes. We have made considerable progress in this direction and two manuscripts on GWPs for quantum dynamics are currently in preparation and will be submitted in 2022.

Relativistic calculation and interpretation of spectroscopic parameters
Relativistic calculation and interpretation of spectroscopic parameters represent another long-term project

pursued within RT3. The relativistic methodology based on the Dirac four-component formalism has been developed and implemented in the in-house quantum-chemistry program ReSpect, with details published in a 2020 article [10] and described in the 2020 Annual Report of the Hylleraas Centre. We have continued the methodological developments, with applications to chemically relevant systems.

In a project led by Lukas Konecny and Michal Repisky, focus has been on the accurate calculation and interpretation of X-ray spectra where the relevant absorption, emission, and scattering processes involve core orbitals, for which relativistic corrections are indispensable. This includes scalar relativistic effects manifested by shifts of orbital energies and large spin–orbit splittings in the case of core p and d

orbitals. The spin–orbit splittings, observed in spectra near $L_{2,3}$-, $M_{2,3}$- and $M_{4,5}$ edges, call for an accurate multi-component relativistic methodology from the outset. ReSpect is one of the very few programs that offer such capabilities.

In collaboration with Jan Vicha from the Tomas Bata University in Zlin, the Czech Republic, and Stanislav Komorovsky from the Slovak Academy of Sciences in Bratislava, Slovakia, a team of researchers from the Hylleraas Centre performed an extensive theoretical study of X-ray absorption spectroscopy (XAS) parameters. The study was published in *Inorganic Chemistry* [11] and focused on transition-metal and actinide compounds with different central atoms, ligands, and oxidation states, employing the relativistic damped-response time-dependent density-

4c-DR-TDDFT

✔ scalar relativistic effects
✔ spin–orbit coupling
✔ direct access to X-ray spectra
✔ large systems
✔ interpretation
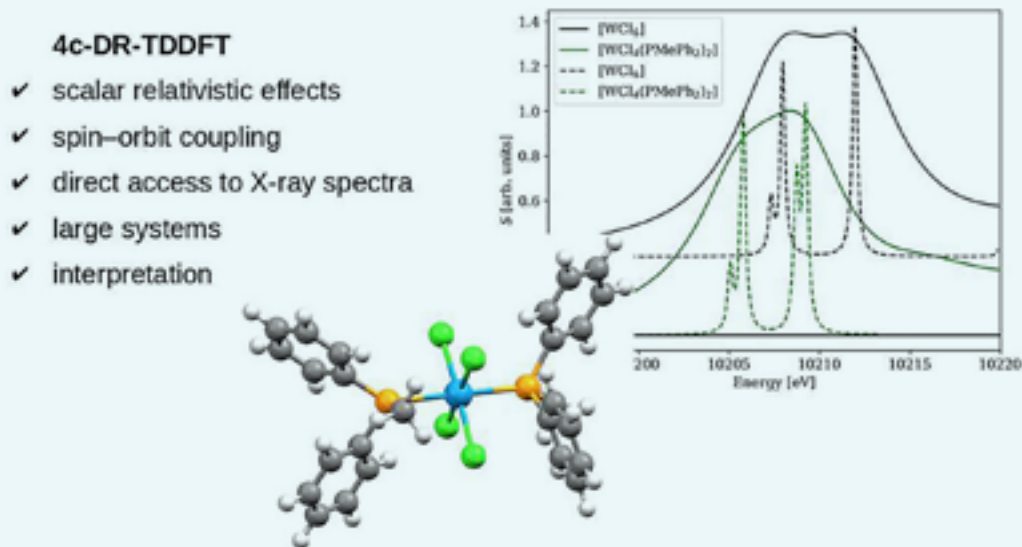
Figure 7: Tungsten IV complex $WCl_4(PMePh_2)_2$ (left) and its X-ray absorption spectrum near W L_2-edge compared with the spectrum of tungsten VI compound WCl_6 [11]. The spectra were calculated using four-component relativistic DR-TDDFT with the aim to reproduce experimental line shape (solid lines), which were then resolved into individual transitions (dashed lines) by changing the damping parameter. The number of spectral lines reflects the occupancy and ligand-field-influenced degeneracy of tungsten 5d orbitals as well as allowed and forbidden transitions in these complexes. *Reproduced from Ref. [11] under CC-BY 4.0 license.*

functional theory (DR-TDDFT) method based on the four-component Dirac–Coulomb Hamiltonian developed at the Hylleraas Centre [12]; see Figure 7. Due to the high-level description of relativistic effects, their contribution to the XAS parameters may be considered solved and disentangled from the effect of the electronic-structure model, which also affects the accuracy of the calculated spectra.

Our study revealed a near linear dependence of the spectral shift on the amount of Hartree–Fock exchange in the hybrid exchange–correlation functional, where a prescription of 60% admixture for spectral regions above 1000 eV offered an excellent accuracy both for absolute peak positions and spin–orbit splittings. This simple protocol combined with the use of a relativistic Hamiltonian allows XAS spectra to be obtained computationally within

the experimental spectral range, without the need to apply an empirical shift. Furthermore, thanks to the algorithmic improvements in the ReSpect program, the current relativistic methodology can routinely be applied to heavy-metal complexes with more than 50 atoms. The damped-response technique has allowed experimental spectra to be reproduced and broad peaks to be resolved into well-separated spectral lines, and their interpretation was achieved in terms of molecular-orbital transitions and double point-group symmetry.

Further research has now focused on the application of a recently developed quasi-relativistic two-component X2C Hamiltonian to XAS. While the simplest one-electron X2C approach overestimates the spin–orbit splittings and suffers from additional shifts of spectral lines, the advanced atomic-mean-field

X2C (amfX2C) approach reproduces faithfully four-component results and offers order-of-magnitude savings in computational time. Manuscripts related to the amfX2C Hamiltonian and its application to XAS will be submitted for publication in 2022. Additional efforts in the development and applications of relativistic methods currently in progress at the Hylleraas Centre include the work on alternative solvers for the damped-response equations and their application to X-ray chiroptical spectroscopies pursued in collaboration with researchers at KTH in Stockholm, Sweden.

While delocalized canonical molecular orbitals (MOs) resulting from a standard mean-field Hartree–Fock or Kohn–Sham calculation are useful for understanding electronic excitations and spectroscopic processes, it is of interest to consider localized MOs (LMOs) when

relating first-principles calculations to simple intuitive models of chemical bonding. In addition, localization of MOs is important for local-correlation treatments beyond the mean-field approximations.

In 2021, Michal Repisky in collaboration with Bruno Senjean (University of Leiden, The Netherlands), Gerald Knizia (Pennsylvania State University, USA), and Lucas Visscher (Vrije Universiteit, The Netherlands) published a work that generalizes the concept of intrinsic atomic and bonding orbitals [13] to the relativistic case using complex and quaternion spinors [14]. The proposed methodology has additionally been extended from atomic to molecular fragments, enabling calculations on complex systems to be performed in the reduced orbital-space extent (ROSE), which consists of localized occupied and valence-virtual orbitals. As the intrinsic orbitals form a minimal polarized basis, they are not tied to the parent atomic basis sets and provide a good representation of chemical bonding as well as an effective configurational basis for correlation methods. This scheme has been implemented into a standalone open-source library (ROSE), interfaced with several quantum-chemistry packages (Psi4, ADF, PySCF, DIRAC, ReSpect), and applied to systems of increasing complexity including complexes of heavy elements.

While often sufficiently accurate, DFT does not allow a systematic improvement of its accuracy. This is possible for wave-function-based methods such as the CC method, for which extensions of the single-particle basis combined with an increase in the excitation level leads to systematic accuracy improvements. In relativistic quantum chemistry, the increase in the number of correlated electrons and the switch from real to complex algebra combine to make relativistic CC calculations

demanding. On the other hand, the CC method is well suited to the deployment on supercomputers because its key algorithmic steps can be formulated as contractions of large tensors, which can be carried out with a high computational efficiency.

To realize the full potential of reduced-scaling techniques and parallel computing, it is advantageous to create a modern implementation of the relativistic CC algorithm. Michal Repisky and collaborators reported last year a re-implementation of the core algorithms of relativistic CC theory aimed at modern heterogeneous high-performance computational infrastructures [15]. The code is designed for efficient parallel execution on many compute nodes with optional GPU co-processing, accomplished via a new ExaTENSOR back end developed at the Oak Ridge Leadership Computing Facility (OLCF) by Dmitry Lyakh. The resulting ExaCorr module is primarily intended for CC calculations of electronic structure and properties of molecules with one or more heavy elements, as relativistic effects are included from the outset. The module was designed as a stand-alone program requiring a set of molecular spinor coefficients as a starting point but is also interfaced to the DIRAC and ReSpect programs, which can be used to generate these coefficients.

The year 2021 saw the publication of the main article of the PhD thesis of Dr. Karen Dundas, on the analytic calculation of infrared and Raman vibrational spectra of solvated systems in a polarizable-embedding approach [16]. This atomistic approach allows specific, directional interactions such as hydrogen bonds to be described for solvated molecules, making it possible to address the effects of solvent dynamics and solute–solvent interactions on vibrational band shapes and leading to a greater level of detail in the understand-

ing of vibrational spectra than that offered by dielectric continuum models. The approach was described as a highlight in the 2020 Annual Report of the Hylleraas Centre. Whereas anharmonic corrections can be included at the Hartree–Fock level of theory, we have run into challenges at the level of DFT, most likely due to an increased importance of grid-weight derivatives. Dr. Magnus Ringholm is pursuing this challenge with the aim of calculating grid-weight derivatives at any order using automatic differentiation, as previously applied by us for calculating high-order derivatives of exchange–correlation kernels [17].

