





# The Centre for Theoretical and Computational Chemistry

## CTCC Annual Report 2015

### Table of Contents

<b>A Good Year for Science and Outreach</b> .....	3
<b>From the Board of Directors</b> .....	4
<b>2015 in Brief</b> .....	5
<b>Highlight:</b> Fostering Theoretical-Experimental Collaborations by Means of Accurate Spectra Simulations	7
<b>Highlight:</b> Is Enzyme Design Becoming Less Fiction and More Science?.....	8
<b>Highlight:</b> Changing the Rules of Quantum Chemistry: BIVAQUM.....	10
<b>Highlight:</b> Catalyst Design for Small Molecule Activation.....	11
<b>Almlöf-Gropen Lecture 2015:</b> 2013 Nobel Laureate Professor Arieh Warshel .....	13
<b>Outreach:</b> Hylleraas Exhibition .....	14
<b>Outreach:</b> Hylleraas Symposium .....	15
<b>Outreach:</b> International Year of Light: .....	16
<b>Outreach:</b> CTCC at Drammen Upper Secondary School .....	17
<b>CTCC members</b> .....	18
<b>Fundamental Aspects of DFT</b> .....	21
<b>A Voyage From Molecules to Materials with Numerical Methods for Quantum Chemistry (NMQC)</b> .....	22
<b>CTCC Spring Meeting</b> .....	23
<b>Advances in Electronic Structure Theory</b> .....	23
<b>Annual Meeting of the Division of Quantum Chemistry and Modelling of the Norwegian Chemical Society</b> .....	24
<b>Polarizable Continuum Model (PCM) Workshop</b> .....	25
<b>Visiting Scientists</b> .....	26

<b>Interview with Visiting Scientist:</b> Professor Jeanet Conradie.....	28
<b>Abril Castro, visiting PhD student from Girona</b> .....	29
<b>Dr. Anand Thirumalai, visiting astrophysicist</b> .....	29
<b>Total revenue and expenditure figures</b> .....	30
<b>Appendix A: Publications CTCC 2015</b> .....	31
<b>Appendix B: Activity Reports 2015</b> .....	38

**The Centre for Theoretical and Computational Chemistry (CTCC)** is a Norwegian Centre of Excellence (CoE) established by the Research Council of Norway (RCN) in July 2007. 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 contribute to raising the quality of Norwegian research.

The CTCC is one of 21 national CoEs in Norway and one of two centres in chemistry. It has two nodes of equal size, hosted by UiT The Arctic University of Norway (UiT) and the University of Oslo (UiO). The CTCC receives an annual RCN funding of about 9,5 MNOK for the period July 2007 – June 2017. In addition, it receives substantial financial support from UiT and UiO.

The vision of the CTCC is to become a leading international contributor to computational chemistry by carrying out cutting-edge research in theoretical and computational chemistry at the highest international level.

The CTCC has an extensive visitors program for scientists from around the world, as well as for PhD students and postdocs from other research groups who wish to benefit from the expertise at the centre. In addition, the CTCC has organized a number of international meetings and conferences, bringing together computational and theoretical chemists from all parts of the world. ■



# A Good Year for Science and Outreach

For the third year in a row, the young members of the CTCC continue to impress: in 2015, Ainara Nova at the CTCC received a «Young Research Talent» (YRT) FRIPRO grant from the Research Council of Norway, for her project *Rational catalyst design for transforming CO<sub>2</sub> into industrially attractive products: Formic acid, polycarbonates and polyurethanes*, while Hima Bindu Kolli was awarded a Marie Skłodowska-Curie Grant for her project *Hybrid particle-field approach including electrostatics for large-scale simulations of biological systems*. The CTCC is clearly teeming with young talent, hosting two ERC Starting Grants, two Marie Skłodowska-Curie grants, and four YRT FRIPRO grants (out of five in all of chemistry in Norway). Moreover, Simen Kvaal was in 2015 elected to the newly established Young Academy of Norway, as one of only 20 members. We congratulate all young members of the CTCC with their achievements. Our felicitations are also extended to senior members Kenneth Ruud and Einar Uggerud, who were in 2015 awarded large FRIPRO grants, for their projects *New dimensions in theoretical multiphoton spectroscopy* and *Chemistry of CO<sub>2</sub> activation and fixation*, respectively. The CTCC has become a powerhouse not only of theoretical and computational chemistry but of chemistry as a whole.

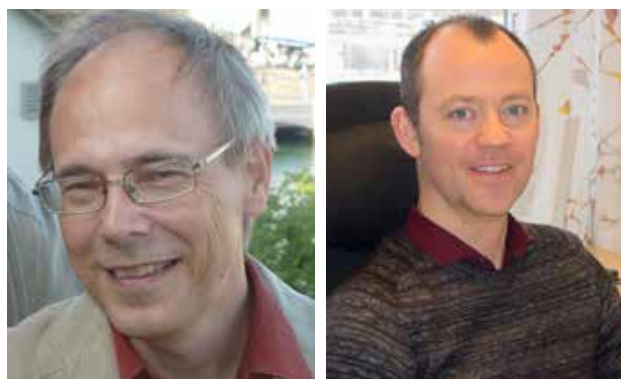
All four *Research Highlights* in this annual report have been written by our young scientists. One of the highlights, *Fostering theoretical-experimental collaborations by means of accurate spectra simulations*, is important not only because it presents excellent independent work carried out by our young researchers but also because it represents collaboration between the two nodes and between theoretical and experimental chemists — in short, everything the CTCC should be.

Scientifically, 2015 was an excellent year for the CTCC, with 88 articles published and nearly 2000 citations to our work in international journals. Moreover, the CTCC hosted three international meetings in Norway, co-organized conferences abroad and contributed to two international summer schools in quantum chemistry. An inspirational visit to the CTCC was that of Nobel Laureate Prof. Arieh Warshel from the University of Southern

California at Los Angeles, whose Almlöf-Gropen Lecture 2015, *How to model the action of complex biological systems on a molecular level*, attracted large audiences in Tromsø and Oslo.

Outreach played an important role last year. A permanent exhibition was opened at the CTCC about the Norwegian physicist Egil Hylleraas (1898–1965), the founding father of Norwegian quantum chemistry and the first to confirm the validity of quantum mechanics for more than one electron. We would like to thank his daughter Inger Hylleraas Bø for help with the preparation of the exhibition, which attracted the interest of national media. Engerdal municipality is now preparing a commemoration of Hylleraas and his work. The CTCC was in 2015 instrumental in organizing a one-day celebration of the *International Year of Light*, also at the Academy. During the fall of 2015, three students from Drammen Upper Secondary School carried out a research project at the CTCC. We would like to thank Heike Fliegl for designing the research project and for her enthusiastic supervision of the young students.

An important task in 2015 was the preparation of an application for a new Centre of Excellence, to follow the CTCC, which terminates in the summer of 2017. Our new proposal builds on the foundations created at the CTCC since 2007 but extends it significantly towards complex systems, with emphasis on matter-field interactions. Fingers crossed! ■



Director Trygve Helgaker and co-director Bjørn Olav Brandsdal.





# From the Board of Directors

The Board of Directors is pleased to note the diversity of activities that now characterises the CTCC: broad research within chemistry, training of students and young researchers, outreach locally and nationally. The CTCC continues to have a strong scientific output with almost 90 publications published each year, it continues to organize successful meetings, conferences and summer schools home and abroad, and it continues to secure national and European grants. We are delighted that its younger members have so convincingly taken the opportunities offered by the Research Council of Norway with the establishment of the Young Researcher Talent program. We congratulate Dr. Ainara Nova with her Young Research Talent grant and Dr. Hima Bindu Kolli with her Marie Skłodowska-Curie grant. Our felicitations are extended to Kenneth Ruud and Einar Uggerud for winning large FRIPRO grants and to last year's ERC Starting Grant winner Simen Kvaal for his election to the Young Academy of Norway. The fact that the CTCC now houses three generations of successful researchers in theoretical and computational chemistry tells us that the centre is not only alive but also kicking.

The Board of Directors is pleased to note the success of recent outreach activities at the CTCC. The Hylleraas Exhibition brought to the attention of the public a Norwegian pioneer of quantum mechanics, the physicist

Egil Hylleraas, on the 50th anniversary of his death. We learned that Egil Hylleraas introduced the term «kvan-tekjemi» («quantum chemistry») into the Norwegian language in a public lecture given in 1931. He would not only have been astonished to see the power and usefulness of computational quantum chemistry today, in a large part due to his own pioneering contributions — he would also have been thrilled to see that quantum chemistry is a prominent field of research in Norway, more than eighty years after he gave it a name and predicted its importance.

When the CTCC terminates as a Norwegian Centre of Excellence in 2017, it is important that what has been built up at the CTCC over the last decade is not lost. The best way to achieve this would be to establish a new Centre of Excellence, hot on the heels of CTCC. The Board is pleased with the proposal for a new Centre of Excellence in theoretical and computational chemistry, submitted to the Research Council of Norway in November 2015. It combines in a balanced manner the current interests and expertise of the CTCC with new directions and opportunities offered by the emerging new experimental facilities in chemistry such as the European Spallation Source and MAX IV Laboratory. We wish the CTCC the best of luck with their application for the proposed Hylleraas Centre. ■



**Professor Fred Godtliebsen**  
*Vice Dean at The Faculty of Science and Technology, UiT. Chairman of the board*



**Professor Anne-Brit Kolsto**  
*University of Oslo*  
Vice-chairman of the board



**Dr. Nina Aas**  
*Det norske oljeselskap ASA*



**Professor Ragnar Winther**  
*University of Oslo*



**Professor Ole Swang**  
*University of Oslo, and Senior Scientist at SINTEF Materials and Chemistry*



## 2015 in Brief

**Research:** In terms of publications, 2015 was our third most productive year, with 88 publications, nearly as many as in the top years 2012 and 2014. Our articles continue to have strong impact, picking up nearly 2000 citations in 2015. The 643 CTCC publications registered by Web of Science have now been cited about 8300 times with an H-index of 39. Three of the papers published by CTCC members are identified as Highly Cited by Web of Science and one paper as Hot, placing it among the top 0.1% of all papers in chemistry. One publication has received a total of 553 citations. Luca Frediani co-edited with Dage Sundholm of the University of Helsinki a themed issue entitled *Real-Space Numerical Grid Methods in Quantum Chemistry* of the journal *Physical Chemistry Chemical Physics*, containing 22 research articles and an introduction by the editors.

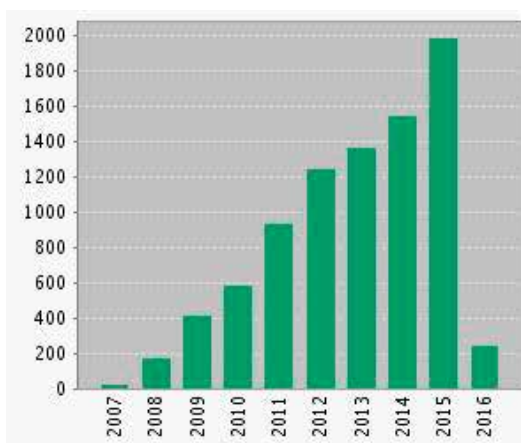
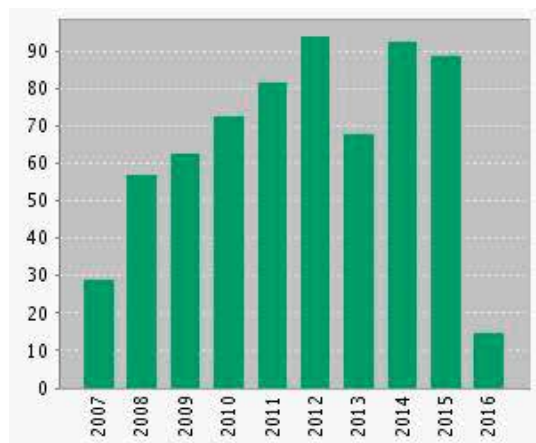
Members of the CTCC continue to attract external funding. In 2015, Ainaro Nova, a postdoctoral fellow at the CTCC in Oslo, received a four-year RCN FRIPRO «Young Research Talent» (YRT) grant of 7.0 million NOK for the project *Rational catalyst design for transforming CO<sub>2</sub> into industrially attractive products: Formic acid, polycarbonates and polyurethanes*, continuing the formidable success of the young CTCC members

in this respect: the CTCC now hosts all but one of the five YRT grant winners in chemistry in Norway, a strong indication of the high quality of the young researchers at the CTCC and the relevance of their work. With the hiring of a PhD student, the YRT grant will allow Ainaro Nova to establish herself as an independent researcher and to remain in Oslo for another four years. In addition, researcher Hima Bindu Kolli was awarded a Marie Skłodowska-Curie Grant of 196 400 EUR for her project *Hybrid particle-field approach including electrostatics for large-scale simulations of biological systems*, senior member Einar Uggerud secured a four-year FRIPRO grant of

9.0 million NOK for the project *The chemistry of CO<sub>2</sub> activation and fixation*, shared with Prof. Knut Børve at the University of Bergen, while Kenneth Ruud received 8.9 million NOK for the four-year project *New dimensions in theoretical multiphoton spectroscopy*. Finally, we add that the project *Molecules in extreme environments* of Trygve Helgaker was selected for the academic year 2017–2018 at the Centre for



CTCC postdoctoral fellow Ainaro Nova was awarded an RCN Young Research Talent grant in 2015,



The number of CTCC publications 2007–2015 (left) and the number of citations to CTCC publications 2007–2015 (right)



Advanced Study (CAS) at the Academy of Science and Letters in Oslo.

The CTCC was host to more than fifty guests and visitors in 2015, including 2013 Nobel Laureate Arieh Warshel.

**Training:** An important part of the training of master students, PhD students, postdocs, and researchers are the regular video-transmitted CTCC seminars, where each Friday one or two progress reports on recent work are given by members of the CTCC. In addition, young centre members receive valuable training at the CTCC spring meetings and the annual meetings of the Computational Chemistry Division of the Norwegian Chemical Society. In 2015, twenty of the lectures given at the spring meeting in Sundvolden and many of the lectures at the Norwegian Chemical Society meeting in Bergen were given by young members of the CTCC.

The CTCC takes an active part in the education and training of students and postdocs by the organization and teaching at international summer schools. From June 29 to July 3, Kenneth Ruud and former CTCC adjunct professor Trond Saue organized together with Daniel Crawford and Patrick Norman *The Molecular Response Properties Summer School* at Virginia Tech, USA, with 25 participants. Trond Saue was also the organiser of the *European Summerschool in Quantum Chemistry* (ESQC) held near Palermo in the period September 9 – 19, with 81 participants. Trygve Helgaker and former CTCC adjunct professor Benedetta Menucci were teachers at the same school, which counted Heike Fliegl and Simen Reine of the CTCC and former CTCC member Stella Stopkowicz among its tutors.

During 2015, two PhD students Sigbjørn Løland Bore (MNF, UiO) and Audun Skau Hansen (FRIPRO, UiO) and five postdocs Gustav Baardsen (FRIPRO, UiO), Geir V. Isaksen (CTCC, UiT), Glenn Miller (FRINATEK, UiO), Hima Bindu Kolli (CTCC, UiO), and Andre Laestadius (ERC, UiO) were hired on projects owned by CTCC members.

**Outreach and dissemination:** In 2015, the CTCC continued its tradition of organizing meetings and conferences. Apart from the *CTCC Spring Meeting* held at Sundvolden April 22–24, the CTCC contributed to the *Annual Meet-*

*ing of the Division for Computational Chemistry* in Bergen 29–30 June. The Division for Computational Chemistry is the youngest division of the Norwegian Chemical Society, established in 2008 at the initiative of the CTCC. In addition, the CTCC organized or co-organized *Fundamental Aspects of DFT* at the Academy of Science and Letters (January 8–10), *A Voyage From Molecules to Materials with Numerical Methods for Quantum Chemistry (NMQC)* on the Coastal Express round trip Tromsø–Kirkenes–Tromsø (January 11–15), *Advances in Electronic Structure Theory* at the Université Pierre et Marie Curie (UPMC) in Paris (April 27–29), *Polarizable Continuum Model (PCM) Workshop* at UiT (July 21–24) and the *Hylleraas Symposium* at the Academy of Science and Letters (November 23), following the opening of the Hylleraas Exhibition at the CTCC on April 15. Michele Cascella co-organized the Psi-k workshop *Computer Simulations for Condensed Phase Systems: From Correlated Electrons to Novel Materials* in honour of Prof. Giovanni B. Bachelet at the CNR headquarters in Rome (May 4–6), and the CECAM workshop *Modelling Activity vs. Selectivity in Metalloproteins* at UPMC, Paris (June 29 – July 1).

Einar Uggerud organized on November 11 the interdisciplinary event *International Year of Light* at the Academy of Science and Letters. John Vedde and Trygve Helgaker of the CTCC helped organize the *Kjemi Grand Prix Day* at the Department of Chemistry in Oslo on November 26. Einar Uggerud continues to serve as a member of the panel of *Abels Tårn* and *Ekko*, a popular-science program on Norwegian Radio. Three young members of the CTCC contributed popular-science articles to *Kjemi*, the journal of the Norwegian Chemical Society, in 2015: Glenn Miller (*Anioniske magnesiumkomplekser og CO<sub>2</sub>*), Geir Villy Isaksen (*Datasimuleringer baner vei for enzymdesign*), and Magnus Ringholm (*Molekylegenskaper med OpenRSP*). Based on an interview of Bjarne Røsjø with Michele Cascella and Thomas Bondo Pedersen, three articles on theoretical chemistry were in 2015 published on titan.no, the online magazine of The Faculty of Mathematics and Natural Sciences at the University of Oslo: *Derfor kan du se infrarødt lys*, *Vi er inne i en kjemisk revolusjon*, and *Kjemikere på stjerne jakt*. The latter was republished nationally on forskning.no. ■



# Highlight: Fostering Theoretical-Experimental Collaborations by Means of Accurate Spectra Simulations

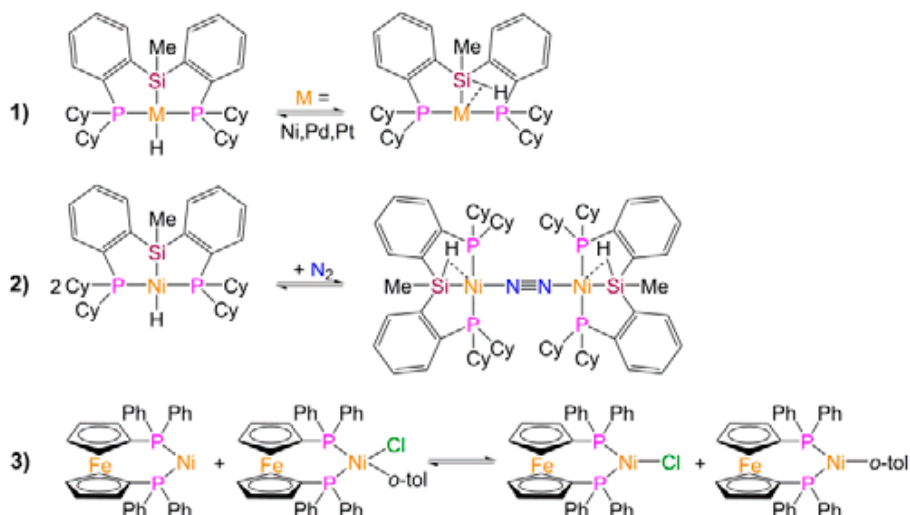
David Balcells and Michal Repisky

Homogeneous catalysis based on transition metals is a key technology in modern chemistry. Catalysts allow for greener industrial processes by giving access to milder reaction conditions and higher product selectivity, thereby reducing the generation of waste and pollution. However, active and robust catalysts based on earth-abundant, cheap and non-toxic metals are still scarce. The development of such catalysts depends on a detailed understanding of the underlying reaction mechanisms. This requires the accurate characterization of the transient intermediates and the kinetics of the elementary steps, which is often challenging or impossible to identify experimentally. In this regard, complementing experimental techniques with the application of computational methods is a powerful approach, since the latter can yield a detailed mechanistic picture of the reactions studied.

The expertise of the CTCC in computational chemistry has been exploited in several collaborations with national and international experimental groups working in the field of homogeneous catalysis, including the group led by Professor Nilay Hazari at Yale University (USA). This collaboration was added to the CTCC net-

work by postdoc Ainara Nova in 2013 and will be further extended in the following years thanks to the FRI-PRO Young Research Talent grant recently awarded to her. The collaboration with Prof. Hazari has focused on three reactions (see Figure), including 1) hydride-agostic equilibria in transition-metal pincer complexes related to high-temperature catalysis, 2) nitrogen fixation triggered by hydride-to-agostic dimerization and 3) generation of nickel(I) transient intermediates in metal-catalyzed cross-coupling reactions used in the synthesis of fine chemicals.

The Oslo node of the CTCC, including researchers Ainara Nova and David Balcells, has worked on these three projects, determining the micro-thermodynamics and kinetics parameters of the reaction mechanisms. These parameters give valuable insight but their interpretation is often encumbered by the lack of experimental values. In contrast, experiments do provide extensive spectral data. These can be used to evaluate the accuracy of the computational methods, which in turn can be used to interpret spectra that are ambiguous or difficult to assign. The nuclear magnetic resonance (NMR) and electron







paramagnetic resonance (EPR) techniques are especially useful in the study of reactions 1–3 (Scheme). However, the reliable prediction and interpretation of magnetic resonance parameters for systems involving transition metals are still a considerable challenge for quantum-chemical methods, because of the large sensitivity of these parameters to the molecular electronic structure as well as to relativistic effects.

The Tromsø node of the CTCC, including senior engineer Michal Repisky and researcher Stanislav Komorovsky, has developed a relativistic density-functional theory (DFT) program for spectroscopic applications, ReSpect ([www.respectprogram.org](http://www.respectprogram.org)). The program is unique in being able to utilize the four-component relativistic Dirac formalism in applications involving large molecular systems (>100 atoms). A variety of molecular properties are available at the Hartree–Fock and DFT

levels, with emphasis on the (paramagnetic) NMR and EPR spectroscopies, where relativistic corrections provide substantial, in some cases dominant, contributions to the spectral parameters; for instance the EPR *g*-shift is a purely relativistic effect induced by spin-orbit coupling.

These techniques have been used to determine the thermodynamics of Reaction 1 and the NMR signature of the species therein. In combination with the experimental data obtained by the Hazari group, this has allowed us to confirm the long-debated preference for the hydride isomers. This work was recently published in *Inorg. Chem.* **54**,11411 (2015). These projects have demonstrated that collaboration between the two CTCC nodes can trigger the application of state-of-the-art computational methods still under development to solve important and challenging chemical problems. ■

## Highlight: Is Enzyme Design Becoming Less Fiction and More Science?

Geir Villy Isaksen

Imagine a designed catalyst that can enhance chemical reaction rates by up to 17 orders of magnitudes, cure diseases, and save energy in industrial processes. Such super catalysts may sound like science fiction, but they do exist. Enzymes are nature's super catalysts and are large biological molecules catalyzing chemical reactions crucial for sustaining life. Nature has iteratively refined catalysts in the course of evolution to function optimally at an impressively wide range of temperatures, pH values, salt concentrations, and pressures. Detailed atomistic knowl-

edge of the mechanisms involved in such adaptation processes can enable the design of enzymes catalyzing any chemical reaction at any given temperature.

As an efficient strategy on the path towards the design of enzymes from chemical principles, we have investigated the mechanisms involved in the evolution of warm- and cold-adapted enzymes. A universal feature of reactions catalyzed by cold-adapted enzymes is a lower enthalpy and a more negative entropy of activation compared with their warm-adapted orthologs. Thus,





computer simulations must determine the experimental observables, which in this case are the thermodynamic activation parameters. These are obtained from extensive all-atom empirical valence bond (EVB) simulations, where the activation free energies are calculated as a function of the temperature. Typically, this involves 600 – 800 independent reaction free-energy simulations distributed over 6 – 8 different temperatures per system. To facilitate the handling of the enormous amount of data in these calculations, we have developed Qgui (Figure 1), a graphical user interface for high-throughput free-energy calculations (Isaksen *et al.*, *J. Mol. Graph. Mod.* **60**, 15–23 (2015)). This software has played a crucial role in allowing us to efficiently examine the temperature dependence of the reaction rates for temperature-adapted enzymes.

Historically, the more negative entropy of activation

in cold-adapted enzymes has been assumed to originate from a more flexible active site than in the warm-adapted counterparts. However, using trypsin from salmon (AST) and cow (BT) as model systems, we have demonstrated that the active sites are virtually identical and that the difference in the enthalpy–entropy balance arises from interactions outside the active site (Isaksen *et al.*, *PLOS Comp. Biol.* **10**(8):e1003813 (2014)). Given that the residues surrounding the substrate are conserved between the two proteins, it is perhaps not surprising that the energetic differences occur farther away. Generally, we find that both enzymes have rather rigid cores with soft surfaces but that the cold-adapted enzyme has softer surface regions (Figure 2). Mutations of conserved residues in either the N $\beta$ 5-N $\beta$ 6 loop or the autolysis loop (Figure 2B) not only change the flexibility of these regions, but also

significantly alter the characteristic enthalpy–entropy balance. It is remarkable that the simulations predict a significant shift of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in, for example, warm-adapted trypsin to become more cold adapted without changing the free energy of activation. Thus, altering the surface softness can fine-tune the enthalpy–entropy balance, and hence the enzyme temperature dependence.

The immediate implication of our findings is that existing enzymes can easily be redesigned to function at lower temperatures by softening strategic surface regions. Doing so would clearly be beneficial in, for example, industrial processes with significant energy savings. However, even though enzyme design has become less science fiction during the last decade, it is still in its infancy. Nevertheless, the quest for enzyme control most certainly holds a promising future. Because proteins and enzymes are involved in many diseases, including cancer, they can also be designed as part of a cure. ■

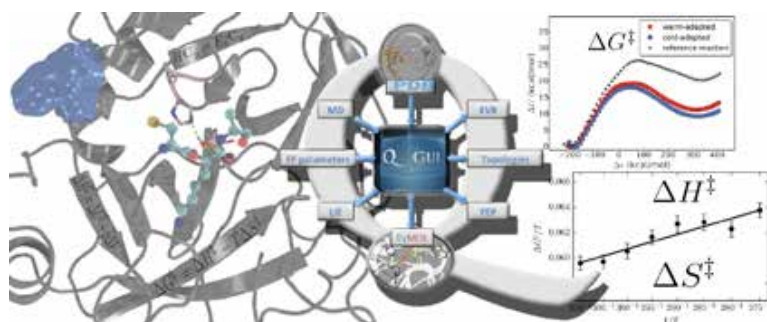


Figure 1: Illustrative overview of Qgui - a high-throughput graphical user interface for free-energy calculations and empirical valence bond simulations.

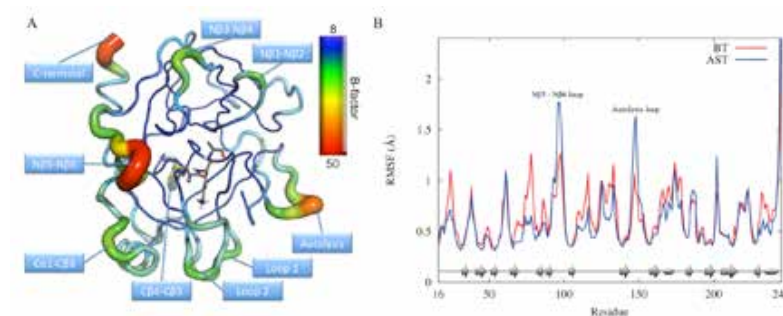


Figure 2: Enzymes generally have soft surface regions and more rigid cores. (A) B-factor representation of cold-active trypsin calculated from 100 ns MD simulation of the reactant state pinpointing soft regions. (B) Average protein backbone fluctuations of warm-adapted bovine trypsin (BT) and cold-adapted salmon trypsin (AST) in the reactant state show that AST has surface regions that are significantly more flexible.



# Highlight: Changing the Rules of Quantum Chemistry: BIVAQUM

Simen Kvaal

BIVAQUM is an acronym for *Bivariational approximations in quantum mechanics and applications to quantum chemistry*, a Starting Grant project funded by the European Research Council (ERC) from April 2015. In addition to the principal investigator, the funding supports two postdoctoral fellows and one PhD student. The BIVAQUM project crosses the borders between computational and theoretical chemistry, physics, and applied mathematics. It aims to explore and apply an unconventional variational principle: *the bivariational principle*. The goal is to develop faster, more accurate, and more robust computational techniques for atoms, molecules, and other many-particle systems governed by the laws of quantum mechanics.

Computer computations are becoming more and more important in all natural sciences, as experiments are often expensive or difficult to perform. In chemistry, the discipline of simulating atoms and molecules and their reactions is called “quantum chemistry”. The fundamental nonrelativistic equation of quantum mechanics, the Schrödinger equation, is a hugely complicated equation to solve. In fact, it is impossible to solve with pen and paper. Instead, we resort to numerical simulations, solving the Schrödinger equation in an approximate manner on a computer.

Already in 1744, the famous mathematician and physicist Leonhard Euler posited that “every effect in nature follows from a maximum or minimum principle”. So far, the prediction has held true: from the standard model of particle physics to the formation of soap bubble films and the propagation of light rays, the physical laws have elegant formulations in terms of variational principles. These principles are powerful, often being the starting point for efficient and robust computational techniques, in a wide range of fields. Quantum mechanics is no exception. Nearly all computational techniques in use today are based on the Rayleigh–Ritz variational principle, which encapsulates the Schrödinger equation: an atom or molecule tends to seek a configuration that minimizes the total quantum-mechanical energy.

However, the Rayleigh–Ritz principle has a major drawback when applied to molecules — the resulting computational techniques tend to be very expensive, manifesting in the half-jokingly named phenomenon “the curse of dimensionality”. The cost of a calculation increases exponentially with the number of electrons in the molecule, making computations on large molecules impossible, even taking into consideration that computers are becoming more powerful each year.

An important exception to this rule is the coupled-cluster (CC) method, which is not based on the conventional Rayleigh–Ritz variational principle. Moreover, it breaks the curse of dimensionality, scaling in a gentler fashion than other methods. Therefore, it is hugely popular, being named “the gold standard of quantum chemistry” due to its excellent balance of accuracy and computational effort. Still, it is too expensive to be applied to larger molecules, and it is difficult to extend and generalize the technique, since it is not based on the Rayleigh–Ritz principle.

Enter the bivariational principle — an unconventional alternative way of rephrasing the Schrödinger equation. It was discovered by the Finnish physicist Jouko Arponen in 1983 that the CC method could be based on the bivariational principle. More than thirty years later, this elegant reformulation is considered highly unconventional, and the bivariational principle has gained little attention.