Together with Assoc. Prof. Swapan Chakrabarti at the University of Kolkata, Kenneth Ruud has continued the study of photophysical properties of transition-metal complexes. In addition to a comprehensive review of this field of research [18], a study has been published that rationalizes the observed vibrational coherence transfer from the lowest singlet-excited state to the lowest triplet-excited state [19] for a platinum complex, $[Pt_2(P_2O_5H_2)_4]^{4-}$. It was found that the spin–orbit coupling between these singlet and triplet states is negligible and therefore cannot explain the vibrational coherence transfer. Instead, it was shown that spin–vibronic interaction is sufficient to explain the observed effect, but that the vibrational transfer goes through the second-lowest triplet state, followed by internal conversion to the lowest triplet state. This is the first documented case of substantial spin–vibronic interactions and can thus form the basis for the development of novel photocatalysts.

Ruud has together with Prof. Magdalena Pecul and her PhD candidate Katarzyna Jakubowska at the University of Warsaw studied relativistic effects on the vibrational frequencies
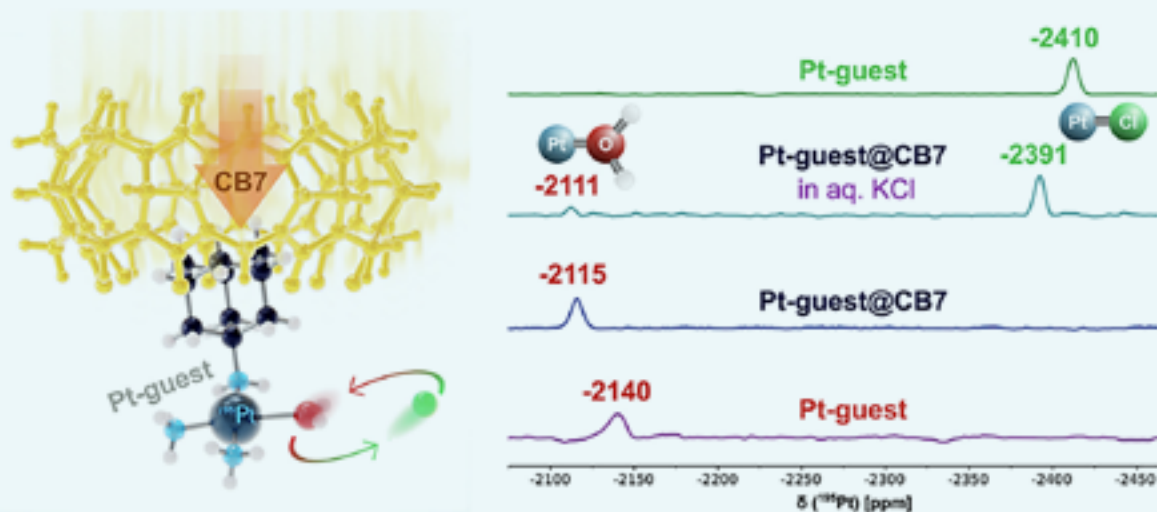
Figure 8: NMR simulations of [195]Pt NMR spectra for platinum complexes encapsulated by the CB7 macrocycle. *Illustration: Abril Castro.*

of the group-14, -15 and -16 hydrides, as well as the $HCCPbH_3$ molecule, going beyond the diatomic molecules that have mostly been studied so far. In general, only the heaviest congeners display significant relativistic effects, which are mostly scalar in nature. The study of $HCCPbH_3$ suggests that only those vibrational modes that involve the heavy element are noticeably affected by relativity.

In the PhD work of Karolina Di Remigio Eikås, a reliable protocol for the calculation of vibrational circular-dichroism spectra for conformationally flexible molecules has been established, focusing on cyclic oligopeptides. Our protocol is based on the conformer–rotamer ensemble sampling tool (CREST) of Grimme and coworkers [21,22]. Using this protocol, we have investigated whether the sensitivity of vibrational circular dichroism would allow the absolute stereochemistry to be unam-

biguously determined as the number of peptides (and hence chiral centres) increases. Preliminary results suggest that this may not be possible. We are currently exploring whether Raman optical activity may aid in obtaining this structural information.

Dr. Julie Héron, who defended her PhD thesis on November 18 2021, collaborated with a number of international researchers in the study of paramagnetic NMR parameters in a series of actinide complexes [$An^{IV}O_2^{2+}$-dipicolinc acid (An = Np, Pu)], with emphasis on the temperature dependence of the proton shielding constants [23]. The combination of open-shell species together with large relativistic effects in actinide compounds makes this a computationally challenging task. Using spin–orbit-coupled restricted-active-space second-order perturbation theory (SO-RASPT2), experimental data were reproduced and analysed. The

latter was particularly important as the results deviated from the expected temperature dependence but could be rationalized based on the computational results.

Hylleraas MSCA postdoctoral fellow Dr. Abril Castro, together with Hylleraas researcher Dr. Michal Repisky and the group of Prof. Radek Marek in The Czech Republic, set out to explore the predictive capabilities of relativistic [195]Pt NMR chemical shift calculations in supramolecular host–guest anticancer drugs [24]. The encapsulation process in the cucurbit[7]uril macrocycle was found to promote the stability of the hydrolysed cationic platinum(II) compounds. Notably, the calculated [195]Pt NMR chemical shifts of the free and encapsulated species provided a valuable tool to interpret the observed structural changes manifested in the NMR spectra (Figure 8).

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RT4

Extreme Environments

Principal investigators:
Trygve Helgaker and Kenneth Ruud
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In 2021, we continued to explore the exotic, squeezed chemistry of ultrastrong magnetic fields and high pressure. Apart from formal developments in current-density functional theory, we introduced several new computational methods and techniques for molecules in a magnetic field, including methods for calculating excited states within a self-consistent field scheme, for geometry optimizations, and for electronic and molecular dynamics. Each methodological development was accompanied by applications, which revealed intriguing new aspects of chemistry in an ultrastrong magnetic field.

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The nine papers published within RT4 in 2021 concern molecular dia- and paramagnetism in a nonuniform magnetic field [1], the fundamentals of current-density functional theory (CDFT) [2–3], self-consistent field methods for

excited states in a magnetic field [4], induced currents in a strong magnetic field [5], geometry optimization in a strong magnetic field [6], molecular dynamics in a magnetic field [7–8], and electron dynamics in a strong magnetic field [9].

Molecules in nonuniform magnetic fields
The article *Benchmarking Density Functional Approximations for Diamagnetic and Paramagnetic Molecules in Nonuniform Magnetic Fields,* by Sangita Sen and Erik Tellgren [1], was published in 2021 but discussed in the 2020 Annual Report and is therefore not considered further here.

Current-density functional theory
Part of the work in RT4 concerns the generalization and development of density-functional theory for molecular calculations in a finite magnetic field — in particular, we have developed current-density-functional theory (CDFT) into a practical method for molecular calculations in a magnetic field. We have previously not only presented the first implementation of CDFT for mo-

lecular calculations in a magnetic field and shown that meta-GGA functionals are well suited for such calculations — we have also made several important theoretical contributions to CDFT, including the development of a Lieb-type convex formulation of the theory [10,11]. In 2021, we showed that the constrained-search functional of CDFT is lower semi-continuous [2], thereby demonstrating its equivalence with the Lieb functional [12]. In a second paper, the role of the total current density in CDFT was clarified [3]. These developments are discussed in more detail in RT1 and are not considered further here.

Excited electron states
Electronic states evolve in a complicated manner with increasing field strength, resulting in a complete reordering of states in the intermediate field regime — that is, at about one atomic unit field strength, B_0 = 235 kT. It is therefore important to be able to calculate such states efficiently. Up until now, excited electronic states have been calculated using full configuration-interaction (FCI) theory [13] or using coupled-cluster (CC) theory [14] and equation-of-motion
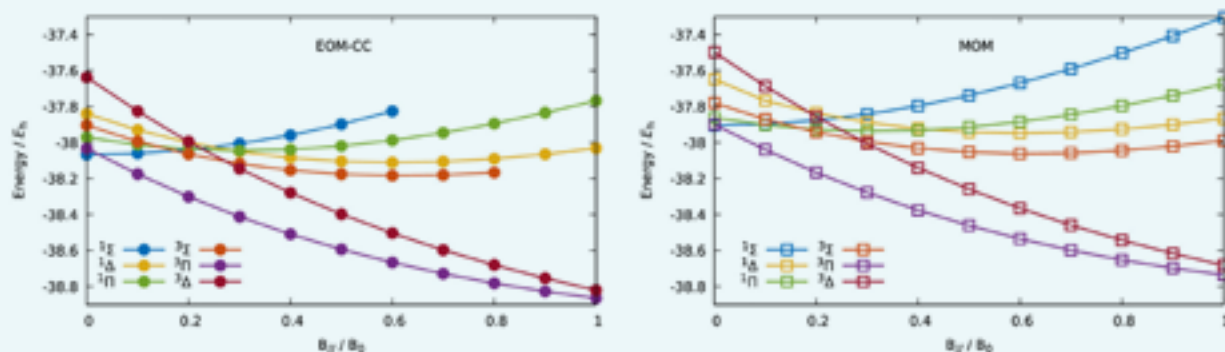
⊙ **Figure 1:** Total energies computed with EOM-CCSD (left) [15] and the MOM-Hartree–Fock (right) [4] methods for CH$^+$ in the u-aug-cc-pCVQZ/AutoAux basis in a magnetic field parallel to the molecular axis. *Reproduced from Ref. [4] under CC-BY 4.0 license.*
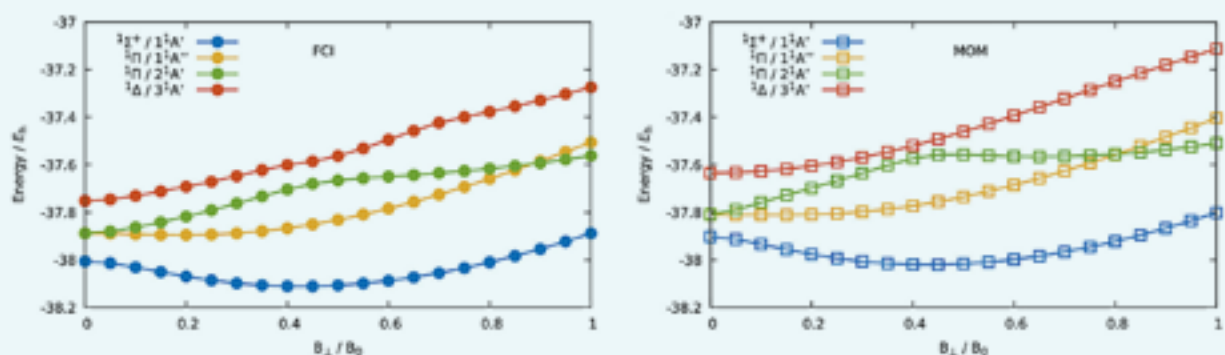
⊙ **Figure 2:** Total energies computed with FCI (left) [16] and the MOM-Hartree–Fock (right) [4] theories for CH$^+$ in the cc-pVDZ/AutoAux basis in a magnetic field perpendicular to the molecular axis. *Reproduced from Ref. [4] under CC-BY 4.0 license.*

coupled-cluster (EOM-CC) theory [15,16]. An important development in 2021 was the implementation of the maximum-overlap method (MOM) for self-consistent field (SCF) methods in a strong magnetic field [4]. Whereas SCF calculations usually converge to ground states (in agreement with the Aufbau principle), MOM avoids collapse to the ground state by constraining orbital occupations.

Using MOM, we will be able to describe excited electronic states more efficiently than before, at a reasonable accuracy. This development is particularly important for molecular dynamics (discussed later in this RT report) as it enables realistic studies of electronic transitions by surface hopping. In Ref. [4], MOM was used at the Hartree–Fock level of theory for a series of small molecules, comparing with high-level FCI

and EOM-CCSD results. Importantly, MOM shows promising performance for excited states under these conditions, yielding results consistent with available benchmark data for a diverse range of electronic states – see Figures 1 and 2 for the lowest electronic states of CH$^+$, a paramagnetic closed-shell molecule that is a good candidate for detection on white dwarf stars.
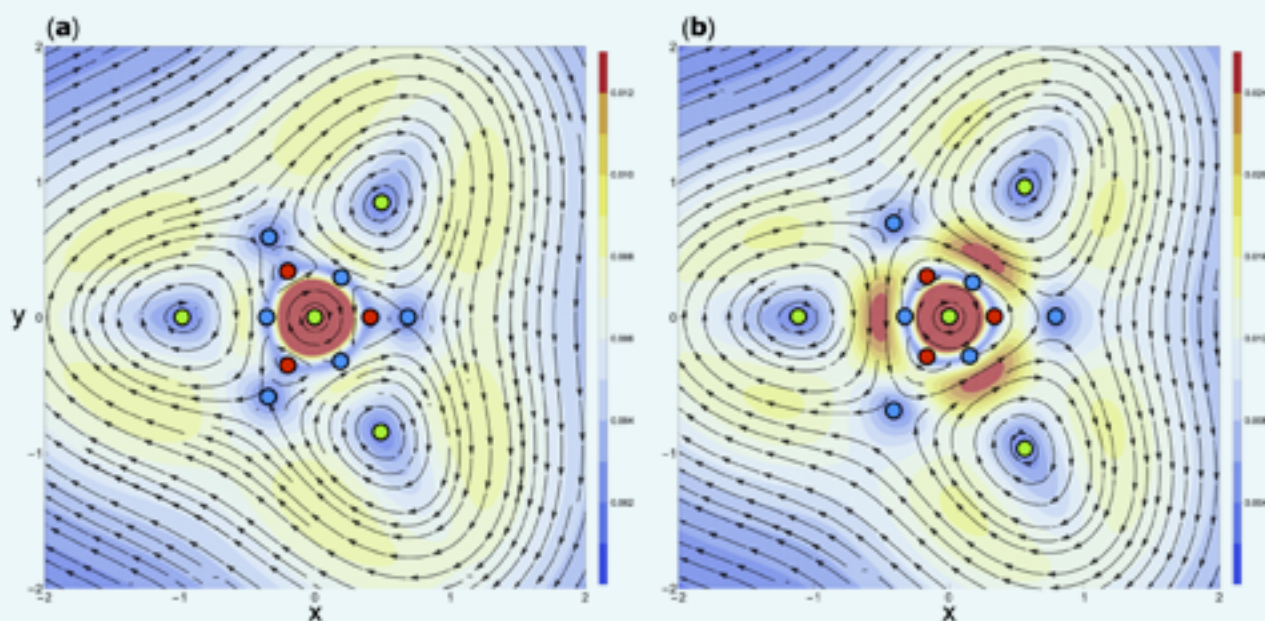
Figure 3: Streamline plots of the current density **j**, with contours of its norm, in the *xy*-plane of the CH_4 molecule in a magnetic field of (a) $0.1B_0$ and (b) $0.2B_0$ along the *z*-axis [5]. Paratropic vortex lines are shown as red circles, diatropic vortex lines as green circles and saddle lines as blue circle. *Reproduced from Ref. [5] under CC-BY 4.0 license.*

Induced currents

A magnetic field induces currents among the electrons in a molecule – in fact, such currents are responsible for the binding of atoms in a strong magnetic field [13]. To be able to understand and interpret the induced currents is therefore important for an appreciation of molecular and electronic structure in a magnetic field.

However, plots of induced currents are often complicated and difficult to analyse. A useful tool for analysing the main topological features of the vector fields associated with magnetically induced currents are stagnation graphs, built up from stagnation points (*i.e.*, points in space where the currents vanish). Such graphs have for a long time been calculated using response theory, as appropriate for weak magnetic fields. In Ref. [5], stagnation graphs have for the first time been cal-

culated in a nonperturbative manner, using CDFT, as appropriate for molecules in a strong magnetic field. The stagnation points of the nonperturbatively calculated currents are identified robustly, using a trust-region second-order optimization method. Our calculations reveal subtle changes in the response to the applied field when the symmetry of the molecule remains constant in the field. By contrast, when the electronic state and symmetry of the equilibrium geometry change with increasing field strength, then the changes in the stagnation graph are substantial.

In Figure 3, the induced currents in CH_4 are plotted in a plane normal to the applied magnetic field, revealing a complicated pattern of diatropic (clockwise) and paratropic (anticlockwise) currents. The positions of the stagnation points are marked by green circles (part of

diatropic vortex lines), by red circles (part of paratropic vortex lines), and by blue circles (part of saddle lines). The marked stagnation points make it easier to make sense of the complicated currents in the system and to understand the changes that occur as the field strength increases – in this case, the paratropic vortices move towards the carbon atom with increasing field strength.

Geometries

For the optimization of molecular structure in a magnetic field, efficient evaluation of molecular gradients (the derivatives of the molecular energy with respect to the positions of the nuclei) is essential. We have previously implemented molecular gradients in the LONDON program package [17] at the Hartree–Fock level of theory. With the implementation of CDFT molecular gradients in the QUEST package [6],
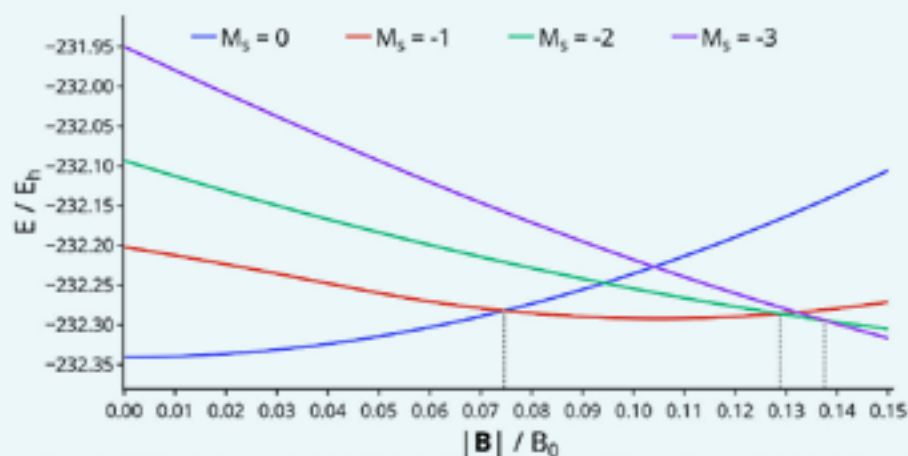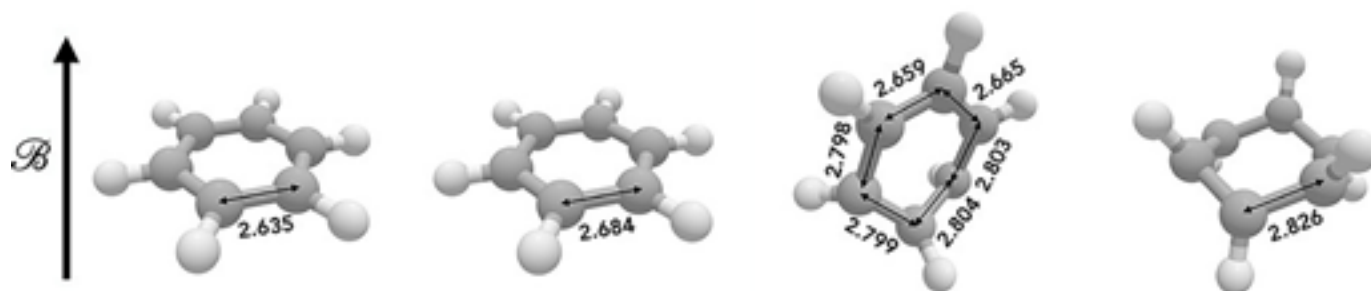
Figure 5: Optimized CDFT geometries of benzene with $M_s = 0$, $M_s = -1$, $M_s = -2$, and $M_s = -3$ (left to right) at field strength $0.1B_0$, calculated with the cTPSS meta-GGA functional [6]. Carbon–carbon bond lengths are given in units of bohr. *Reproduced from Ref. [6] under CC-BY 4.0 license.*

we are now able to carry out geometry optimizations more efficiently, for larger systems and for excited states, with the inclusion of dynamical correlation.