The idea behind the BIVAQUM project is that the bivariational principle may be the key to cheaper and more robust computational techniques. The goal of BIVAQUM is to study the bivariational principle from a mathematical point of view, aiming to develop new computational techniques that “break” the curse of dimensionality. The CC method is the living proof that this is possible. Moreover, we have already developed a generalization of CC theory — namely, orbital-adaptive CC, which is based on the bivariational principle and cannot be derived from the conventional viewpoint. This demonstrates that it is possible to extend the area



of applicability of the unconventional approach.

The BIVAQUM project is thus about exploring a fundamentally different approach to the development of computational methods in chemistry. The project has a large mathematical element, in that the bivariational principle is not well understood from a mathematical perspective. If successful, the BIVAQUM project may have a dramatic impact on how we develop computational techniques in chemistry, as it changes the “rules” of quantum chemistry — that is, the underlying variational principle that we base our tools on. ■



## Highlight: Catalyst Design for Small Molecule Activation

Ainara Nova

The use of small molecules in organic synthesis is an area of great interest because such molecules are readily available and are economical building blocks that can be converted into added-value products. However, they are typically inert and require catalytic activation to be efficiently used. Finding a good catalyst for such reactions is not trivial. Therefore, a protocol designed to achieve this aim will be very attractive.

Rational catalyst design requires a good understanding of the mechanistic aspects of the catalytic processes. A useful starting point is the mechanism of a known catalytic reaction in which improvements are still required. This includes not only the productive catalytic pathway but also unproductive reactions such as catalyst decom-

position and the formation of unreactive species. Once the mechanism is completely understood, rational modification of the catalyst can be performed to reduce the energy barrier of the rate limiting steps, thereby increasing activity and preventing undesirable processes, thus improving robustness.

Computation can play a key role in catalyst design when combined with experiment, by determining the complete reaction mechanism and by evaluating the effects of ligand modifications before these are tested in the lab. At the CTCC in Oslo, improvements of Pd catalysts for cross-coupling reactions have already been accomplished by following this strategy by David Balcells and myself in collaboration with the experimental group of



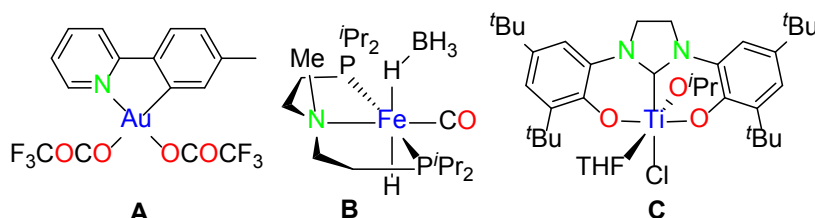
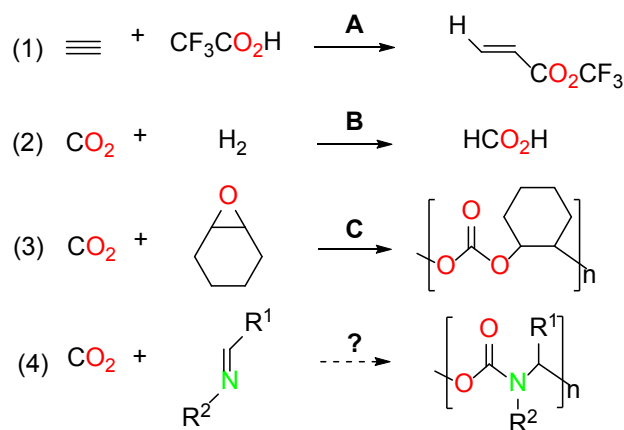


Prof. Nilay Hazari at Yale University (J. Am. Chem. Soc., 2014, 136, 7300; Organometallics, 2015, 34, 381; ACS Catal., 2015, 5, 3680; ACS Catal., 2015, 5, 5596). The same protocol is currently being used to develop an efficient Ni-catalyst for the same type of reactions. The change from Pd to Ni is motivated by the present need to use earth-abundant, cheap, and non-toxic metals. In addition, we are working towards developing an efficient borylation catalyst based on cross-coupling reactions in collaboration with Prof. Simon Aldridge at the University of Oxford.

Ethylene and acetylene are two of the target molecules that we are currently working on in collaboration with the group of Mats Tilset at the CTCC in Oslo. The functionalization of ethylene by using the gold complex **A** has been accomplished by means of trifluoroacetic acid (TFA, J. Am. Chem. Soc., 2014, 136 10104), trifluoroethanol (TFE) and a mixture of acetonitrile and water. However, we are still working on making these transformations catalytic by following the rational design approach. In this case, the insight required is obtained from the mechanistic study of three different processes, including the stoichiometric reactions with ethylene, the catalytic functionalization of acetylene by TFA (Eq 1), and the most common decomposition processes observed in related Au(III) complexes.

Thanks to the awarded FRIPRO Young Research Talent grant, CO<sub>2</sub> functionalization will be the new small-molecule activation target in the next three years. Use of CO<sub>2</sub> as a building block in organic synthesis is especially important for the development of a carbon-recycling economy. In this project, two reactions will be studied: the hydrogenation of CO<sub>2</sub> to form formic acid catalyzed by **B** (Eq 2)

and the generation of poly(cyclohexene-alt-carbonate) from CO<sub>2</sub> and epoxides catalyzed by **C** (Eq 3). Improvements of the efficiency of **B** and **C** to make these reactions industrially attractive will be made in collaboration with the experimental groups of Profs. Hazari (Eq 2) and Le-Roux at the UiB (Eq 3). In addition, the development of a new reaction for the synthesis of poly-carbamates from CO<sub>2</sub> and imines (Eq 4) will be explored. This will be done by optimizing the mechanism proposed for the synthesis of poly-carbonates, replacing the epoxide by an imine — first computationally and then experimentally in collaboration with Mats Tilset. If successful, it will give access to a new class of polyurethanes by a green process incorporating CO<sub>2</sub>, demonstrating the power of computational chemistry for designing new chemical processes. ■





# Almlöf–Gropen Lecture 2015: Nobel Laureate Professor Arie Warshel

The Almlöf–Gropen Lecturer of 2015 was Professor Arie Warshel, University of Southern California, USA. Warshel was born in 1940 in Israel. He did his MSc and PhD with Shneior Lifson at the Weizmann Institute of Science in Israel and carried out postdoctoral work with Martin Karplus at Harvard University 1969–1972. His work the next four years was shared between the Weizmann Institute and the Laboratory of Molecular Biology in Cambridge, where he collaborated with Michael Levitt. In 1976 he moved to California and joined the Department of Chemistry at University of Southern California (USC). Warshel holds the Dana and David Dornsife Chair in Chemistry and is a Distinguished Professor of Chemistry and Biochemistry at USC. For his contributions to computational methods for structure-function studies of biological molecules — in particular, multi-scale models for complex chemical systems such as the QM/MM method — Arie Warshel was awarded the Nobel Prize in Chemistry in 2013 together with Martin Karplus and Michael Levitt.

In his lecture, *How to Model the Action of Complex Biological Systems on a Molecular Level*, delivered in Oslo and Tromsø on June 23 and 25, respectively, Professor Warshel gave a historical overview of how the action of complex biological molecules has been studied and the enormous progress witnessed in this exciting area from its inception in the early 1970s. With the emergence of powerful computers, the development of computational methods combining different levels of theory, ranging from classical force fields to quantum mechanics, has enabled structure-function relationship in biological systems to be deduced. Much of his talk was devoted to the study of enzymes and their reactions.



Arie Warshel (left) and Bjørn-Olav Brandsdal (right)

Enzymes play a key role in nearly all biological processes, accelerating a variety of reactions. They possess the remarkable capacity to accelerate reactions by many orders of magnitude when compared with the uncatalyzed reactions, enabling cells to carry out reactions that would otherwise not occur on biologically relevant timescales. Professor Warshel provided strong evidence that enzymatic catalysis is primarily caused by electrostatic preorganization, and that dynamical effects do not change the rate of chemical steps in enzyme reactions. He also showed how computer simulations help to understand the preferred directions among a set of complex molecular motions and that such machines work by exploiting free-energy gradients.

The Almlöf–Gropen Lecture Series was established by the CTCC to honour the memory of two pioneers of quantum chemistry in Norway: Professor Jan Almlöf (1945–1996) at the University of Oslo and Professor Odd Gropen (1941–2005) at the University of Tromsø. Previous Almlöf–Gropen speakers are Prof. Bjørn Roos, (University of Lund, 2008), Tom Ziegler (University of Calgary, 2009), Michele Parrinello (ETH Zürich, 2010), Pekka Pyykkö (University of Helsinki, 2011), Harry B. Gray (Caltech, 2012), Fritz Schaefer (University of Georgia, 2013), and Leo Radom (University of Sydney, 2014). ■



Audience in Tromsø



# Outreach: Hylleraas Exhibition

Department of Chemistry, University of Oslo, April 15 2015

On April 15 2015, a permanent exhibition on the life and work of the Norwegian physicist Egil A. Hylleraas was opened at the CTCC, University of Oslo. Several members of the Hylleraas family were present at the opening, including Hylleraas' daughter, Inger Hylleraas Bø, who has donated photos, books, and Hylleraas' calculator to the exhibition. Present were also officials from the Department of Chemistry and The Faculty of Mathematics

and Natural Science at the University of Oslo. The event began with a popular talk about Hylleraas, his life and contributions by Trygve Helgaker. The exhibition itself had been designed and prepared by Chloé Turlotte, Ellen Christina Sjøwall, and Trygve Helgaker with help from Jan Ingar Johnsen. ■



*Egil Hylleraas daughter Inger Hylleraas Bø and family members at the opening of the Hylleraas Exhibition*



*This Dalton calculator was used by Hylleraas from the 1930s to 1951, when it was given to his nephew for use in a grocery store. It was donated by Inger and Philippe Caquet to the Hylleraas Exhibition*





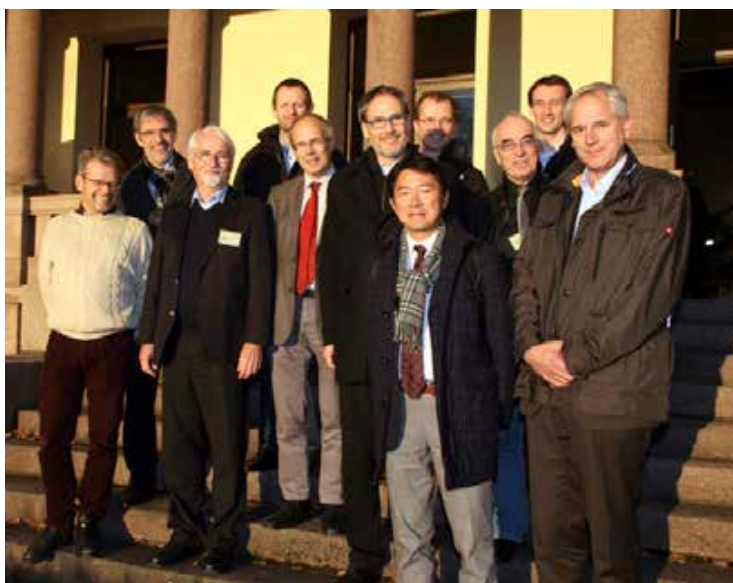
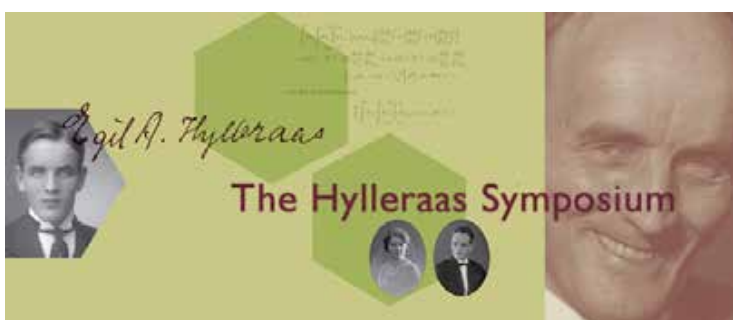
# Outreach: Hylleraas Symposium

Norwegian Academy of Science and Letters, Oslo, November 23 2015

On November 23, the CTCC and Norwegian Academy of Science and Letters organized a one-day symposium in honour of Egil Hylleraas. The speakers were seven prominent quantum chemists (see photo), who have contributed decisively to the revival and development of the method of explicit electron correlation, pioneered by Hylleraas in the late 1920s and early 1930s. Together, their presentations painted a broad and detailed picture of the current state of the art: *Can Hylleraas coordinates be used in density-functional theory?* (Prof. W. Klopper, Karlsruhe Institute of Technology), *Singular coincidences and electron correlation* (Prof. P. Taylor, University of Melbourne), *The impact of explicitly correlated F12 theory on modern electronic structure calculations* (Prof. S. Ten-no, Kobe University), *Practical explicitly correlated methods in LCAO and non-LCAO representations* (Prof. E. Valeev, Virginia Tech), *Explicitly correlated coupled-cluster methods for large molecules* (Prof. H.-J. Werner, University of Stuttgart), *Explicit electron correlation in molecules and crystalline materials* (Dr. D. Tew, Bristol University), and *Explicit correlation for connected triple excitations in coupled-cluster theory* (Prof. A. Köhn, University of Stuttgart). Each presentation created a lively discussion among the speakers and the 50 participants of the symposium.

The evening program consisted of a popular talk by Trygve Helgaker, after which the Mayor of Engerdal Lars Erik Hyllvang outlined the plans for a park and science trail bearing the name of Hylleraas, partly financed by a generous gift of 2 MNOK from Sparebanken Hedmarks Kunstfond to the municipality of Engerdal, as announced by Wenche Høye at the meeting. The 90 guests, including the speakers, members of Hylleraas family, the Mayor of Engerdal, representatives of the University of

Oslo and the Research Council of Norway, then sat down for banquet, being welcomed by the President of the Norwegian Academy of Science and Letters Kirsti Strøm Bull.



Left to right: Prof. Trond Saue (organizer, University of Toulouse), Prof. Jürgen Gauss (organizer, University of Mainz), Prof. Hans-Joachim Werner (speaker, University of Stuttgart), Prof. Thomas B. Pedersen (organizer, CTCC), Prof. Trygve Helgaker (organizer, CTCC), Prof. Andreas Köhn (speaker, University of Stuttgart), Prof. Seiichiro Ten-no (speaker, Kobe University), Prof. Edward Valeev (speaker, Virginia Tech), Prof. Peter R. A. Taylor (speaker, University of Melbourne), Dr. David Tew (Bristol University), Prof. Wim Klopper (speaker, Karlsruhe Institute of Technology).



# Outreach: International Year of Light

Norwegian Academy of Science and Letters, Oslo, November 11 2015

In proclaiming 2015 to be the International Year of Light, the UN has recognized the importance of raising global awareness about how light-based technologies promote sustainable development and provide solutions to global challenges in energy, education, agriculture and health, see (<http://www.light2015.org>). The year 2015 was the 200th anniversary of Fresnel's suggestion that light propagates in space as a travelling wave, the 150th anniversary of Maxwell's electromagnetic theory, and the 100th anniversary of Einstein's theory of general relativity. Furthermore, light plays an important role as a metaphor in religion and philosophy, and affects our health, senses and minds.