In the new implementation, the integral derivatives are constructed using a hybrid McMurchie–Davidson and Rys quadrature approach, combining the amenability of the former to the evaluation of derivative integrals with the efficiency of the latter for high angular momentum. Gradients may be calculated using the resolution-of-the-identity approach, enabling efficient optimization of molecular structure for many-electron systems in a strong magnetic field. The CDFT contributions have been implemented for a wide range of density functionals, including the meta-GGA level and (range-separated) hybrids for the first time.

As an illustration, we consider the benzene molecule in a magnetic field. As the field strength increases, more and more π electron pairs are unpaired. In Figure 4, we have plotted the ground-state energies for the lowest states of $M_s = 0$, $M_s = -1$, $M_s = -2$, and $M_s = -3$, revealing the reordering of electronic states in the magnetic field. The corresponding molecular structures are given in Figure 5, beginning with the familiar D_{6h} benzene structure at zero field. At a field strength of $0.15B_0$, all π electrons are unpaired, and the molecule assumes a chair-like conformation of S_6 symmetry. In the absence of a magnetic field, the corresponding point-group symmetry is D_{3d}, which is precisely that of cyclohexane in its most stable, chair conformation.

Molecular dynamics

An important development in 2021 was the back-to-back publication of two articles on the theory and implementation of molecular dynamics in a magnetic field [7,8]. The papers, which were promoted as Editor's Picks in the
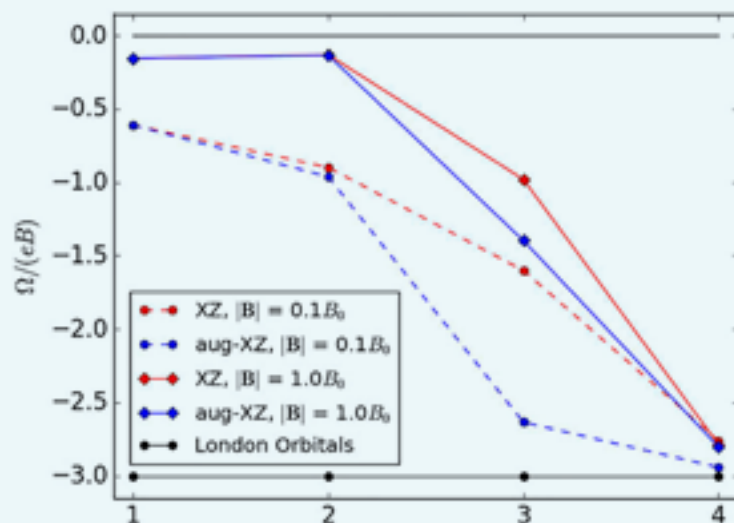
⬆ **Figure 6:** The electronic charge of the Li atom calculated from the Berry curvature at two different field strengths as a function of basis-set size without London orbitals (coloured lines) and with London orbitals (black line) [7]. *Reprinted from Ref. [7], with the permission of AIP publishing.*

Journal of Chemical Physics, report the first *ab initio* molecular dynamics calculations of molecules in a uniform magnetic field, with integration of the classical equations of motion of the molecule in the presence of the Lorentz force.

The two papers overcome several challenges to such calculations, including the gauge-invariant *ab initio* calculation of the screened Lorentz force acting on the nuclei within the Born–Oppenheimer approximation and the propagation of the classical equations of motion in the presence of the velocity-dependent Lorentz force. As an illustration, the vibrational spectrum of H_2 in the presence of a magnetic field was calculated, providing the first glimpse into the complicated rovibrational spectra of molecules in a magnetic field.

The first paper [7] discusses the theory of molecular dynamics in a magnetic

field, beginning with the Born–Oppenheimer separation and the derivation of the time-dependent Born–Oppenheimer Schrödinger equation, followed by a transition to the semi-classical equations of molecular dynamics with the velocity-dependent Lorentz force. In a magnetic field **B**, the force acting on nucleus I of charge $Z_I e$ and velocity $\mathbf{v}_I$ is given by

$$\mathbf{F}_I = \underbrace{-\boldsymbol{\nabla}_I U(\mathbf{R})}_{\text{gradient force}} - \underbrace{Z_I e\, \mathbf{B} \times \mathbf{v}_I}_{\text{Lorentz force}}$$
$$+ \underbrace{\sum_J \boldsymbol{\Omega}_{IJ}(\mathbf{R})\mathbf{v}_J}_{\text{Berry force}}$$

Here $U(\mathbf{R})$ is the Born–Oppenheimer potential energy at nuclear positions $\mathbf{R}$ and $\Omega_{IJ}(\mathbf{R})$ is the IJth three-by-three block of the Berry curvature tensor

$$\boldsymbol{\Omega}_{IJ}(\mathbf{R}) = -2\hbar\Im\langle \boldsymbol{\nabla}_I \Psi | \boldsymbol{\nabla}_J \Psi \rangle$$

calculated from the electronic wave function Ψ. The Berry force represents

the screening of the Lorentz force by electrons in the system. Without the Berry force included, the dynamics of an atom or molecule becomes qualitatively wrong in a magnetic field, the external field affecting the atoms too strongly. In Ref. [7], the nonadiabatic matrix elements needed for the Berry curvature are calculated by a finite-difference approach in a basis of London atomic orbitals. London orbitals are needed to ensure gauge invariance and are essential for an accurate calculation of the Berry curvature.

In atoms, the Berry curvature is related to the number of electrons in a simple manner. In Figure 6, we have used this relationship to extract the number of electrons from the Berry curvature. In the London basis, we obtain the correct number of electrons even in the smallest basis. Without London orbitals, by contrast, the convergence towards the correct number of electrons is very
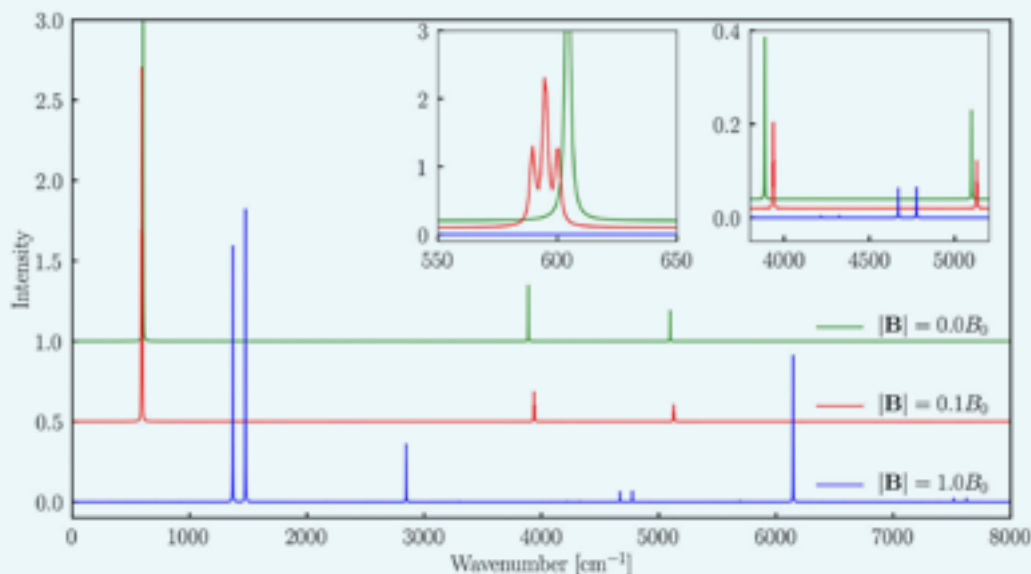
⊕ **Figure 7:** Rovibrational spectra obtained from molecular dynamics simulations of H_2 at three different field strengths [8]. The insets show the fine structure of the selected regions. *Reprinted from Ref. [8], with the permission of AIP publishing.*

slow, demonstrating the need for using London orbitals in atomic and molecular dynamics calculations in a magnetic field.

In Ref. [8], we presented *ab initio* molecular dynamics simulations of molecules in a magnetic field, at the Hartree–Fock level of theory in a basis of London orbitals, with no restrictions on field orientation and basis-set size. To include the nonconservative Lorentz forces in the dynamics, a propagator was developed, based on Tao's symplectic propagator for nonseparable Hamiltonians [18]. The scheme is about three times more expensive than a standard Verlet scheme. The Berry curvature, needed for a proper screening of the external Lorentz force, was calculated as described in Ref. [7].

As in the field-free case, rovibrational spectra of molecules in a magnetic field can be determined as the Fourier trans-

form of the velocity autorcorrelation function obtained from nuclear kinetic momenta along a molecular dynamics path. Unlike static calculations based on second derivatives of the electronic energy (and the diagonalization of a mass-weighted Hessian), this approach captures anharmonic features of the spectrum and vibrational overtones are visible.

As a first application, we analysed simulations of He and H_2 at two field strengths characteristic of magnetic white dwarfs. While the He simulations demonstrate the importance of electron screening of the Lorentz force in the dynamics, the extracted rovibrational spectra of H_2 reveal several fascinating features not observed in the field-free case: couplings of rotations/vibrations with the cyclotron rotation, overtones with unusual selection rules, and hindered rotations that transmute into librations with increasing field strength.

In Figure 7, we compare the field-free rovibrational spectrum of singlet H_2 with spectra calculated at two different field strengths. At a field strength of $0.1B_0$, the spectrum is like the field-free spectrum, with a slight redshift of the lowest mode (because of hindered rotation) and blueshift of higher modes (because of stronger binding). The fine structure is strongly affected by the magnetic field − the rotational mode couples to the cyclotron mode and becomes a triplet, for example.

At a field strength of B_0, the changes are more dramatic, with a strong blueshift of all peaks. Importantly, the rotation is now fully hindered and has become a libration, whose coupling to the cyclotron rotation gives a doublet. Overtones of libration are visible but with a twist: even multiples are singlets, while odd multiples are doublets. Hence, just like electronic spectra, rovibrational spectra are altered in a

fundamental way in the presence of a magnetic field.

Electron dynamics
An important activity at the Hylleraas Centre is the development of methods for modelling ultrafast electron dynamics, as discussed in RT3. In RT4, we have considered such dynamics in the presence of a strong magnetic field, using real-time time-dependent Hartree–Fock (RT-TDHF) and real-time time-dependent CDFT (RT-TDCDFT) methods [9]. A range of current-dependent exchange–correlation functionals based on the TPSS functional were considered, including a range-separated variant, which is particularly suitable for application to excited states. The performance of a range of propagator algorithms for real-time methods was investigated.

The RT-TDCDFT method was applied to the calculation of absorption spectra of the N_2 and H_2O molecules; see Figure 8. The complex evolution of the absorption spectra is rationalized using a molecular orbital-pair decomposition analysis previously developed by members of the Hylleraas Centre [19]. Bearing in mind the often dramatic changes in the spectra with the application of a strong magnetic field, such a tool is indispensable. The accurate evaluation of such spectra is essential if molecules are to be detected on magnetic white dwarf stars.

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RT5

Chemical Transformations

Principal investigators:
David Balcells and Ainara Nova
—

RT5 applies computational methods to understand chemical reactions, often in collaboration with experimental groups. A key goal is to simulate reactivity in complex environments, including reaction networks, spectroscopic processes in solution, and metal–organic frameworks. Machine learning is being introduced with the goal of exploring large chemical spaces in homogeneous catalysis.
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Catalytic oxidations
Bastian Skjelstad studied the C–H activation of di-hydro-anthracene and other alkanes by cobalt-oxo cubane complexes doped with ruthenium [1]. These high-valent multimetallic compounds are experimental models of the intermediates observed in natural systems that catalyse oxidation reactions, like the photosystem II. Metal-catalysed oxidations involve complex proton-coupled electron-transfer (PCET) mechanisms with metal–oxo intermediates. The high reactivity of these species hinders their characterization, limiting the in-depth understanding required to improve catalytic activity, robustness, and selectivity. In this context, we combined calculations using density-functional theory (DFT) with experiments to shed light on the reaction mechanism. This study is part of the collaboration begun in 2017 with the experimental group of Prof. T. Don Tilley at UC Berkeley (USA) [2–4].

The calculations showed that the reactive centre of the cubane is centred over the ruthenium vertex of the cubane, which, in the reactive state, is a Ru(V)-oxyl with radical character in the oxo ligand; see Figure 1. The mechanism starts as expected, with a H atom abstraction (HAA) yielding an organic radical and a Ru(IV)-hydroxyl intermediate. After this step, the system follows an unusual reaction pathway, in which the radical does not undergo rebound to the alcohol but a barrierless radical-coupling with the Ru(V)-oxyl, yielding a Ru(III)-O-R product. This coupling is preferred over the rebound by 12.3 kcal/mol. Further, for the HAA reaction, we demonstrated the existence of structure–activity relationships between the experimental kinetics and DFT descriptors, including natural charges and spin densities. By modelling the influence of the ligands coordinated to the copper atoms at the other vertices of the cubane, we were also able to prove the presence of cooperativity effects
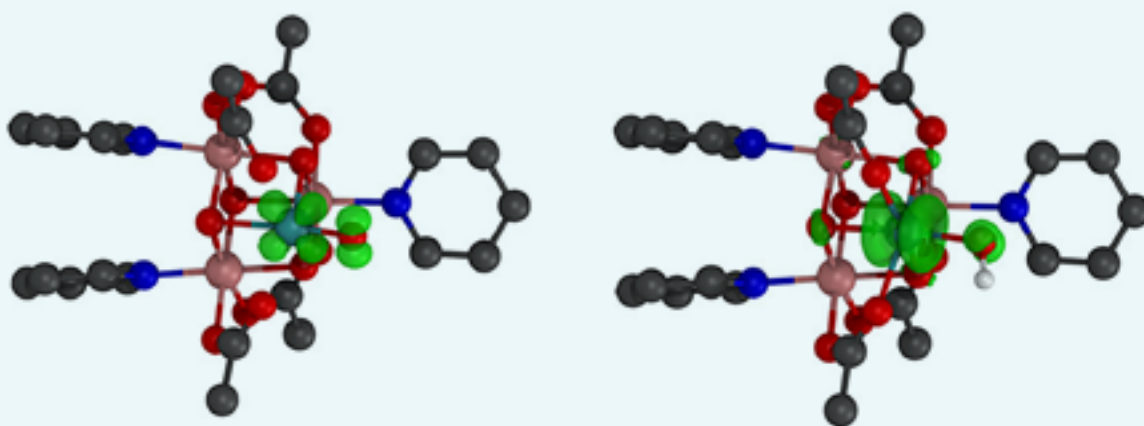
Figure 1: Spin densities (isovalue = 0.02 a.u.) of the Ru(V)-oxyl species (left) and the Ru(IV)-hydroxyl species (right) in oxidation reactions promoted by Ru-doped cobalt–oxo cubanes. *Reprinted with permission from J. Am. Chem. Soc., 2021, 143, 12108–12119. Copyright 2021 American Chemical Society.*

between these metal centres and the reactive Ru(V) oxyl moiety. The work of Skjelstad was performed under the supervision of David Balcells and published in the *Journal of the American Chemical Society* [1]. Skjelstad is a former MSc student from the Hylleraas Centre currently working on his PhD project with Prof. Satoshi Maeda at the Institute for Chemical Reaction Design and Discovery (ICReDD) at Hokkaido University, Japan. He continues to collaborate with the Hylleraas Centre, in a machine-learning project led by Balcells.

The selective oxidation of methane represents an important challenge because it requires the activation of the strongest C–H bond, while avoiding overoxidation of the methanol product. The ERC-SyG CUBE project led by Prof. Unni Olsbye at the University of Oslo aims at achieving this reaction by using metal-organic-framework (MOF) catalysts mimicking LPMO enzymes. The computational part of the CUBE project

is led by Ainara Nova. In 2021, PhD candidate Ning Cao was hired to study the nature of the copper active sites and their reactivity within MOF nanopores. PhD candidate Vanda Le was hired for working in the same project from the Tromsø node of the Hylleraas Centre, focusing on the simulation of spectra used to characterize the copper catalysts and transient intermediates. Both Cao and Le will be supervised by Nova, while Le will be co-supervised by researchers Michal Repisky and Magnus Ringholm.

Base-metal catalysis
PhD candidate Julie Héron worked on a computational study of the copper-catalysed azide–alkyne cycloaddition (CuAAC). This reaction is a paradigm of 'click chemistry' and is used in the synthesis of derivatives needed in the production of several drugs and materials. The work of Héron focused on a dinuclear copper(I) system supported by a nonsymmetric naphthyri-

dine, which acts as a mixed phosphine/amine pentadentate ligand.

Héron's DFT calculations revealed the mechanism underlying the C–H activation of the alkyne (Figure 2). This step plays a key role in both the activation of the catalyst and in the catalytic cycle that transforms the reactants into the product. The cleavage of the C–H bond takes place in a single concerted step, in which the H atom is transferred to a phenyl ligand bridging the two metal centres. Approximately one third of the effective energy barrier (9.8 of 22.9 kcal/mol) is associated with the formation of a prereaction intermediate, in which the alkyne is inserted between the two copper atoms, weakening the coordination of the phenyl ligand. The computational study also revealed a complex interplay between the position of the substrate and the counterion relative to the catalyst, and the partial dissociation of the naphthyridine ligand. This work required
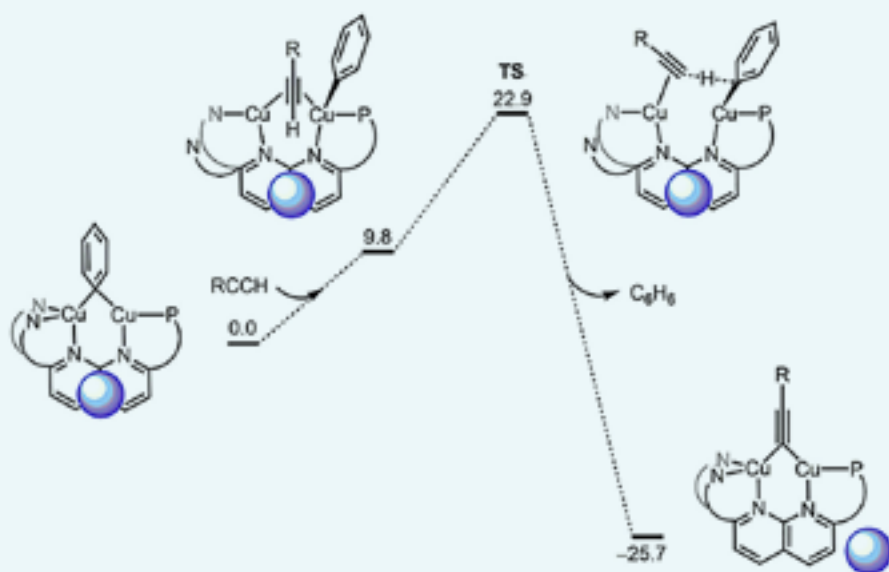
Figure 2: Energy profile, in kcal/mol, for the C–H activation of alkynes by dicopper-naphthyridine complexes involved in the CuAAC reaction. *Reprinted with permission from Organometallics, 2021,* **40***, 1866-1873. Copyright 2021 American Chemical Society.*

the computation of many transition states, which proved to be essential for finding the lowest energy pathway.