INTERNATIONAL  
YEAR OF LIGHT  
2015

On November 11, The Norwegian Academy of Science and Letters hosted an interdisciplinary seminar on light with a program intended for a wide audience, with Einar Uggerud of the CTCC as the main organizer. Eleven invited lecturers covering chemistry, physics, astrophysics, biology, medicine, light technology, art history, theology,

and philosophy gave well prepared and inspiring lectures (titles translated to English):

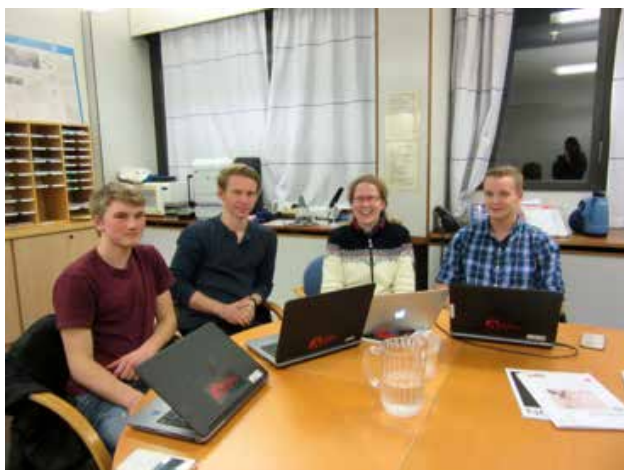
- Johannes Skaar: *Maxwell's theory and Hertz's experiment: the basis of modern telecommunications was created 150 years ago*
- Hans Kristian Eriksen: *Light from the creation of the universe*
- Johan E. Moan: *Light as a cancer causative agent and as therapy for cancer*
- Linda Haugen: *A new era for light microscopy*
- Øivind Storm Bjerke: *Light and the visual arts*
- Erik Marstein: *From light to electricity and back: photovoltaics and LEDs*
- Søren Rud Keiding: *Light and chemistry: «survival of the fastest»*
- Björn Åkermark: *Natural and artificial photosynthesis*
- Mari Nerhus: *Does light excite us? Seasonal variations and the role of vitamin D in mental disorders*
- Anders Runesson: *«Let there be light!»: on the struggle against darkness in the Bible*
- Trond Berg Eriksen: *«Mehr Licht!»: light as a metaphor in philosophy* ■





# Outreach: CTCC at Drammen Upper Secondary School

In 2010, Drammen Upper Secondary School (videregående skole) established a science research line (forskerlinje), whose students attend several more lessons per week in natural sciences and mathematics than do other students. In addition, they follow a special subject “Technology and Research”, learning about research in general and carrying out their own research project. The three students, Ola Solli Grønningsæter, Sveinar Hammer and Chris Andre Reierth Røgeberg completed their research project at the CTCC, under the supervision of Dr. Heike Fliegl.

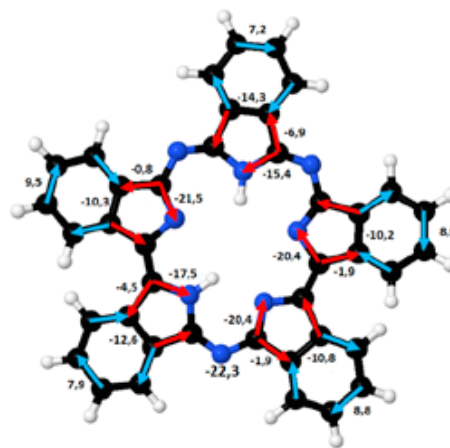


From left: Sveinar Hammar, Chris Andre Reierth Røgeberg, Dr. Heike Fliegl, and Ola Solli Grønningsæter

Their task was to calculate the currents induced by a magnetic field in the pentabenzotriazasmaragdyrin (PBTAS) molecule, determine the current pathways and thereby classify the molecules as aromatic or antiaromatic. In the process, the students learned about the theory and application of state-of-the-art quantum-chemical

methods with an emphasis on aromaticity studies. Ola, Sveinar, and Chris calculated the induced current density of PBTAS with the gauge-including magnetically-induced-current (GIMIC) method, using density functional theory. Their calculations showed that PBTAS is antiaromatic, carrying paratropic ring currents of  $-22.3$  nA/T, with currents flowing predominantly along the inner nitrogen atoms. In addition, its outer benzene rings carry local diatropic currents, see Figure. The students successfully completed their project, submitting a 40-page report *GIMIC analyse av pentabenzotriazasmaragdyrin viser antiaromatisk klassifisering*, to be graded.

The unusual topic and learning impact of the project have already attracted attention. The project was selected for a research-line highlight presentation, demonstrating the success of the school's research line. CTCC's youngest students have also been invited to present their work at a research evening (forskerkveld) at their school and at the CTCC weekly seminar series. ■



Molecular structure and B3LYP/def2-TZVP integrated current strength susceptibilities of PBTAS.





# CTCC members

## Principal Scientists

---



**Bjørn Olav Brandsdal**  
Professor  
UiT



**Tor Flå**  
Professor  
UiT



**Luca Frediani**  
Associate  
Professor  
UiT



**Michele Cascella**  
Associate Professor  
UiO



**Abhik Ghosh**  
Professor  
UiT



**Trygve Helgaker**  
Professor  
UiO



**Thomas Bondo Pedersen**  
Associate  
Professor  
UiO



**Kenneth Ruud**  
Professor  
UiT



**Mats Tilset**  
Professor  
UiO



**Einar Uggerud**  
Professor  
UiO

## Researchers

---



**Hima Bindu Kolli**  
UiO



**Simen Kvaal**  
UiO



**David Balcells**  
UiO



**Erik Tellgren**  
UiO



**Kathrin Hopmann**  
UiT



**Heike Fliegl**  
UiO



**Bin Gao**  
UiT



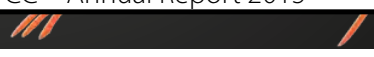
**Peter Wind**  
UiT



**Ulf Egil Ekström**  
UiO























**Mauritz Ryding**  
UiO























## Postdocs

 <b>Gustav Baardsen</b> UiO	 <b>Elke Fasshauer</b> UiT	 <b>Andre Laestadius</b> UiO	 <b>Elisa Rebolini</b> UiO
 <b>Alex Borgoo</b> UiO	 <b>Daniel Friese</b> UiT	 <b>Hugo Vazquez Lima</b> UiT	 <b>Magnus Ringholm</b> UiT
 <b>Yann Cornaton</b> UiT	 <b>Geir Isaksen</b> UiT	 <b>Elena Malkin</b> UiT	 <b>Arnfinn Hykkerud Steindal</b> UiT
 <b>Andrea Debnarova</b> UiO	 <b>Stig Rune Jensen</b> UiT	 <b>Ainara Nova</b> UiO	 <b>Stella Stopkowicz</b> UiO
 <b>Taye Demissie</b> UiT	 <b>Stanislav Komorovsky</b> UiT	 <b>Elena Platania</b> UiO	 <b>Clemens Woywod</b> UiT

## PhD students

 <b>Marco Anelli</b> UiT	 <b>Maarten Beerepoot</b> UiT	 <b>Audun Skau Hansen</b> UiO	 <b>Jon Austad</b> UiO
 <b>Roberto Di Remigio</b> UiT	 <b>Tor-Arne Andberg</b> UiT	 <b>Patrick Merlot</b> UiO	 <b>Chandan Kumar</b> UiO
 <b>Kai K. Lange</b> UiO	 <b>Karl R. Leikanger</b> UiO	 <b>Marius Kadek</b> UiT	 <b>Raphael Mathias Peltzer</b> UiO
 <b>Davide Michetti</b> UiT	 <b>Glenn B.S. Miller</b> UiO	 <b>Krzysztof Mozgawa</b> UiT	 <b>Sarah Reimann</b> UiO
 <b>Johannes Rekkedal</b> UiO	 <b>Sigbjørn Løland Bore</b> UiO		



## Affiliates

---



**Arne Karlsson**  
Professor II  
UiO



**Harald Møllendal**  
Professor emeritus  
UiO



**Claus Jørgen Nielsen**  
Professor  
UiO



**Peter Klæboe**  
Professor emeritus  
UiO



**Inge Røeggen**  
Professor emeritus  
UiT



**Svein Samdal**  
Professor  
UiO

## Administrative Staff

---



**Stig Eide**  
Head of Administration  
UiT



**Jan Ingar Johnsen**  
Head of Administration  
UiO

## Senior Engineers

---



**Niels H. Andersen**  
UiO



**Simen Reine**  
UiO



**John Vedde**  
UiO



**Michal Repisky**  
UiT



**Osamu Sekiguichi**  
UiO

## Adjunct Professors

---



**Odlie Eisenstein**  
Professor II  
UiO



**Andrew Teale**  
Associate Professor II  
UiO



**Espen Sagvolden**  
Associate Professor II  
UiO

## Board of Directors

---



**Professor Fred Godtliebsen**  
*Vice Dean of the Faculty of Science, UiT*  
Chairman of the board



**Professor Anne-Brit Kolstø**  
*University of Oslo*  
Vice-chairman of the board



**Dr. Nina Aas**  
*Det norske oljeselskap ASA*



**Professor Ragnar Winther**  
*University of Oslo*



**Professor Ole Swang**  
*Innovative Natural Gas Processes and Products, inGAP, and Senior Scientist at SINTEF Materials and Chemistry*

## Scientific Advisory Board

---

**Professor Kersti Hermansson**  
*Uppsala University, Sweden*

**Professor Vidar Remi Jensen**  
*University of Bergen, Norway*

**Professor Gunnar Nyman**  
*University of Gothenburg, Sweden*

**Professor Mike Robb**  
*Imperial College London, UK*





# Fundamental Aspects of DFT

The Norwegian Academy of Science and Letters, Oslo, January 8–10 2015

An international workshop dedicated to fundamental aspects of density-functional theory (DFT) was organized by CTCC members Simen Kvaal and Trygve Helgaker, on 8 – 10 January 2015, at The Norwegian Academy of Science and Letters. The workshop focused on recent developments in DFT, with emphasis on theoretical and fundamental aspects (including formal developments)

rather than applications. The workshop attracted 57 participants from 14 countries, who gave a total of 25 oral presentations. Among the speakers were several important contributors to modern DFT, including Paul Ayers, Evert Jan Baerends, Andreas Görling, Mel Levy, Andreas Savin, and David Tozer. Three young members of the CTCC gave presentations. ■



*Participants of Fundamental Aspects of DFT outside the Academy Building*



# A Voyage From Molecules to Materials with Numerical Methods for Quantum Chemistry (NMQC)

Coastal Express Tromsø–Kirkenes–Tromsø, January 11–15 2015

A coastal adventure into the recent progress in numerical methods for quantum-chemical calculations

The NMQC conference took place on board the MS *Midnattsol* ship of the Hurtigruten fleet from Tromsø to Kirkenes and back, from January 11 to 15. The goal of the conference was to gather scientists who make use of real-space numerical methods in quantum chemistry. The conference covered six main topics, from wavelet and multiwavelet methods, to density-functional theory, correlation, molecular properties and fundamental mathematical aspects. Applying real-space methods to quantum chemistry is challenging (memory requirements, computational overhead, etc.) pushing the limits of such methods to the extreme — as extreme as the conference venue: the voyage took place during the arctic night when the sun does not rise and crossed North Cape to reach Kirkenes, at the Norwegian border with Russia. Thanks to the cold ( $-27^{\circ}\text{C}$  in Kirkenes) but beautiful weather, the

participants could admire the beautiful arctic nature and the spectacular northern lights.

More than 50 scientists from all over the world took part in the conference, attending the 30 lectures and a poster session. Those who dared face the arctic climate joined an excursion in Kirkenes (dog sledding, snowmobile, ice hotel).

The conference was a success both scientifically and socially: never before had a conference been organized on this topic. The conference was organized by Luca Frediani (UiT), Dage Sundholm (Univ. of Helsinki), Kathrin Hopmann (UiT), Stig-Rune Jensen (UiT), Roberto Di Remigio (UiT), and Stig Eide (UiT). Financial support was provided by a conference grant from UiT, the CTCC, and the Department of Chemistry at UiT.

In connection with the workshop, Luca Frediani and Dage Sundholm edited a themed issue of *Physical Chemistry Chemical Physics* entitled *Real-Space Numerical Grid Methods in Quantum Chemistry*, with 22 articles. ■







# CTCC Spring Meeting

Sundvolden Hotel, Sundvollen April 22–24 2015

The CTCC spring meeting was held at Sundvolden Hotel April 22–24 2015. The meeting saw 23 seminars, divided in 7 sessions, including 2 keynote lectures by Prof. Franca Fraternali from King's College of London, and Prof. Truls Norby from the University of Oslo. One special session was devoted to seminars by young scientists from CTCC who were permanently employed and/or received personal funding in the past year. In particular, Bin Gao presented *Density-functional tight-binding (DFTB)*; Erik Tellgren presented *Non-relativistic and relativistic current-density functional theory*; Simen Kvaal presented *The bivariational principle for approximating the Schrödinger equation*; and Michal Repisky presented *Modelling fast electron dynamics with relativistic real-time time-dependent density functional theory*.

In addition to the official program, the senior CTCC members and the two guest speakers held a round-table discussion on the present challenges for theoretical and

computational chemistry, envisaging future plans to continue the successful experience of CTCC in the years to come. ■



Evening at Steinsfjorden at Sundvollen

# Advances in Electronic Structure Theory

Jussieu Campus, Université Pierre et Marie Curie, Paris, April 27–29 2015

Together with Prof. Paola Gori-Giorgi (Vrije Universiteit Amsterdam), Prof. Gustavo Scuseria (Rice University) and Associate Professor Julien Toulouse (UPMC, Paris), Trygve Helgaker organised a three-day international conference in honour of CNRS Research Professor Andreas Savin at UPMC in Paris in April 2015, on the occasion of his 65th birthday. Andreas Savin has made numerous contributions to density-functional theory, including the introduction of range-separated methods. He is the co-author of three CTCC publications. The meeting concentrated on recent developments in density-functional theory, wave-function methods and quantum Monte-Carlo methods, attracting more than 100 participants. A total of 32 presentations were given. The organizers of the meeting have edited a special issue of *Molecular Physics* in honour of Andreas Savin, to be published in 2016. ■



Andreas Savin at the conference dinner, Restaurant Les Tablettes





# Annual Meeting of the Division of Quantum Chemistry and Modelling of the Norwegian Chemical Society

Grand Hotel Terminus, Bergen, June 29–30 2015

The division of Quantum Chemistry and Modelling of the Norwegian Chemical Society (NKS) held its annual meeting in Bergen 29–30 June 2015, with 47 participants, including Margareta Blomberg from KTH (Sweden) and Ove Christiansen from University of Aarhus (Denmark) as international invited speakers.

The annual meeting of the NKS division for Quantum Chemistry and Modelling is a platform where in particular young PhD students, postdocs, and researchers are encouraged to present their work. The organization of the meeting rotates between the Universities of Oslo, Bergen, Tromsø and Trondheim. This time, the annual meeting was organized by Giovanni Occhipinti, Knut Børve and Vidar Remi Jensen at the University of Bergen. In her presentation, Margareta Blomberg gave an overview on how quantum chemistry can be used to explain mechanisms of enzymatic reactions important to energy storage in cells; Ove Christiansen discussed the advantages of using optimized coordinates rather than normal coordinates when investigating molecular vibrations using quantum-chemical methods.