In 2021, Héron finished and published this work under the supervision of Balcells [5]. She defended her thesis successfully on November 18. Other publications related to her PhD work are in preparation.

Machine learning
Following his work on the Vaska's complex chemical space [6] and the tmQM data set [7], Balcells focused in 2021 on the design of new automation methods enhanced by machine learning. Together with Skjelstad and Prof. Daniel Ess, a new collaborator from Brigham Young University, USA, we developed a method for the automated optimization of transition states [8], the most critical step in the generation of the large data sets needed in data-driven discovery of new catalysts. The method is based on a transition-state core concept, in which ligands and substituents are added to 'decorate' a molecular frag-

ment that contains only the metal and the few atoms involved in bond cleavage and formation (Figure 3). This approach was tested for platinum complexes that catalyse the activation of methane. A fundamental component of our method is use of a random-forest machine-learning model that predicts the distances of the bonds activated in the transition state. This method recovered a significant amount of the transition-state calculations that failed to converge in a chemical space containing 973 systems.

In 2021, Dr. Lucas Lang from Frank Neese's group at the Max Planck Institute in Mülheim was hired as an MSCA postdoc on the project ML4Catalysis. Lang will be co-supervised by Balcells and Thomas Bondo Pedersen, in a collaboration between RT5 and RT1. In addition, Hannes Kneiding, with an MSc from the Free University of Berlin, was in 2021 hired as a PhD candidate in the MSCA CompSci program at the University in Oslo under the supervision of Balcells. Pedersen and Prof. Riccardo

De Bin from the Department of Mathematics will act as co-supervisors in this project, promoting interdisciplinary collaboration of the Hylleraas Centre. Lang and Kneiding have started working on graph representations and deep-learning models for transition-metal complexes.

In 2021, our machine-learning research was boosted by the external funding brought in by an RCN FRIPRO grant awarded to Balcells. With a budget of 12 MNOK, this project will expand our research in the three key domains: 1) data, including quantum properties for chemical spaces with 10^4–10^5 systems; 2) representations, including new molecular graphs; and 3) models, including deep Gaussian processes and inverse design. The project supports three new positions (one PhD candidate and two postdocs). Balcells is also part of the HySTrAm consortium funded by 6 million euros from the EU Resilience program. This project aims at building a demonstration plant for the synthesis of ammonia from nitrogen and
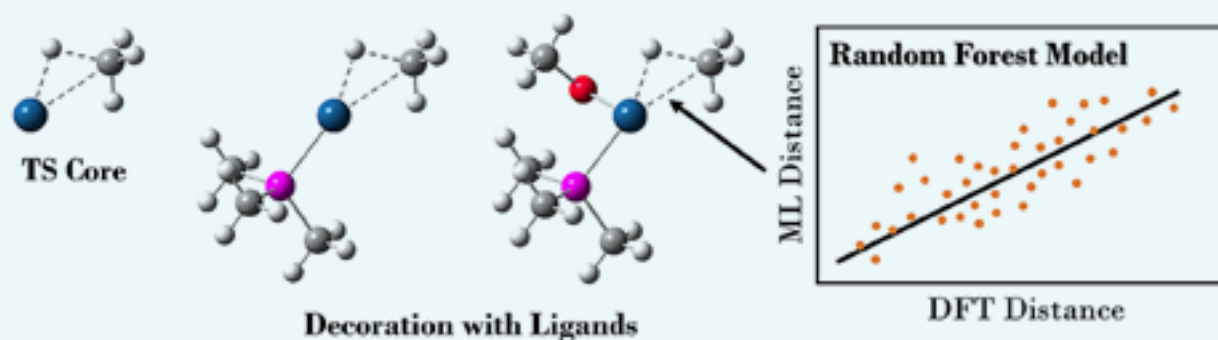
Figure 3: Automated workflow for transition-state optimization in metal-catalysed reactions including distance prediction by machine learning. *Illustration: Shusen Chen and David Balcells.*

hydrogen, using renewable energy. At the Hylleraas Centre, HySTrAm supports the hiring of one postdoc for developing machine-learning models for the virtual screening of MOFs for efficient hydrogen storage.

Grignard reaction
The year 2021 was a year of transition for the Grignard project, following the award of the FRIPRO grant *Revealing the Elusive World of Main-Group Organometallic Chemistry: An Adventure with Computational Chemistry* to Odile Eisenstein and Michele Cascella in 2020. This grant builds on our successful study of the Grignard reaction [9], which showed that computational chemistry is now well equipped to study structures and reaction mechanisms in the challenging world of solvated alkali and alkaline-earth complexes.

The first study of the Grignard reaction [9] considered the pure RMgX reagent is an ethereal solvent, as it was originally used by Victor Grignard in 1900 [10]. Today, however, this reaction is run under experimental conditions that are different from those used at the time of its discovery. The purpose of the FRIPRO project is to understand how and why the modified experimental conditions (additives, change of solvent) are profitable to the reaction and thus contribute to the design of better alkylating reagents. We began our work by modeling the consequence of adding LiCl to the reactive media, with promising results.

Another relevant activity in 2021 has been the hiring of new personnel for the Grignard project, including PhD candidate Marinella de'Giovanetti and postdoc Sondre Eliasson, to be supervised by Eisenstein and Cascella in a collaboration between RT2 and RT5. Collaboration between RT2 and RT5 is also becoming important in other research projects at the Hylleraas Centre, including research on MOFs and CO_2 reduction.

Cross-coupling reactions
Cross-coupling reactions have been a research line in our group since the Centre for Theoretical and Computational Chemistry, as summarized in a review published in *ACS Catalysis* in 2018 [11]. Traditionally, our studies have focused on the interplay between chemical reactions taking place within and outside the catalytic cycle. In 2021, we extended our research towards the prediction and rationalization of selectivity – in particular, we studied the origin of the selectivity in the synthesis of triarylmethanes with palladium-catalysed Suzuki–Miyaura cross-coupling reactions [12].

A puzzling feature of these reactions is that OC–OAr bond cleavage occurs with Ar = Ph, whereas OCO-Ar cleavage occurs with Ar = Bz. DFT calculations on the mechanism of this reaction showed that this difference originates from the different stabilization of the metal centre in the oxidative addition transition state. With Ar = Ph, palladium is more strongly stabilized by the
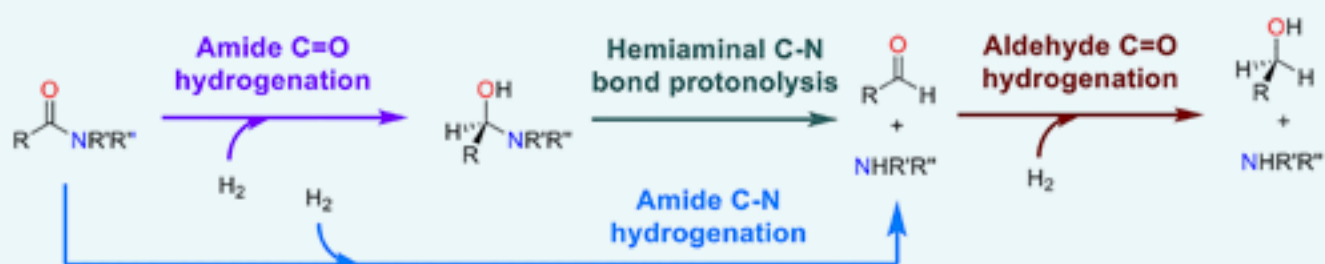
Figure 4: Reaction pathways proposed for the hydrogenation of amides to alcohols with bi-functional catalysts. *Illustration: Ainara Nova.*

OPh fragment from OC–OAr bond cleavage than by the Ph fragment from OCO–Ar cleavage. This trend is reversed by Ar = Bz because this fragment acts as a strong η^3-coordinating ligand. Our calculations also allowed us to rationalize other experimental observations, including the faster reaction rates observed with fluorinated esters and the ion-pair nature of some of the key intermediates involved in the mechanism.

This work was carried out by Irene Casademont-Reig, a PhD exchange student from the Matito group in the Basque Country University (Spain), in collaboration with the experimental group of Prof. Nilay Hazari at Yale University (USA).

Conversion of CO_2 to fuels

A critical step in the hydrogenation of CO_2 to methanol using homogeneous catalysts is the hydrogenation of amides. Understanding this complex mechanism by means of DFT was the topic of the PhD work of Dr. Luís Artús

Suàrez, carried out under the supervision of Ainara Nova and successfully defended in May 2021. His work resulted in three publications [13–15] and was summarized in a review article published in a special issue of *Topics in Catalysis* entitled *Computational Catalysis – A Land of Opportunities* |16].

The review article is divided into three sections describing the fundamental steps of this reaction: 1) the C=O and C–N hydrogenation of the amide, 2) the protonolysis of the hemiaminal, and 3) the hydrogenation of the aldehyde; see Figure 4. This work highlighted the importance of using microkinetic models for identifying the critical steps owing to the high complexity of the reaction mechanisms, which, in these systems, include deactivation processes that affect the robustness of the catalyst.

The insight obtained from this work will be used in the CO2pCat project to design more efficient homogeneous

and heterogeneous catalysts for CO_2 hydrogenation reactions. This project began in August 2021 with the hiring of the PhD candidate Inga Lena Schmidtke and researchers Raquel Jiménez Rama and Tamal Das. In October 2021, PhD candidate Mohamed Eid Safy also joined the project.

Safy is part of the EU-COFUND CompSci program, in which he will be trained in computational and data sciences, developing a new approach to catalyst design based on large data sets and machine-learning models. Jiménez will use her expertise in the synthesis of organometallic complexes and mechanistic experiments to benchmark in the wet lab the efficiency of the catalysts designed computationally. Schmidtke will use DFT methods to study reactions involving the selective insertion of CO_2 into C–H bonds in collaboration with Prof. Pedro Perez (Universidad de Huelva, Spain), while Das will study CO_2 hydrogenation reactions involving MOF-based single-site cata-

lysts using static and molecular-dynamics calculations. All these new projects began in 2021 under the supervision of Ainara Nova.

In addition to thermal processes, there is an increased interest in performing CO_2 reduction with water using electrochemical catalysts to avoid the additional step of generating green hydrogen. This reaction presents many challenges that reduce yield and selectivity. One strategy for increasing the reaction yield is to use amines, which, as shown in our previous studies [13–15], can play several roles. In the case of Mn-bpy complexes, amines can change the product selectivity from CO to formic acid or hydrogen. PhD candidate Mahika Luthra, hired on the EU-ITN CO2PERATE project under the supervision of Nova, has worked on the computational study to determine how cyclic amines prevent the formation of CO and formic acid, yielding only hydrogen. This work is done in collaboration with Prof. Troels Skrydstrup and

Kim Daasbjerg at Aarhus University (Denmark).

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RT6

Multiphase Systems

Principal investigators:
Bjørn Olav Brandsdal and Michele Cascella
—

The RT6 team applies computer simulations to important problems in chemistry, biology and physics. Activities in 2021 focused on antimicrobial resistance, temperature dependence of chemical rates, and aggregation of charged surfactants and lipids.
—

In 2021, we pushed forward a set of new projects related to antimicrobial drugs and to cell mitosis, in collaboration with experimental groups at the UiO campus.

Lipid flip–flop induced by antimicrobial peptides
Antimicrobial peptides are short amino-acid oligomers that show antimicrobial activity. To date, there exist a plethora of known such peptides (both natural and artificial), characterized by different sequences and different architectures (linear chains, circular chains, dendritic chains, *etc.*). The general understanding of the action of such peptides is that they interact with cellular membranes, interfering in some manner with their biological functions. In fact, there is no consensus about how antimicrobial peptides function, the mechanisms present in the literature including membrane distortion, poration, solubilization, lipid extraction, and so on. Possibly there exists a redundancy of effects, depending on the type of membrane, type of peptide and

relative concentrations, which together contribute to the mechanism of action of such peptides.

Recently, combining small-angle neutron-scattering (SANS) and thermochemical measurements on pre-constituted asymmetric deuterated/nondeuterated phospholipid bilayers, Hylleraas affiliate Prof. Reidar Lund characterized the change in the lipid flip–flop rate as various antimicrobial peptides adhere onto the surface of the bilayer [1]. Strikingly, even at low concentration rates, peptide binding significantly enhances lipid flipping between the two leaflets. Given the highly dynamic features involved in the process, the detailed mechanism and relative energetics by which these processes occur are not easy to characterize experimentally. Nonetheless, the measured temperature dependency of the reaction-rate constant suggests that the catalytic role of the peptide acts mostly on the entropic component of the free-energy barrier rather than on the enthalpic one.
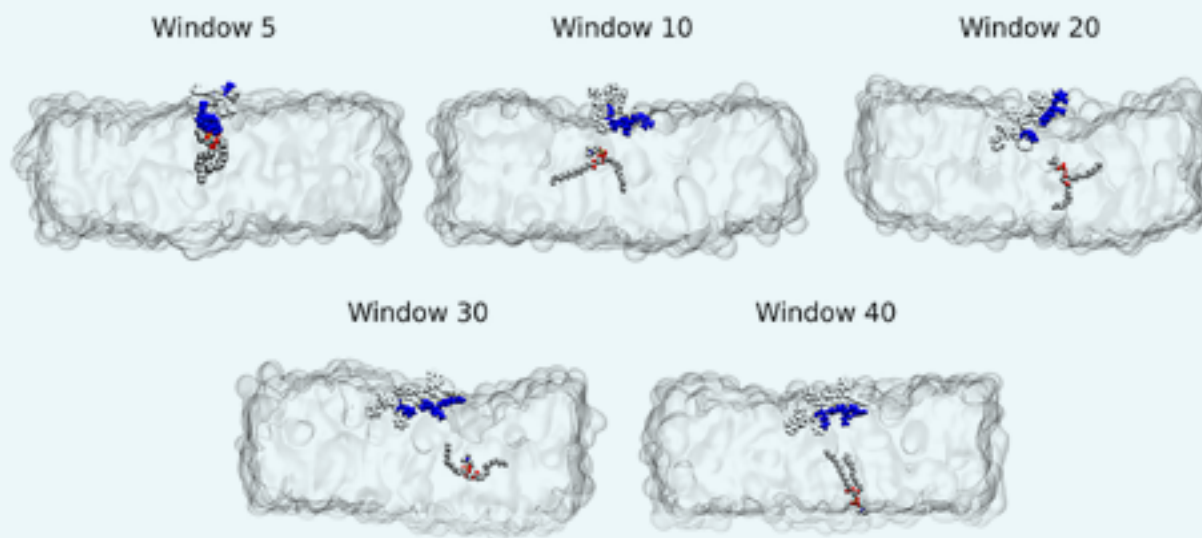
Figure 1: Selected umbrella-sampling windows highlighting the translocation steps of DMPC during a flip–flop event in the presence of inolicidin peptide.

During 2021, PhD candidate Manuel Carrer performed all-atom simulations of indolicidin, adsorbed on a mixed 3:1 DMPC:DPMG lipid bilayer, corresponding to a similar set-up in the experiment by Lund. Molecular-dynamics (MD) simulations revealed that peptide binding occurs via formation of salt bridges between positively charged peptide side chains and the negatively charged phosphate groups of the lipids. By repeating umbrella sampling simulations, Carrer characterized the activation energies for the flip–flop event when a lipid is bound or not bound to the peptide, finding indeed that the initial interaction with the peptide reduces the reaction barrier in quantitative agreement with experiment. Moreover, MD simulations showed that the lipid–peptide interaction is lost before the lipid reaches the transition state (TS). At the TS, corresponding to the lipid flipping around the middle of the bilayer, the peptide has recovered the lost interaction with another neighbouring lipid. As such, the TS structure of the flipping lipid and of the peptide is the same regardless of the starting position of the lipid (in contact or not in contact with the peptide), suggesting minor changes in the activation enthalpy (Figure 1). Instead, we observed that the local distortion of the membrane is significantly different in the two cases, with only a minor invagination of the leaflet on the flipping side when the lipid is at initial contact with the peptide but with a prominent deformation when flipping from a free position.

Thus, MD simulations confirm that the catalytic role of the peptide is mostly in preorganizing the lipid for the flipping dynamics, by accompanying the insertion of the polar head into the hydrophobic core region of the bilayer through peristaltic fluctuations, and by reducing the required reorganization of the leaflet when the lipid flips. A manuscript is in preparation [2].

Investigations on key molecular aspects of cellular mitosis
In 2021, we reinforced the collaboration with the research group of Dr. Nikolina Sekulić at the Centre for Molecular Medicine Norway (NCMM), combining experiment and simulations to explore the molecular biology of cell division. We have focused on the Aurora B kinase (computational work done by former master student Oda Hovet) and on the centromeric nucleosome complex (computational work done by postdoc Xinmeng Li).

Aurora B is a component of the chromosome passenger complex that controls multiple events during cell division. Together with IN-box, a C-terminal part of the inner centromere protein (INCENP), Aurora B constitutes a catalytic component of the complex. In the cell, Aurora B–IN-box is activated by autophosphorylation, while removal of the phosphoryl groups by phosphatases is inhibitory for the kinase activity. However, the effect of phosphorylation on the structural and internal dynamic properties of the enzymatic complex is not clear. We used a combination of experimental (hydrogen-deuterium exchange, enzyme kinetics) and computational (MD simulations) approaches to assess how the internal dynamics

A.

PDB 4C2W   Aurora B/IN-box^no-P   Aurora B/IN-box^IN-P   Aurora B/IN-box^loop-P   Aurora B/IN-box^all-P
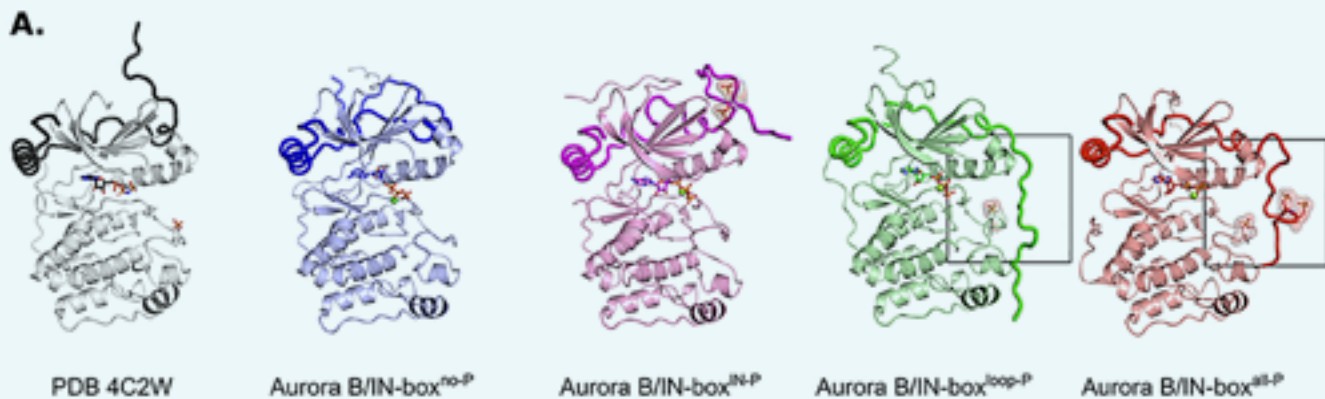
Figure 2: Folding of the C-terminal portion of the IN-box protein in a complex with Aurora B protein, as a function of the phosphorylation state of the complex, as predicted by MD. no-P, IN-P, loop-P, and all-P correspond to the complex being phosphorylated nowhere, at the IN-box, at the Aurora B loop, or everywhere, respectively.

and function of the Aurora B–IN-box complex change with phosphorylation.