In addition, the organizers had invited five national speakers to present their research: Bjørn-Olav Brandsdal

(UiT, CTCC), Nathalie Reuter (UiB), Simen Kvaal (UiO, CTCC), Per-Olof Åstrand (NTNU) and Anand Thirumalai (Arizona State University, USA), a CTCC guest researcher. The meeting had in total seven sessions and covered a wide spectrum of research topics ranging from studies of reaction mechanisms to the calculation of large molecules and lipids as well as the development of new quantum-chemical methods for molecular properties. In the course of two days, 32 speakers presented their research. In lieu of posters, seven-minute flash talks were presented, which were well received by an enthusiastic audience. The next meeting will take place at NTNU in Trondheim. ■



*Lecture hall at the Grand Hotel Terminus*



# Polarizable Continuum Model (PCM) Workshop

UiT The Arctic University of Norway, Tromsø, July 21–24 2015

A recent activity in the group of Luca Frediani is the development of a stand-alone module PCMSolver for solvation calculations with the polarizable continuum model (PCM). The module has been successfully interfaced with several quantum chemistry programs, opening a wide spectrum of scientific possibilities, including real-time propagation, relativity and correlation. A workshop (July 21-24) was therefore organized to coordinate the development lines that the PCM modularization has opened. Local participants from Tromsø were Luca Frediani, Roberto Di Remigio, Kenneth Ruud, Michal Repisky, Marius Kadek, Krzysztof Mozgawa, while the international guests were Stefano Corni (Univ. of Mode-

na), Silvio Pipolo (ENS, Paris), Christan Pomelli (Univ. of Pisa). Several topics were discussed during the workshop, such as the inclusion of the TessLess model for the molecular cavities, the interface between ReSpect and PCMSolver for real-time propagation, and the combination of complex response theory with solvation in the presence of metal nanoparticles.

Apart from the scientific program, a social dinner was organized at the newly established Mathallen restaurant in Tromsø and a relaxing excursion was taken on the ferry from Bellvik to Vengsøy, to enjoy the Northern Norwegian landscape in the evening sun. ■



*Left to right: Stefano Corni (Univ. of Modena), Silvio Pipolo (ENS, Paris), Christian Pomelli (Univ. of Pisa)*



# Visiting Scientists

## Visitors in Tromsø

Name	Title	Period from-to
Monica Bugeanu	PhD student	10.01.2015 – 11.02.2015
Lukas Konecny	PhD student	14.01.2015 – 28.02.2015
Pawel Kozlowski	Professor	31.05.2015 – 28.06.2015
Petr Bour	Professor	22.05.2015 – 09.06.2015
Monika Krupova	PhD student	22.05.2015 – 09.06.2015
Swapan Chakrabarti	Professor	23.07.2015 – 21.08.2015
Sayantanu Koley	Junior Research Fellow	01.09.2015 – 30.09.2015
Lopa Paul	Junior Research Fellow	01.09.2015 – 30.09.2015
Jeanet Conradie	Professor	10.08.2015 – 10.09.2015
Penny Brothers	Professor	20.04.2015 – 01.05.2015
Stefano Corini	Researcher	22.07.2015 – 26.07.2015
Christian Pomelli	Researcher	20.07.2015 – 27.07.2015
Silvio Pipolo	Postdoc	22.07.2015 – 27.07.2015
Trygve Helgaker	Professor	18.06.2015 – 19.06.2015
Florian Rupp	Professor	25.08.2015 – 15.09.2015
Peter Cherry	PhD student	01.08.2015 – 23.08.2015
Radek Marek	Professor	17.08.2015 – 22.08.2015
Jan Novotny	Postdoc	17.08.2015 – 22.08.2015
Ankan Paul	Professor	18.08.2015 – 14.09.2015
Markus Rauhalhti	Master student	30.08.2015 – 06.09.2015
Jeanet Conradie	Professor	01.11.2015 – 21.11.2015
Arieh Warshel	Professor	24.06.2015 – 27.06.2015





## Visitors in Oslo

Name	Title	Period from – to
Thereza A. Soares	Professor	02.02.2015 – 06.02.2015
Petros Souvatzis	Researcher	04.02.2015 – 05.02.2015
Jürgen Gauss	Professor	20.02.2015 – 06.03.2015
Róbert Iszák	Researcher	25.03.2015 – 28.03.2015
Kathrin Helen Hopmann	Researcher	19.03.2015 – 20.03.2015
Lalita Uribe	PhD student	01.04.2015 – 15.07.2015
Oleksii Rebrov	PhD student	10.04.2015 – 17.04.2015
Anand Thirumalai	Postdoctoral Fellow	13.04.2015 – 22.04.2015
Nathalie Reute	Professor	17.04.2015 – 17.04.2015
Andrew Teale	Associate Professor II	19.04.2015 – 26.04.2015
Franca Fraternali	Professor	22.04.2015 – 24.04.2015
Odile Eisenstein	Professor	23.05.2015 – 01.06.2015
Anand Thirumalai	Postdoctoral Fellow	29.05.2015 – 17.07.2015
Ludwig Adamowicz	Professor	08.06.2015 – 26.06.2015
Israel Fernández López	Researcher	15.06.2015 – 15.08.2015
Arieh Warshel	Professor	22.06.2015 – 24.06.2015
Andrea Correa	Researcher	01.08.2015 – 31.08.2016
Giuseppe Milano	Professor	01.08.2015 – 31.08.2015
David Tozer	Professor	08.08.2015 – 22.08.2015
Odile Eisenstein	Professor	14.08.2015 – 04.09.2015
Jean-Claude Guillemin	Professor	21.08.2015 – 28.08.2015
Keiji Morokuma	Professor	31.08.2015 – 02.09.2015
Taku Onishi	Assistant Professor	31.08.2015 – 18.09.2016
Abril Castro	PhD student	01.09.2015 – 15.01.2016
Ankan Paul	Assistant Professor	01.09.2015 – 11.09.2015
James Talman	Professor	04.09.2015 – 11.09.2015
Sangita Sen	PhD student	17.09.2015 – 30.09.2015
Debashis Mukherjee	Professor	19.09.2015 – 30.09.2015
Odile Eisenstein	Professor	30.09.2015 – 05.10.2015
Anthony Scemama	Research Associate	07.10.2015 – 09.10.2015
Peter Schmelcher	Professor	24.11.2015 – 24.11.2015
Odile Eisenstein	Professor	02.12.2015 – 09.12.2015



# Interview with Visiting Scientist: Professor Jeanet Conradie

Professor Jeanet Conradie, Professor of Chemistry at the University of the Free State in the Republic of South Africa, has been a regular visitor at the UiT over the last 14 years. One of the top researchers at her University in terms of scientific output, she is also the first female professor at her Department. In 2014, she was elected to the Academy of Science of South Africa (ASSAf). Her research involves a combined experimental and computational approach to coordination chemistry and transition metal catalysis.



## 1. Why did you choose to visit CTCC and how did you learn about the CTCC and its visitor program?

I first visited the Department of Chemistry at the University of Tromsø toward the end of 2002, when I did a 6-month postdoc with Professor Abhik Ghosh. We quickly completed a few important projects in the area of NO chemistry and published our results in high-impact journals. Our common interest in NO chemistry as well as other areas has endured and deepened over the last 14 years so Abhik and I together have co-authored nearly 50 papers to date! Today, we are pursuing ever more fundamental and exotic topics, with an important new project on superheavy elements. In recent years, I have also collaborated with and co-authored a few papers with Dr. Kathrin Hopmann. A number of other collaborative projects are also underway with other CTCC staff members.

## 2. In what way was the stay at CTCC important for your scientific activities?

The CCTC has been important to me in two ways. Firstly, I have been exposed to a large community of researchers focusing on computational chemistry – the daily discussions and exchange of knowledge have been extremely useful and pleasant. Second, the excellent supercomputing facilities and support staff at the University of Tromsø have made our scientific work smooth and pleasant.

## 3. How did you find the working conditions and social and scientific environment at the CTCC?

The working conditions are very pleasant indeed and I deeply appreciate the friendliness and helpfulness of everyone at the CTCC. I perceive the Centre as a large family with a common interest in life – theoretical and computational chemistry.

## 4. How did you find Norway in general and Tromsø in particular?

Norway is a wonderful country with breath-taking scenery and solid traditions. I have taken the coastal steamer from Bergen to Tromsø and seen the spectacular coastline. In Tromsø, I have enjoyed each season, the winters brightened by lots of snow and the northern lights and the summers with the midnight sun and beautiful flowers. It is a unique part of the world and very different from my homeland, South Africa. I want to thank the CTCC for allowing me to visit Tromsø on a regular basis. ■



## Abril Castro, Visiting PhD Student from Girona

From September until December 2015, Abril Castro, a PhD student in the group of Marcel Swart at University of Girona, visited the CTCC. As part of her PhD project, she investigates solvent and relativistic effects on NMR shielding constants applying in-house developed CTCC software such as ReSpect and state of the art molecular dynamics computations. She is working together with Trygve Helgaker (UiO), Michele Cascella (UiO), Michal Repisky (UiT), Stano Komorovsky (UiT) and Heike Fliegl (UiO). ■



## Dr. Anand Thirumalai, Visiting Astrophysicist from Arizona

Dr. Anand Thirumalai, an astrophysicist from Arizona State University, visited the CTCC April 13–22 and May 29 – July 17, collaborating with CTCC researcher Erik Tellgren and Trygve Helgaker. Thirumalai works with atoms in the atmospheres of rapidly rotating neutron stars and white dwarfs and has developed a pseudospectral software package for calculations on atoms in the strong magnetic fields encountered on such stellar objects. During his visits to the CTCC, Thirumalai calculated electronic spectra of H<sub>2</sub>, with the aim to identify signals from such species in the spectra from magnetic white dwarfs. ■





# Total Revenue and Expenditure Figures

<b>FAKTISK FINANSIERING AV ALL FAGLIG AKTIVITET VED SENTERET ( i tusen kroner)</b>		<b>2015</b>
Egenfinansiering		7 186
Innbetaling fra samarbeidspartner(e) til vertsinstusjonen		0
Egenfinansiering hos samarbeidspartnere (in kind)		0
Forskningsrådet (SFF-bevilgning)		8 280
Eksterne prosjektmidler som inngår i kontrakten		0
<i>Sum finansiering av senteret som avtalt i kontrakten</i>		<i>15 466</i>
<b>Finansiering av prosjekter med faglig tilknytning til senteret</b>		
Andre prosjektmidler fra Forskningsrådet		11 150
Internasjonale prosjektmidler		7 777
Offentlige prosjektmidler og annen offentlig finansiering		0
Private prosjektmidler og annen privat finansiering		808
<i>Sum finansiering fra ekstern prosjekter</i>		<i>19 735</i>
<i>Finansiering av samlet faglig aktivitet</i>		<i>35 201</i>

<b>REGNSKAPSFØRTE KOSTNADER PÅ CTCC i tusen kroner</b>		<b>2015</b>
Lønn og sosiale kostnader		14 347
Driftskostnader		1 846
<i>Sum kostnader</i>		<i>16 193</i>
<b>Personellressurser på CTCC</b>		
Personellressurser i årsverk		45,7
Professorer, forskere o.l.		15,0
Doktorgradstipendiater		12,6
Postdoktorstipendiater		11,0
Gjedeforskere		3,0
Teknisk/adm. Ansatte		4,1



# Appendix A: Publications CTCC 2015

1. Norheim, Hans-Kristian; Capar, Jan; Einrem, Rune F; Gagnon, Kevin J; Beavers, Christine M; Vazquez-Lima, Hugo; Ghosh, Abhik, *Ligand noninnocence in FeNO corroles: insights from beta-octabromocorrole complexes.*, Dalton transactions (Cambridge, England : 2003), **45**, 681 - 9 (2015) <http://dx.doi.org/10.1039/c5dt03947a>
2. Frediani, Luca; Sundholm, Dage, *Real-space numerical grid methods in quantum chemistry*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 31357 - 31359 (2015) <http://dx.doi.org/10.1039/c5cp90198g>
3. Erichsen, Marius Westgard; Morten, Magnus; Svelle, Stian; Sekiguchi, Osamu; Uggerud, Einar; Olsbye, Unni, *Conclusive Evidence for Two Unimolecular Pathways to Zeolite-Catalyzed De-alkylation of the Heptamethylbenzenium Cation*, CHEMCATCHEM, **7**, 4143 - 4147 (2015) <http://dx.doi.org/10.1002/cctc.201500793>
4. Friese, Daniel H.; Mikhaylov, Alexander; Krzeszewska, Maciej; Poronik, Yevgen M.; Rebane, Aleksander; Ruud, Kenneth; Gryko, Daniel T., *Pyrrolo[3,2-b]pyrroles-From Unprecedented Solvatofluorochromism to Two-Photon Absorption*, CHEMISTRY-A EUROPEAN JOURNAL, **21**, 18364 - 18374 (2015) <http://dx.doi.org/10.1002/chem.201502762>
5. Suh, Hee-Won; Balcells, David; Edwards, Alison J.; Guard, Louise M.; Hazari, Nilay; Mader, Elizabeth A.; Mercado, Brandon Q.; Repisky, Michal, *Understanding the Solution and Solid-State Structures of Pd and Pt PSiP Pincer-Supported Hydrides*, INORGANIC CHEMISTRY, **54**, 11411 - 11422 (2015) <http://dx.doi.org/10.1021/acs.inorgchem.5b02073>
6. Thomassen, Ivar K.; Vazquez-Lima, Hugo; Gagnon, Kevin J.; Ghosh, Abhik, *Octaiodoporphyrin*, INORGANIC CHEMISTRY, **54**, 11493 - 11497 (2015) <http://dx.doi.org/10.1021/acs.inorgchem.5b02127>
7. Capar, Jan; Berg, Steffen; Thomas, Kolle E; Beavers, Christine M; Gagnon, Kevin J; Ghosh, Abhik, *Improved syntheses of beta-octabromo-meso-triarylcorrole derivatives.*, Journal of inorganic biochemistry, **153**, 162 - 6 (2015) <http://dx.doi.org/10.1016/j.jinorgbio.2015.07.017>
8. Demissie, Taye B.; Kostenko, Nataliya; Komorovsky, Stanislav; Repisky, Michal; Isaksson, Johan; Bayer, Annette; Ruud, Kenneth, *Experimental and four-component relativistic DFT studies of tungsten carbonyl complexes*, JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, **28**, 723 - 731 (2015) <http://dx.doi.org/10.1002/poc.3476>
9. Thomas, Kolle E.; Vazquez-Lima, Hugo; Fang, Yuyanyuan; Song, Yang; Gagnon, Kevin J.; Beavers, Christine M.; Kadish, Karl M.; Ghosh, Abhik, *Ligand Noninnocence in Coinage Metal Corroles: A Silver Knife-Edge*, CHEMISTRY-A EUROPEAN JOURNAL, **21**, 16839 - 16847 (2015) <http://dx.doi.org/10.1002/chem.201502150>
10. Thomas, Kolle E; Vazquez-Lima, Hugo; Fang, Yuyanyuan; Song, Yang; Gagnon, Kevin J; Beavers, Christine M; Kadish, Karl M; Ghosh, Abhik, *Ligand Noninnocence in Coinage Metal Corroles: A Silver Knife-Edge.*, Chemistry (Weinheim an der Bergstrasse, Germany), **21**, 16705 - 16705 (2015) <http://dx.doi.org/10.1002/chem.201503939>
11. Fla, Tor; Rupp, Florian; Woywod, Clemens, *Bifurcation patterns in generalized models for the dynamics of normal and leukemic stem cells with signaling*, MATHEMATICAL METHODS IN THE APPLIED SCIENCES, **38**, 3392 - 3407 (2015) <http://dx.doi.org/10.1002/mma.3345>
12. Kvaal, Simen; Helgaker, Trygve, *Ground-state densities from the Rayleigh-Ritz variation principle and from density-functional theory*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4934797>
13. Nielsen, Claus J.; Klæboe, Peter; Andersen, Niels H.; Guirgis, Gamil A.; Hickman, Daniel V.; Morris, Tamia B., *Infrared and Raman spectra, DFT-calculations and spectral assignments of 1,1,3,3,5,5-hexafluoro-1,3,5-trisilacyclohexane*, JOURNAL OF MOLECULAR STRUCTURE, **1099**, 399 - 406 (2015) <http://dx.doi.org/10.1016/j.molstruc.2015.05.065>
14. Peach, Michael J. G.; Teale, Andrew M.; Helgaker,