Our results provided evidence that the unphosphorylated, inhibited form is more entropic, with the active centre only partially assembled. Auto-phosphorylation is associated with structural reorganization in both the active centre and the allosteric parts of the enzyme complex. We used a chemical-ligation approach to generate partially phosphorylated intermediates and assess the individual contribution of the two major phosphorylation sites: Aurora B Thr248 in the activation loop of Aurora B, and the TSS motif in the IN-box. We found that phosphorylation in the activation loop primes the active form of the enzyme, whereas phosphorylation in both sites act synergistically to activate the enzyme complex by progressive folding the structure (Figure 2) and by helping it adopt a productive breathing motion. Our study provided insight into the intertwined and unique communication between

the mitotic protein kinase Aurora B and its binding partner IN-box. It reveals how phosphorylation regulates their internal communication allosterically and enables tight control of this essential mitotic enzyme. A manuscript has been submitted for publication [3].

Centromeric chromatin

Nucleosomes are protein–DNA complexes that play crucial roles in chromatin organization and as gatekeepers for genetic readouts during DNA replication and transcription. Minor differences in the histone protein or DNA sequences give rise to specialized nucleosomes that can also recruit other binding partners that define the final chromatin structure. To understand how epigenetics works, it is necessary to characterize how sequence variations affect nucleosome structure, stability and functional behaviour. With several high-resolution structures known, there is nevertheless a need to understand inherent dynamic properties such as conformational dynamics ('nucle-

osome breathing') and dissociation behaviour, which are important factors for their specific functional roles.

In this study, we present a comprehensive characterization of canonical and centromere nucleosomes using native mass spectrometry in combination with ion mobility (IM–MS) and collisional activation to investigate nucleosome shape, architecture, and stability and to analyse whether changes in their composition — that is, a different histone variant or DNA sequence — influence the dynamic behaviour of the nucleosome. More specifically, we focus on the H3 histone and its variant centromere protein A (CENP-A), in combination with the superpositioning 601 DNA sequence and a naturally occurring AT-rich sequence present in centromeres.

Experimental collision cross section (CCS) from IM–IS spectrometry indicated that centromeric structures tend to be less compact than noncentromer-
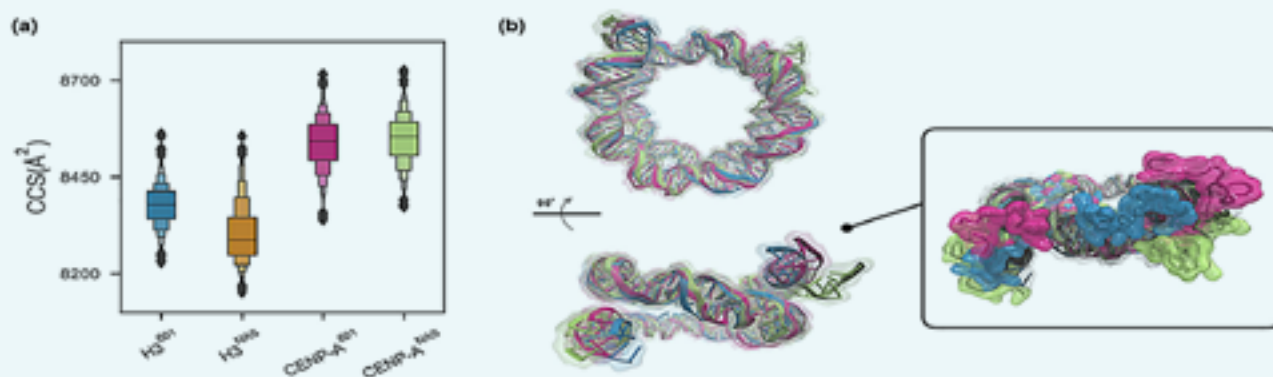
⊕ **Figure 3:** (a) Calculated CCS for H3 (noncentromeric) and CENP-A (centromeric) nucleosomes wrapped with 601 and NAS DNA sequences from MD simulations. (b) Wrapping of histone tails around DNA for different sequences.

ic ones, regardless of the specific DNA sequence wrapped into them. MD simulations confirm this trend. Importantly, they reveal that the compactness of the nucleosomes is not so much dependent on the protein sequence in the histone core as it depends on the different topological wrapping of the unfolded histone tails around DNA (Figure 3).

Our combined experimental–computational study showed that nucleosomes are mainly observed in a compact conformation, while a small portion exists in an extended form. Most likely, this extended form arises from a combination of histone tails unfolding and terminal DNA unwrapping. By determining the experimental CCS of all nucleosomes, we found that the CENP-A histone and the NAS DNA sequence both contribute to a less compact nucleosome form. The CENP-A^{NAS} nucleosome was found to be the most open and dynamic nucleosome in the study.

The determination of the molecular details making centromeric nucleosome units different from noncentromeric units is a key step towards the identification of druggable sites for the therapy of diseases associated to abnormal cell division, prominently cancer.

A manuscript on the presented work is in preparation [4].

Personnel

In 2021, Professor Thereza A. Soares joined the Hylleraas Centre in a Professor II position. She will reinforce the collaboration with affiliate Assoc. Prof. Reidar Lund on the combined computational and experimental investigation of antimicrobial drugs and the bacterial cell wall. The work on nucleosomes was continued in 2021 by postdoc Dr. Xinmeng Li and by master student Mira Mors at UiO.

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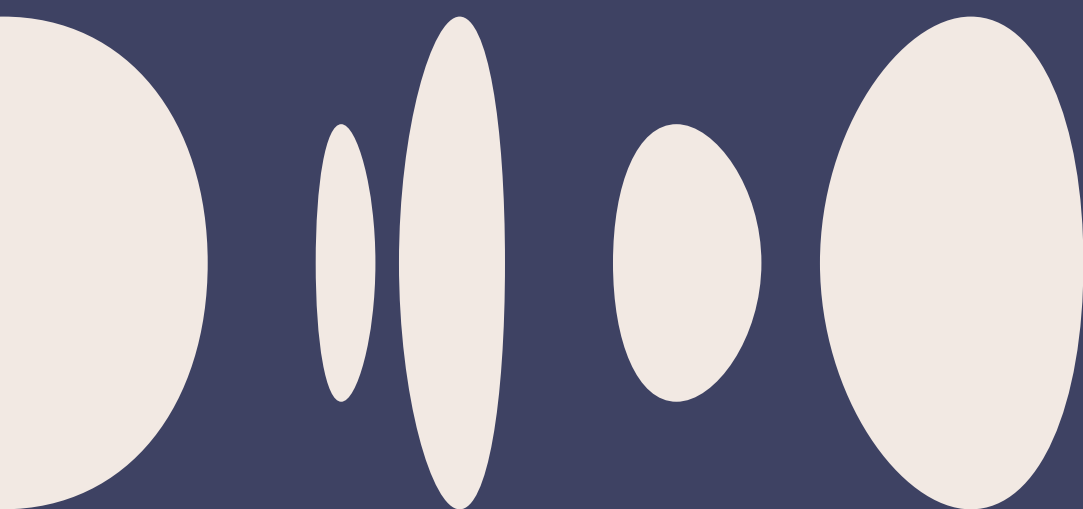
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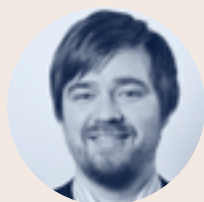
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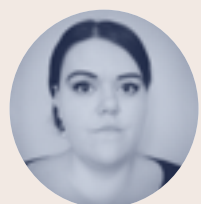
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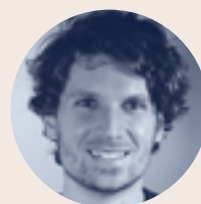
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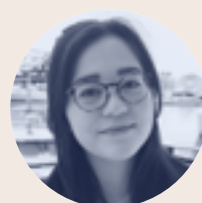
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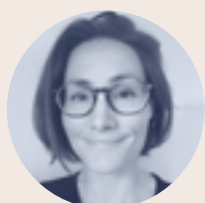
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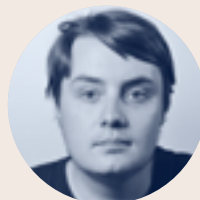*UiT*

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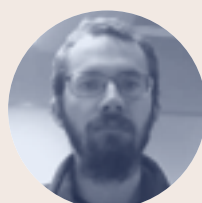
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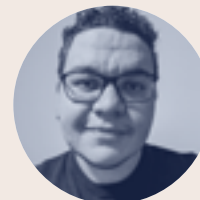
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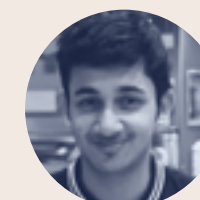*UiO*

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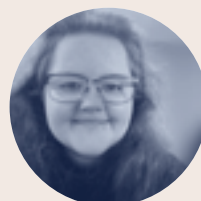**Aleksandar Davidov**
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Funding and
Staff Report

Funding 2021
(in NOK 1000)

Basic funding as agreed in the Centre contract	
Funding from Research Council (CoE grant)	13 281
Funding from home institutions	8 482
Total basic funding	**21 763**
Additional funding from external projects	
Research Council funding	17 440
International funding	3 166
Public funding	
Private funding	2 997
Total additional funding	**23 603**
Total funding	**45 336**

Staff Report 2021
(in man-years)

Professors and Researchers	15.6
PhD Candidates	21.7
Postdoctoral Fellows	9.1
Visiting Researchers	0.6
Administrative and Technical Staff	4.6
All staff	**51.5**