- Trygve; Tozer, David J., *Fractional Electron Loss in Approximate DFT and Hartree-Fock Theory*, JOURNAL OF CHEMICAL THEORY AND COMPUTATION, **11**, 5262 - 5268 (2015) <http://dx.doi.org/10.1021/acs.jctc.5b00804>
15. Demissie, Taye B.; Jaszunski, Michal; Komorovsky, Stanislav; Repisky, Michal; Ruud, Kenneth, *Absolute NMR shielding scales and nuclear spin-rotation constants in (LuX)-Lu-175 and (AuX)-Au-197 (X=F-19, Cl-35, Br-79 and I-127)*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4934533>
16. Adamowicz, Ludwik; Tellgren, Erik I.; Helgaker, Trygve, *Non-Born-Oppenheimer calculations of the HD molecule in a strong magnetic field*, CHEMICAL PHYSICS LETTERS, **639**, 295 - 299 (2015) <http://dx.doi.org/10.1016/j.cplett.2015.09.051>
17. Friese, Daniel H.; Ringholm, Magnus; Gao, Bin; Ruud, Kenneth, *Open-Ended Recursive Calculation of Single Residues of Response Functions for Perturbation-Dependent Basis Sets*, JOURNAL OF CHEMICAL THEORY AND COMPUTATION, **11**, 4814 - 4824 (2015) <http://dx.doi.org/10.1021/acs.jctc.5b00646>
18. Kadek, Marius; Konecny, Lukas; Gao, Bin; Repisky, Michal; Ruud, Kenneth, *X-ray absorption resonances near L-2,L-3-edges from real-time propagation of the Dirac-Kohn-Sham density matrix*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 22566 - 22570 (2015) <http://dx.doi.org/10.1039/c5cp03712c>
19. Mennucci, Benedetta; Eisenstein, Odile; Fliegl, Heike; Hopmann, Kathrin H.; Helgaker, Trygve; Ruud, Kenneth, *FemEx-Female Excellence in Theoretical and Computational Chemistry*, INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, **115**, 1195 - 1196 (2015) <http://dx.doi.org/10.1002/qua.24961>
20. Hopmann, Kathrin H., *Quantum Chemical Studies of Asymmetric Reactions: Historical Aspects and Recent Examples*, INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, **115**, 1232 - 1249 (2015) <http://dx.doi.org/10.1002/qua.24882>
21. Demissie, Taye B.; Ruud, Kenneth; Hansen, Jorn H., *DFT as a Powerful Predictive Tool in Photoredox Catalysis: Redox Potentials and Mechanistic Analysis*, ORGANOMETALLICS, **34**, 4218 - 4228 (2015) <http://dx.doi.org/10.1021/acs.organomet.5b00582>
22. Friese, Daniel H., *Note: Derivation of two-photon circular dichroism (vol 62, pg 1006, 1975)*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4930017>
23. Mollendal, Harald; Samdal, Svein; Guillemin, Jean-Claude, *Microwave and Quantum Chemical Study of the Hydrazino Group as Proton Donor in Intramolecular Hydrogen Bonding of (2-Fluoroethyl)hydrazine (FCH2CH2NHNH2)*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 9252 - 9261 (2015) <http://dx.doi.org/10.1021/acs.jpca.5b06095>
24. Melvin, Patrick R.; Balcells, David; Hazari, Nilay; Nova, Ainara, *Understanding Precatalyst Activation in Cross-Coupling Reactions: Alcohol Facilitated Reduction from Pd(II) to Pd(0) in Precatalysts of the Type (eta(3)-allyl)Pd(L)(Cl) and (eta(3)-indenyl)Pd(L)(Cl)*, ACS CATALYSIS, **5**, 5596 - 5606 (2015) <http://dx.doi.org/10.1021/acscatal.5b01291>
25. Furness, James W.; Verbeke, Joachim; Tellgren, Erik I.; Stopkowicz, Stella; Ekstroem, Ulf; Helgaker, Trygve; Teale, Andrew M., *Current Density Functional Theory Using Meta-Generalized Gradient Exchange-Correlation Functionals*, JOURNAL OF CHEMICAL THEORY AND COMPUTATION, **11**, 4169 - 4181 (2015) <http://dx.doi.org/10.1021/acs.jctc.5b00535>
26. Garbuio, Viviana; Cascella, Michele; Kupchak, Igor; Pulci, Olivia; Seitsonen, Ari Paavo, *Proton disorder in cubic ice: Effect on the electronic and optical properties*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4929468>
27. Samdal, Svein; Mollendal, Harald; Carles, Sophie, *Rotational Spectrum, Conformational Composition, and Quantum Chemical Calculations of Cyanomethyl Formate (HC(O)OCH2C N), a Compound of Potential Astrochemical Interest*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 9070 - 9077 (2015) <http://dx.doi.org/10.1021/acs.jpca.5b05285>
28. Stopkowicz, Stella; Gauss, Juergen; Lange, Kai K.;





- Tellgren, Erik I.; Helgaker, Trygve, *Coupled-cluster theory for atoms and molecules in strong magnetic fields*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4928056>
29. Epifanovsky, Evgeny; Klein, Kerstin; Stopkowicz, Stella; Gauss, Juergen; Krylov, Anna I., *Spin-orbit couplings within the equation-of-motion coupled-cluster framework: Theory, implementation, and benchmark calculations*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4927785>
30. Komorovsky, Stanislav; Repisky, Michal; Malkin, Elena; Demissie, Taye B.; Ruud, Kenneth, *Four-Component Relativistic Density-Functional Theory Calculations of Nuclear Spin-Rotation Constants: Relativistic Effects in p-Block Hydrides*, JOURNAL OF CHEMICAL THEORY AND COMPUTATION, **11**, 3729 - 3739 (2015) <http://dx.doi.org/10.1021/acs.jctc.5b00276>
31. Hopmann, Kathrin H.; Conradie, Jeanet; Tangen, Espen; Tonzetich, Zachary J.; Lippard, Stephen J.; Ghosh, Abhik, *Singlet-Triplet Gaps of Cobalt Nitrosyls: Insights from Tropocoronand Complexes*, INORGANIC CHEMISTRY, **54**, 7362 - 7367 (2015) <http://dx.doi.org/10.1021/acs.inorgchem.5b00901>
32. Conradie, Jeanet; Berg, Steffen; Ghosh, Abhik, *Mechanisms of Oxygen Atom Transfer between Main-Group Elements*, EUROPEAN JOURNAL OF INORGANIC CHEMISTRY, , 4138 - 4144 (2015) <http://dx.doi.org/10.1002/ejic.201500591>
33. Delcey, Mickael G.; Pedersen, Thomas Bondo; Aquilante, Francesco; Lindh, Roland, *Analytical gradients of the state-average complete active space self-consistent field method with density fitting*, JOURNAL OF CHEMICAL PHYSICS, **143**, - (2015) <http://dx.doi.org/10.1063/1.4927228>
34. Reimann, Sarah; Ekstrom, Ulf; Stopkowicz, Stella; Teale, Andrew M.; Borgoo, Alex; Helgaker, Trygve, *The importance of current contributions to shielding constants in density-functional theory*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 18834 - 18842 (2015) <http://dx.doi.org/10.1039/c5cp02682b>
35. Abboud, Jose-Luis M.; Koppel, Ilmar A.; Uggerud, Einar; Leito, Ivo; Koppel, Ivar; Sekiguchi, Osamu; Kaupmees, Karl; Saame, Jaan; Kuett, Karl; Mishima, Masaaki, *Solution and Gas-Phase Acidities of all-trans (all-E) Retinoic Acid: An Experimental and Computational Study*, CHEMISTRY-A EUROPEAN JOURNAL, **21**, 11238 - 11243 (2015) <http://dx.doi.org/10.1002/chem.201500717>
36. Demissie, Taye B.; Jaszunski, Michal; Malkin, Elena; Komorovsky, Stanislav; Ruud, Kenneth, *NMR shielding and spin-rotation constants in XCO (X = Ni, Pd, Pt) molecules*, MOLECULAR PHYSICS, **113**, 1576 - 1584 (2015) <http://dx.doi.org/10.1080/00268976.2014.993343>
37. Rebolini, Elisa; Toulouse, Julien; Teale, Andrew M.; Helgaker, Trygve; Savin, Andreas, *Excited states from range-separated density-functional perturbation theory*, MOLECULAR PHYSICS, **113**, 1740 - 1749 (2015) <http://dx.doi.org/10.1080/00268976.2015.1011248>
38. Anelli, Marco; Jonsson, Dan; Fliegl, Heike; Ruud, Kenneth, *The origin dependence of the material constants: the permittivity and the inverse permeability*, MOLECULAR PHYSICS, **113**, 1899 - 1913 (2015) <http://dx.doi.org/10.1080/00268976.2015.1021728>
39. Cheng, Chi Y.; Ryley, Matthew S.; Peach, Michael J. G.; Tozer, David J.; Helgaker, Trygve; Teale, Andrew M., *Molecular properties in the Tamm-Dancoff approximation: indirect nuclear spin-spin coupling constants*, MOLECULAR PHYSICS, **113**, 1937 - 1951 (2015) <http://dx.doi.org/10.1080/00268976.2015.1024182>
40. Beerepoot, Maarten T. P.; Friese, Daniel H.; List, Nanna H.; Kongsted, Jacob; Ruud, Kenneth, *Benchmarking two-photon absorption cross sections: performance of CC2 and CAM-B3LYP*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 19306 - 19314 (2015) <http://dx.doi.org/10.1039/c5cp03241e>
41. Hopmann, Kathrin H, *Frontispiece: Iron/Bronsted Acid Catalyzed Asymmetric Hydrogenation: Mechanism and Selectivity-Determining Interactions.*, Chemistry (Weinheim an der Bergstrasse, Germany), **21**, - (2015) <http://dx.doi.org/10.1002/chem.201582862>
42. Hopmann, Kathrin H, *Iron/Bronsted Acid Catalyzed Asymmetric Hydrogenation: Mechanism and Selec-*



- tivity-Determining Interactions.*, Chemistry (Weinheim an der Bergstrasse, Germany), **21**, 10020 - 30 (2015) <http://dx.doi.org/10.1002/chem.201500602>
43. Isaksen, Geir Villy; Andberg, Tor Arne Heim; Aqvist, Johan; Brandsdal, Bjorn Olav, *Qgui: A high-throughput interface for automated setup and analysis of free energy calculations and empirical valence bond simulations in biological systems*, JOURNAL OF MOLECULAR GRAPHICS & MODELLING, **60**, 15 - 23 (2015) <http://dx.doi.org/10.1016/j.jmgm.2015.05.007>
44. Ryding, Mauritz J.; Debnarova, Andrea; Fernandez, Israel; Uggerud, Einar, *Nucleophilic Substitution in Reactions between Partially Hydrated Superoxide Anions and Alkyl Halides*, JOURNAL OF ORGANIC CHEMISTRY, **80**, 6133 - 6142 (2015) <http://dx.doi.org/10.1021/acs.joc.5b00651>
45. Vazquez-Lima, Hugo; Norheim, Hans-Kristian; Einrem, Rune F.; Ghosh, Abhik, *Cryptic noninnocence: FeNO corroles in a new light*, DALTON TRANSACTIONS, **44**, 10146 - 10151 (2015) <http://dx.doi.org/10.1039/c5dto1495f>
46. Melvin, Patrick R.; Nova, Ainara; Balcells, David; Dai, Wei; Hazari, Nilay; Hruszkewycz, Damian P.; Shah, Hemali P.; Tudge, Matthew T., *Design of a Versatile and Improved Precatalyst Scaffold for Palladium-Catalyzed Cross-Coupling: (eta(3)-1-Bu-t-indenyl)(2)(mu-Cl)(2)Pd-2*, ACS CATALYSIS, **5**, 3680 - 3688 (2015) <http://dx.doi.org/10.1021/acscatal.5b00878>
47. Christen, Monika; Marcaida, Maria J.; Lamprakis, Christos; Aeschmann, Walter; Vaithilingam, Jathana; Schneider, Petra; Hilbert, Manuel; Schneider, Gisbert; Cascella, Michele; Stocker, Achim, *Structural insights on cholesterol endosynthesis: Binding of squalene and 2,3-oxidosqualene to supernatant protein factor*, JOURNAL OF STRUCTURAL BIOLOGY, **190**, 261 - 270 (2015) <http://dx.doi.org/10.1016/j.jsb.2015.05.001>
48. Durdek, Antoine; Jensen, Stig Rune; Juselius, Jonas; Wind, Peter; Fla, Tor; Frediani, Luca, *Adaptive order polynomial algorithm in a multiwavelet representation scheme*, APPLIED NUMERICAL MATHEMATICS, **92**, 40 - 53 (2015) <http://dx.doi.org/10.1016/j.apnum.2014.12.006>
49. Di Remigio, Roberto; Bast, Radovan; Frediani, Luca; Saue, Trond, *Four-Component Relativistic Calculations in Solution with the Polarizable Continuum Model of Solvation: Theory, Implementation, and Application to the Group 16 Dihalides H<sub>2</sub>X (X = O, S, Se, Te, Po)*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 5061 - 5077 (2015) <http://dx.doi.org/10.1021/jp507279y>
50. Olsen, Jogvan Magnus Haugaard; Steinmann, Casper; Ruud, Kenneth; Kongsted, Jacob, *Polarizable Density Embedding: A New QM/QM/MM-Based Computational Strategy*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 5344 - 5355 (2015) <http://dx.doi.org/10.1021/jp510138k>
51. Remigio, Roberto Di; Bast, Radovan; Frediani, Luca; Saue, Trond, *Four-component relativistic calculations in solution with the polarizable continuum model of solvation: theory, implementation, and application to the group 16 dihalides H<sub>2</sub>X (X = O, S, Se, Te, Po).*, The journal of physical chemistry. A, **119**, 5061 - 77 (2015) <http://dx.doi.org/10.1021/jp507279y>
52. Samdal, Svein; Mollendal, Harald; Reine, Simen; Guillemin, Jean-Claude, *Ring Planarity Problem of 2-Oxazoline Revisited Using Microwave Spectroscopy and Quantum Chemical Calculations*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 4875 - 4884 (2015) <http://dx.doi.org/10.1021/acs.jpca.5b02528>
53. Friese, Daniel H.; Bast, Radovan; Ruud, Kenneth, *Five-Photon Absorption and Selective Enhancement of Multiphoton Absorption Processes*, ACS PHOTONICS, **2**, 572 - 577 (2015) <http://dx.doi.org/10.1021/acsp Photonics.5b00053>
54. Fasshauer, Elke; Kolorenc, Premysl; Pernpointner, Markus, *Relativistic decay widths of autoionization processes: The relativistic FanoADC-Stieltjes method*, JOURNAL OF CHEMICAL PHYSICS, **142**, - (2015) <http://dx.doi.org/10.1063/1.4917255>
55. Valente, Sergio; Rodriguez, Veronica; Mercurio, Ciro; Vianello, Paola; Saponara, Bruna; Cirilli, Roberto; Ciossani, Giuseppe; Labella, Donatella; Marrocco, Biagina; Monaldi, Daria; Ruoppolo, Giovanni; Tilset, Mats; Botrugno, Ortona A.; Dessanti, Paola; Minucci, Saverio; Mattevi, Andrea; Varasi, Mario; Mai, Antonello, *Pure enantiomers of benzoylamino-tranylcyclo-*



- promine: LSD1 inhibition, gene modulation in human leukemia cells and effects on clonogenic potential of murine promyelocytic blasts*, EUROPEAN JOURNAL OF MEDICINAL CHEMISTRY, **94**, 163 - 174 (2015) <http://dx.doi.org/10.1016/j.ejmech.2015.02.060>
56. Samdal, Svein; Mollendal, Harald; Guillemin, Jean-Claude, *Conformational Properties of cis- and trans-N-Cyclopropylformamide Studied by Microwave Spectroscopy and Quantum Chemical Calculations*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 3375 - 3383 (2015) <http://dx.doi.org/10.1021/acs.jpca.5b00542>
57. Capar, Jan; Conradie, Jeanet; Beavers, Christine M.; Ghosh, Abhik, *Molecular Structures of Free-Base Corroles: Nonplanarity, Chirality, and Enantiomerization*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 3452 - 3457 (2015) <http://dx.doi.org/10.1021/jp511188c>
58. Rebolini, Elisa; Toulouse, Julien; Teale, Andrew M.; Helgaker, Trygve; Savin, Andreas, *Calculating excitation energies by extrapolation along adiabatic connections*, PHYSICAL REVIEW A, **91**, - (2015) <http://dx.doi.org/10.1103/PhysRevA.91.032519>
59. Kristkova, Anezka; Komorovsky, Stanislav; Repisky, Michal; Malkin, Vladimir G.; Malkina, Olga L., *Relativistic four-component calculations of indirect nuclear spin-spin couplings with efficient evaluation of the exchange-correlation response kernel*, JOURNAL OF CHEMICAL PHYSICS, **142**, - (2015) <http://dx.doi.org/10.1063/1.4913639>
60. Fliegl, Heike; Pichierri, Fabio; Sundholm, Dage, *Antiaromatic Character of 16 pi Electron Octaethylporphyrins: Magnetically Induced Ring Currents from DFT-GIMIC Calculations*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 2344 - 2350 (2015) <http://dx.doi.org/10.1021/jp5067549>
61. Nilsson, Elna J. K.; Heimdal, Jimmy; Bache-Andreassen, Lihn; Johnson, Matthew S.; Nielsen, Claus J., *Tropospheric Photolysis Rates of the Acetaldehyde Isotopologues CD<sub>3</sub>CHO and CD<sub>3</sub>CDO Relative to CH<sub>3</sub>CHO Measured at the European Photoreactor Facility*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 2562 - 2567 (2015) <http://dx.doi.org/10.1021/jp509050d>
62. Tarakanov, Pavel A.; Simakov, Anton O.; Tolbin, Alexandr Yu.; Salashova, Irina O.; Shestov, Vladimir I.; Tomilova, Larisa G., *Novel A(3)B-type tert-butyl-substituted tribenzodiazepinoporphyrazine: Synthesis, spectral properties and DFT study*, SPECTROCHIMICA ACTA PART A-MOLECULAR AND BIOMOLECULAR SPECTROSCOPY, **139**, 464 - 470 (2015) <http://dx.doi.org/10.1016/j.saa.2014.12.054>
63. Bunkan, Arne Joakim C.; Hetzler, Jens; Mikoviny, Tomas; Wisthaler, Armin; Nielsen, Claus J.; Olzmann, Matthias, *The reactions of N-methylformamide and N,N-dimethylformamide with OH and their photooxidation under atmospheric conditions: experimental and theoretical studies*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 7046 - 7059 (2015) <http://dx.doi.org/10.1039/c4cp05805d>
64. Repisky, Michal; Konecny, Lukas; Kadek, Marius; Komorovsky, Stanislav; Malkin, Olga L.; Malkin, Vladimir G.; Ruud, Kenneth, *Excitation Energies from Real-Time Propagation of the Four-Component Dirac-Kohn-Sham Equation*, JOURNAL OF CHEMICAL THEORY AND COMPUTATION, **11**, 980 - 991 (2015) <http://dx.doi.org/10.1021/ct501078d>
65. Komorovsky, Stanislav; Repisky, Michal; Malkin, Elena; Ruud, Kenneth; Gauss, Juergen, *Communication: The absolute shielding scales of oxygen and sulfur revisited*, JOURNAL OF CHEMICAL PHYSICS, **142**, - (2015) <http://dx.doi.org/10.1063/1.4913634>
66. Hoffmann, Mark R.; Helgaker, Trygve, *Use of Density Functional Theory Orbitals in the GVVPT2 Variant of Second-Order Multistate Multireference Perturbation Theory*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 1548 - 1553 (2015) <http://dx.doi.org/10.1021/jp507554v>
67. Friese, Daniel H.; Beerepoot, Maarten T. P.; Ringholm, Magnus; Ruud, Kenneth, *Open-Ended Recursive Approach for the Calculation of Multiphoton Absorption Matrix Elements*, JOURNAL OF CHEMICAL THEORY AND COMPUTATION, **11**, 1129 - 1144 (2015) <http://dx.doi.org/10.1021/ct501113y>
68. Pikulska, Anna; Steindal, Arnfinn Hykkerud; Beerepoot, Maarten T. P.; Pecul, Magdalena, *Electron-*





- ic Circular Dichroism of Fluorescent Proteins: A Computational Study*, JOURNAL OF PHYSICAL CHEMISTRY B, **119**, 3377 - 3386 (2015) <http://dx.doi.org/10.1021/jp511199g>
69. Ryding, Mauritz Johan; Izsak, Robert; Merlot, Patrick; Reine, Simen; Helgaker, Trygve; Uggerud, Einar, *Geometry of the magic number  $H^+(H_2O)_n$  water cluster by proxy*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 5466 - 5473 (2015) <http://dx.doi.org/10.1039/c4cp05246c>
70. Valiev, Rashid R.; Fliegl, Heike; Sundholm, Dage, *Aromatic Pathways in Carathiaporphyrins*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 1201 - 1207 (2015) <http://dx.doi.org/10.1021/jp5120652>
71. Conradie, Jeanet; Patra, Ashis K.; Harrop, Todd C.; Ghosh, Abhik, *Square-Antiprismatic Eight-Coordinate Complexes of Divalent First-Row Transition Metal Cations: A Density Functional Theory Exploration of the Electronic Structural Landscape*, INORGANIC CHEMISTRY, **54**, 1375 - 1383 (2015) <http://dx.doi.org/10.1021/ic502287m>
72. Landman, Marile; Buitendach, Blenerhassitt E.; Conradie, Murrigje M.; Fraser, Roan; van Rooyen, Petrus H.; Conradie, Jeanet, *Fischer mono- and biscarbene complexes of tungsten with mono- and dimeric heteroaromatic substituents*, JOURNAL OF ELECTROANALYTICAL CHEMISTRY, **739**, 202 - 210 (2015) <http://dx.doi.org/10.1016/j.jelechem.2014.12.019>
73. Guirgis, Gamil A.; Dukes, Horace W.; Wyatt, Justin K.; Nielsen, Claus J.; Horn, Anne; Aleksa, Valdemaras; Klæboe, Peter, *Vibrational spectra, quantum chemical calculations and spectral assignments of 1,1-difluoro-1-silacyclohexane*, SPECTROCHIMICA ACTA PART A-MOLECULAR AND BIOMOLECULAR SPECTROSCOPY, **136**, 51 - 57 (2015) <http://dx.doi.org/10.1016/j.saa.2013.10.058>
74. Mollendal, Harald; Samdal, Svein; Guillemin, Jean-Claude, *Microwave and Quantum-Chemical Study of Conformational Properties and Intramolecular Hydrogen Bonding of 2-Hydroxy-3-Butynenitrile (HC equivalent to CCH(OH)C equivalent to N)*, JOURNAL OF PHYSICAL CHEMISTRY A, **119**, 634 - 640 (2015) <http://dx.doi.org/10.1021/jp5112923>
75. Schwabe, Tobias; Beerepoot, Maarten T. P.; Olsen, Jogvan Magnus Haugaard; Kongsted, Jacob, *Analysis of computational models for an accurate study of electronic excitations in GFP*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 2582 - 2588 (2015) <http://dx.doi.org/10.1039/c4cp04524f>
76. List, Nanna Holmgaard; Beerepoot, Maarten T. P.; Olsen, Jogvan Magnus Haugaard; Gao, Bin; Ruud, Kenneth; Jensen, Hans Jorgen Aagaard; Kongsted, Jacob, *Molecular quantum mechanical gradients within the polarizable embedding approach-Application to the internal vibrational Stark shift of acetophenone*, JOURNAL OF CHEMICAL PHYSICS, **142**, - (2015) <http://dx.doi.org/10.1063/1.4905909>
77. Hruszkewycz, Damian P.; Guard, Louise M.; Balcells, David; Feldman, Nicola; Hazari, Nilay; Tilset, Mats, *Effect of 2-Substituents on Allyl-Supported Precatalysts for the Suzuki-Miyaura Reaction: Relating Catalytic Efficiency to the Stability of Palladium(I) Bridging Allyl Dimers*, ORGANOMETALLICS, **34**, 381 - 394 (2015) <http://dx.doi.org/10.1021/om501250y>
78. Bugeanu, Monica; Di Remigio, Roberto; Mozgawa, Krzysztof; Reine, Simen Sommerfelt; Harbrecht, Helmut; Frediani, Luca, *Wavelet formulation of the polarizable continuum model. II. Use of piecewise bilinear boundary elements*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 31566 - 31581 (2015) <http://dx.doi.org/10.1039/c5cp03410h>
79. Miller, Glenn B. S.; Faseke, Vincent; Uggerud, Einar, *Unimolecular dissociation of anions derived from maleic acid (MaH(2)) in the gas phase: MaH(-) and MaMgCl(-)-relationship to Grignard chemistry and reductive CO<sub>2</sub> fixation*, EUROPEAN JOURNAL OF MASS SPECTROMETRY, **21**, 545 - 556 (2015) <http://dx.doi.org/10.1255/ejms.1325>
80. Geng, Yan; Yi, Chenyi; Bircher, Martin Peter; Decurtins, Silvio; Cascella, Michele; Graetzel, Michael; Liu, Shi-Xia, *Anthanthrene dye-sensitized solar cells: influence of the number of anchoring groups and substitution motif*, RSC ADVANCES, **5**, 98643 - 98652 (2015) <http://dx.doi.org/10.1039/c5ra21917e>
81. Sharninghausen, Liam S.; Mercado, Brandon Q.; Crabtree, Robert H.; Balcells, David; Campos, Je-





- sus, *Gel-assisted crystallization of [Ir-4(IME)(7)(CO)H-10](2+) and [Ir-4(IME)(8)H-9](3+) clusters derived from catalytic glycerol dehydrogenation*, DALTON TRANSACTIONS, **44**, 18403 - 18410 (2015) <http://dx.doi.org/10.1039/c5dt03302k>
82. Vicha, Jan; Novotny, Jan; Straka, Michal; Repisky, Michal; Ruud, Kenneth; Komorovsky, Stanislav; Marek, Radek, *Structure, solvent, and relativistic effects on the NMR chemical shifts in square-planar transition-metal complexes: assessment of DFT approaches*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 24944 - 24955 (2015) <http://dx.doi.org/10.1039/c5cp04214c>
83. Freitag, Leon; Knecht, Stefan; Keller, Sebastian F.; Delcey, Mickael G.; Aquilante, Francesco; Pedersen, Thomas Bondo; Lindh, Roland; Reiher, Markus; Gonzalez, Leticia, *Orbital entanglement and CASSCF analysis of the Ru-NO bond in a Ruthenium nitrosyl complex*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 14383 - 14392 (2015) <http://dx.doi.org/10.1039/c4cp05278a>
84. Valiev, Rashid R.; Fliegl, Heike; Sundholm, Dage, *Predicting the degree of aromaticity of novel carbaporphyrinoids*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 14215 - 14222 (2015) <http://dx.doi.org/10.1039/c5cp01306b>
85. Ghosh, Abhik; Conradie, Jeanet, *Pentafluorosulfanyltrimethylsilane: A Nonexistent Molecule?*, EUROPEAN JOURNAL OF INORGANIC CHEMISTRY, , 207 - 209 (2015) <http://dx.doi.org/10.1002/ejic.201402928>
86. Nicovich, J. M.; Mazumder, S.; Laine, P. L.; Wine, P. H.; Tang, Y.; Bunkan, A. J. C.; Nielsen, C. J., *An experimental and theoretical study of the gas phase kinetics of atomic chlorine reactions with CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, and (CH<sub>3</sub>)<sub>3</sub>N*, PHYSICAL CHEMISTRY CHEMICAL PHYSICS, **17**, 911 - 917 (2015) <http://dx.doi.org/10.1039/c4cp03801k>



# Appendix B: Activity Reports 2015

## WP1: Large periodic and nonperiodic systems

Scientists in charge: Trygve Helgaker and Thomas Bondo Pedersen

The work on fast and accurate approximations to the important exchange contribution in Kohn–Sham density-functional theory has continued in 2015. We have conducted a benchmark comparing three approximations: chain of spheres (COSX), pair-atomic resolution of the identity (PARI-K), and the auxiliary density matrix method (ADMM). Though not available in most quantum-chemistry software packages, the potential of the COSX method has been exhausted and, at present, it offers the best balance between accuracy and efficiency. Unfortunately, the COSX method does not provide sufficient speedup and the exchange contribution remains the computational bottleneck. The PARI-K and ADMM methods, on the other hand, have the potential to remove this bottleneck but are currently not sufficiently accurate. Consequently, these methods are candidates for further development. We have during 2015 continued the important development of tailored basis sets for the ADMM method, and expect to have these ready for extensive benchmark studies during 2016. We have also initiated a revitalisation of the PARI method, aiming at a linear-scaling algorithm that includes the semi-exact correction to improve accuracy. This has been made possible by the realisation that the PARI method, although unstable for the Coulomb contribution in rare cases, can be used for the exchange term indiscriminately.

The development of quantum-chemistry methods for periodic systems has been significantly strengthened in 2015 through the NFR-FRIPRO researcher project PBCCC. Two postdoctoral fellows, Elisa Rebolini and Gustav Baardsen, and one PhD student, Audun Skau Hansen, were hired in fall of 2015 to work on coupled-cluster methods for periodic systems. Initial efforts have been directed towards the calculation of localised Wannier orbitals within Hartree–Fock and Kohn–Sham theories, and towards design and prototype implementation of a massively

parallel framework supporting a periodic extension of the divide-expand-consolidate approach to linear-scaling coupled-cluster methods. The massively parallel framework will be based on a fault-tolerant messaging system, zeroMQ, which allows for simultaneous utilisation of physically separated computer systems – such as different HPC clusters and individual work stations.

The ERC Starting Grant project BIVAQUM commenced in April 2015. Andre Laestadius was hired as a postdoctoral fellow in September 2015, working on mathematical aspects of coupled-cluster theory. Three international workshops (in Germany, USA, and Denmark) have been attended, exposing the project to a wide scientific audience.

The ERC Advanced Grant ABACUS made great strides in 2015. In particular, we presented the first successful calculations of molecules in magnetic fields using current-density-functional theory (CDFT). Previous attempts using the Vignale-Rasolt-Geldart (VRG) functional, based on the response of the uniform electron gas to a magnetic field, had been unsuccessful, strongly underestimating the electronic energy of diatomic molecules. With the Tao-Perdew-Staroverov-Scuseria (TPSS) functional with the kinetic-energy density properly modified for magnetic fields, electronic energies in excellent agreement with high-level ab-initio methods for paramagnetic bonding in strong magnetic fields are obtained, giving us the possibility of studying large systems in strong magnetic fields. A second important development was the implementation of the coupled-cluster singles-and-doubles (CCSD) and coupled-cluster singles-doubles-perturbative-triples (CCSD(T)) models for finite magnetic fields. Indeed, without these methods, it would be impossible to check the quality of the CDFT calculations in magnetic fields.

An on-going project related to WP1 is the development in Tromsø of the open-ended Kohn–Sham response code, OpenRSP — a long-term endeavour that is now beginning to bear fruits. A significant effort of making a good interface between the LSDALTON code and the OpenRSP code has been made in 2015. We expect a fully working version of this joint effort during 2016. This will



enable calculations of high-order properties of molecules of unprecedented size. Additionally, solvent effects have been made available in LSDALTON through an interface to the PCM module developed in Tromsø. This module is currently only available for energies, but forces are in progress. We have also worked on modularisation of LSDALTON, important for long-term flexibility and portability of the various components. Finally, we have contributed to the development of state-average CASSCF gradients and non-adiabatic coupling matrix elements in the MOLCAS software package.

[WP2: defunct]

### WP3: Multiwavelets

Scientist in charge: Tor Flå

The work of the group in 2015 focussed on further development of MRChem, a program for solving the Hartree–Fock and Kohn–Sham self-consistent field (SCF) equations with the goal of linear scaling calculations of molecular electronic orbitals. Our approach is based on an integral reformulation of the SCF equations that makes it possible (1) to use powerful separation-of-variable techniques for the integral kernels, allowing these operators to be expanded with the same complexity as in one dimension, and (2) to employ multiwavelets combined with the non-standard representation of operators. The code is able to treat small molecular systems with unprecedented accuracy, at the Hartree–Fock and Kohn–Sham levels of theory. It has been interfaced to the XCFun library, making a wide range of exchange–correlation functionals available.

On the theoretical side, Luca Frediani and postdoc Stig Rune Jensen have worked on the linear-response formalism for electric and magnetic molecular properties, while Tor Flå has worked on the formalism for representing the complex Helmholtz kernel, required for frequency-dependent molecular properties. Jensen and Senior Engineer Dan Jonsson have worked on the theory for non-linear

response properties, making use of the OpenRSP platform. The linear-response formalism has been completed, whereas the work on the complex Helmholtz kernel and non-linear response is in progress.

The implementation of a multiwavelet SCF scheme is now complete. In particular, in 2015, Jensen achieved quadratic precision in the energy accuracy with respect to the orbital error. Currently, Jensen and Senior Engineer Peter Wind are working on the parallel implementation for larger systems with near linear complexity by combining multiwavelet methods, orbital localization, and Gaussian-smoothed representations for the nuclear potential and the Poisson operator.

Orbital localization has been successfully implemented (Jensen and Wind) and the current algorithm is able to solve the Kohn–Sham equations directly for localized molecular orbitals (MOs), without reference to canonical MOs. To achieve linear scaling, the most critical part is evaluation of exact exchange for Hartree–Fock and hybrid functionals. To treat larger systems, we need to improve the parallel performance so as to exploit large cluster architectures. This work is in progress.

The implementation of the linear response solver for static and low-frequency dynamic properties (Jensen) has been completed. We are working on including several perturbation operators to apply our model to a wide range of molecular properties.

Recently, an interface to the GIMIC program has been written by Jensen and Ass. Prof. Jonas Juselius, making it possible to compute and visualize magnetically induced currents. We have also started interfacing MRChem with dielectric continuum models, by incorporating the dielectric properties of the environment in the Poisson equation.

Thanks to the achieved quadratic accuracy of the energy, we are now collaborating with the group of Prof. Stefan Gödecke (University of Basel, Switzerland) to produce highly accurate atomization energies at the generalized-gradient-approximation (GGA) level of theory, for a number of small molecules. These values are important benchmarks for the development of accurate pseudopotentials.

A manuscript on an adaptive-order algorithm was pub-



lished in 2015. The goal was to reduce the complexity of the representation of a function by allowing for a reduction of the polynomial order at finer scales (A. Durdek *et al.*, *Adaptive order polynomial algorithm in a multiwavelet representation scheme*, Applied Numerical Mathematics, **92**, 2015.)

In the beginning of 2015, we organized an international conference *Real-Space Numerical Methods for Quantum Chemistry (NMQC)* on Hurtigruten from Tromsø to Kirkenes and back. At the conference, Jensen presented our work on magnetic properties, whereas Juselius gave an overview of the MRChem-GIMIC implementation for current densities.

During 2015, we also recruited three master students to the MRChem group: Magnar Bjørgve from mathematics, who will work on the frequency-dependent Helmholtz operator, Rune Monstad from chemistry, who will work on the implementation of solvent effects, and Raymond Bomstad from informatics, who will work on optimization and parallelization of the code.

To meet the need for new multiscale property models in WP3, Flå continued in 2015 a project based on Clebsch parameterization of density matrix theory via operator brackets from a reference state. This method includes linear response both for static and periodic forcing, but is more flexible. It can also potentially be used to explore response to time dependent pulses even in a finite magnetic field background. This method is also a natural framework for understanding the paramagnetic and diamagnetic parts of the response on the same footing. It is also a step forward towards a versatile parameterization of multiscale coarse graining for large molecules, with possibilities to extract heterogeneous variation of observables in time and/or space.

## WP4: Molecular properties

**Scientists in charge:** Luca Frediani and Kenneth Ruud

The goal of WP4 is to develop and employ methods to compute molecular properties for a wide range of applications: elucidation of molecular structure through the understanding of structure-to-properties relationships, rational design of molecules and materials with tailor-made properties, assisting experimental work by providing modelling results that are complementary to experimental investigations.

The method-development activity comprises a wide spectrum of tools to achieve an accurate and faithful representation of the properties of the molecular targets being investigated: for a correct description of the molecular electronic structure, a wide range of electronic-structure methods is employed, ranging from density-functional theory (DFT) to coupled-cluster methods; for a correct description of heavy elements, relativistic effects are included through two- and four-component methods; to reproduce environmental effects, polarizable embedding, polarizable density embedding and the polarizable continuum model (PCM) are employed.

A central component of most of these developments is the OpenRSP code, capable of computing molecular properties of arbitrary order in the perturbations for self-consistent-field methods such as Hartree-Fock theory and DFT. During 2015, CTCC researcher Bin Gao has been exploring the extension of this framework to the coupled-cluster theory. Whereas such an extension was realized many years ago for one-electron perturbations, the inclusion of perturbation dependence in the basis set is not straightforward. This work is on-going.

During 2015, CTCC postdocs Magnus Ringholm and Yann Cornaton have been exploring the many avenues that are being opened through the functionality of OpenRSP, with a focus on anharmonic effects on vibrational spectra (infrared, Raman, hyper-Raman and Raman optical activity spectra). This work has demonstrated the superiority of the analytic approach in terms of reliability compared with the numerical schemes so far used in the literature. The initial focus on anharmonicities in vibrational spectroscopy is motivated in part by their importance and in part because of the possibility to benchmark and validate the results obtained using DFT methods. The goal is to include medium effects, and the exploration of nonlinear and multidimensional vibrational spectroscopies.

Building on the work by PhD student Marco Anelli on the definition of molecular magnetizabilities in frequency-dependent magnetic fields, we have included in the analytic calculation of harmonic and anharmonic vibrational spectra also higher orders in the multipolar expansion describing the interaction of light with a molecular electron density. We are now finalizing the first use of this approach in the study of electric field-induced second-harmonic generation circular intensity difference of a series of model compounds. This novel spectroscopic technique has potential for use in the study of chiral complexes adsorbed at





surfaces and interfaces, combining chiral sensitivity with specificity towards surfaces and interfaces.

CTCC postdoc Daniel Friese has extended the OpenRSP scheme to the calculation of residues of response functions of arbitrary order – that is, transition moments – including perturbation dependence in the basis set. This has been applied to calculate gauge-origin independent two- and three-photon circular dichroism. The code has now been verified to work for excited-state gradients and Hessians, allowing vibrational structures and properties to be obtained from knowledge of the ground-state electron density only. Our initial applications of this formalism focus on analytic calculation of vibronic effects on absorption spectra of linear and nonlinear properties.

In the activities directed towards relativistic effects, 2015 has seen a broad exploration of the breakdown of the non-relativistic relation between nuclear spin-rotation constants (observed experimentally in microwave spectra) and absolute shielding constants, which can only indirectly be observed in nuclear magnetic resonance (NMR) spectroscopy, but which are important for determining the nuclear magnetic moments of atoms. CTCC researchers Taye Demissie, Stanislav Komorovsky and Michal Repisky have explored a wide range of compounds, ranging from simple molecules such as water to compounds containing third-row transition metals and lanthanides, in most cases leading to a substantial revision of the absolute shielding scales of these nuclei. Even for an element as light as oxygen in the water molecule, the effects of the breakdown of the non-relativistic relation between nuclear spin-rotation constants and absolute shielding constants is as large as 1 ppm.

The activity in the group has also to an increasing extent involved the interaction with experimental groups, both at the local host departments and internationally. We have explored the effects of relativity on NMR shielding and spin-spin coupling constants using our newly developed methods on compounds synthesized in the laboratory of Assoc. Prof. Annette Bayer. Together with Assoc. Prof. Jørn Hansen, we have explored the use of DFT calculations for predicting photoredox catalysis. We have also collaborated with Prof. Radek Marek at Mazaryk University in the Czech Republic in the exploration of heavy-element shieldings for compounds that are potential cancer drugs. In the domain of multiphoton absorption, CTCC postdoc Daniel Friese together with Prof. Daniel Gryko at the Polish Academy of Sciences have used modelling to rational-

ize observation of the two-photon absorption properties of newly synthesized pyrrolopyrroles.

We have in 2015 combined the development of novel approaches for modelling solvent effects with the development of two- and four-component relativistic DFT. PhD student Roberto Di Remigio together with CTCC researchers Michal Repisky and Stanislav Komorovsky have implemented the PCM for four-component DFT, allowing for the study of solvent effects on electron-paramagnetic resonance (EPR) g tensors and hyperfine coupling constants.

Another development within the continuum solvation model has been the extension to solvent surfaces of the calculation of energetics and molecular properties. PhD Student Krzysztof Mozgawa has shown that, for the energetics and properties of molecules at solvent surfaces, all contributions to the solvation energy (electrostatic, cavitation, dispersion and repulsion) are essential to yield a correct picture of solvation. Moreover, PhD students Roberto Di Remigio and Krzysztof Mozgawa have implemented and tested a module for spherical electrostatic interfaces.

In parallel, PhD student Maarten Beerepoot has benchmarked the performance of the polarizable embedding approach against accurate coupled-cluster results, as well as explored different computational models/approximations to large and complex systems, studying how the size of the quantum system, the truncation of the virtual space, and the polarizable embedding approach affect the calculated absorption properties.

## WP5: Dynamics and time-development

### Scientist in charge: Einar Uggerud

Postdoctoral fellow Andrea Debranova has contributed with key reaction dynamics calculations to a publication in *Journal of Organic Chemistry* in 2015, on reactions of superoxide water with alkyl halides – for example,  $O_2^{\cdot-}(H_2O)_n + CH_3Cl \rightarrow Cl^-(H_2O)_n + CH_3O_2^{\cdot}$  ( $n = 0, 1, 2, \dots$ ). Besides elucidating fundamental aspects of such reactions, including how the degree of hydration affects reactivity, our study showed that superoxide anion dissolved in water has a high potential for practical use by decomposing environmentally harmful chlorinated and brominated organic substances. During the spring semester of 2016, Dr. Debranova will finish a detailed and complex computational study



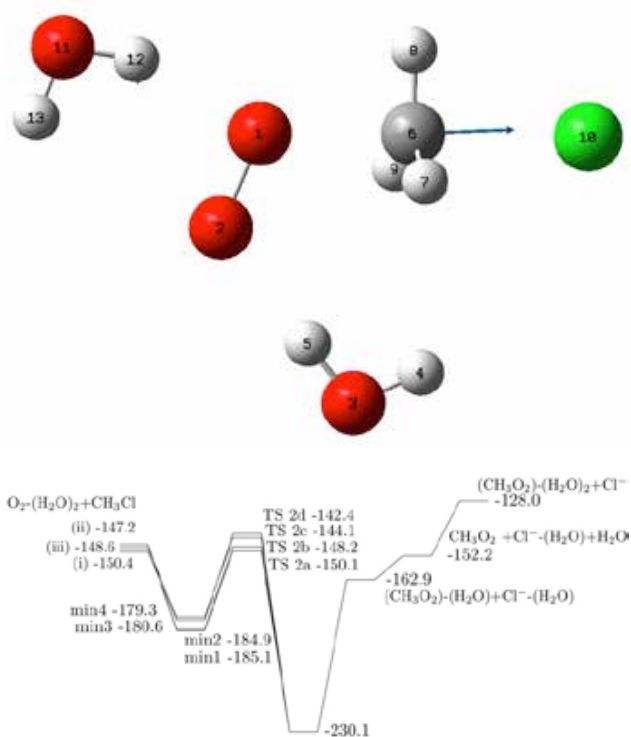
on Fenton chemistry, leading to a second publication. In addition, she has made progress in developing a computational method for ring-polymer molecular dynamics. When completed, this method will enable us to describe more accurately quantum-mechanical effects (tunnelling and zero-point energy issues), important to the real-time dynamics of hydrogen-bonded species—a topic of great significance to our experimental efforts on water cluster chemistry.

Regarding water clusters, a paper entitled *Geometry of the magic number  $H^+(H_2O)_{21}$  water cluster by proxy* was published in 2015, in collaboration with WP1. In this paper, we demonstrated how t-butyl groups of a key species,  $H^+(TB)_9(H_2O)_{12}$ , form a tight hydrophobic outside layer with an interior water core, essentially a nano-colloid particle, providing new insight into the structure and properties of gas hydrates.

NFR-research scholar Dr. Mauritz Ryding is completing a study on oxidation of NO into  $NO_2$  by  $HO_2^-(H_2O)_n$  and  $O_2^-(H_2O)_n$  ( $n = 0-4$ ) with NO. NO and  $NO_2$  are spontaneously formed from air gases at high temperatures, as in lightening and in the Birkeland–Eyde process for saltpetre production. Prof. Israel Fernandez, who visited CTCC this summer, has provided very valuable quantum-chemical modelling of the reactions.

Glenn Miller continues to work on his Ph.D.-project on  $CO_2$  activation chemistry. A paper was published in European Mass Spectrometry in 2015 on gas-phase Grignard reactions with  $CO_2$ . In addition, a comprehensive manuscript describing the unimolecular dissociation of deprotonated  $\alpha$ -ketoacids, studied by mass spectrometric techniques and supported by quantum-chemical and kinetics calculations, will be submitted for publication in January 2016. For the moment, Miller is systematically surveying the periodic table for putative  $M(\eta^2-O_2C)$  structures by doing quantum-chemical calculations. The structure of prototype  $[ClMg(\eta^2-O_2C)]^-$  was identified by free-electron laser infrared spectroscopy, as reported here last year. Such elusive and highly reactive species represent a novel metal- $CO_2$  binding motif, giving rise to a new principle for activating carbon dioxide for chemical reaction. Thanks to a new NFR FRIPRO grant, we will be able to extend Miller's project to study bond breaking and bond forming reactions relevant to the photosynthetic dark reaction and reductive  $CO_2$  fixation, and artificial photosynthesis. One student, Joakim Jestilä, does his master thesis work on related chemistry, by studying decarboxylation

and dehydration of magnesium complexes of succinic acid and similar molecular systems.

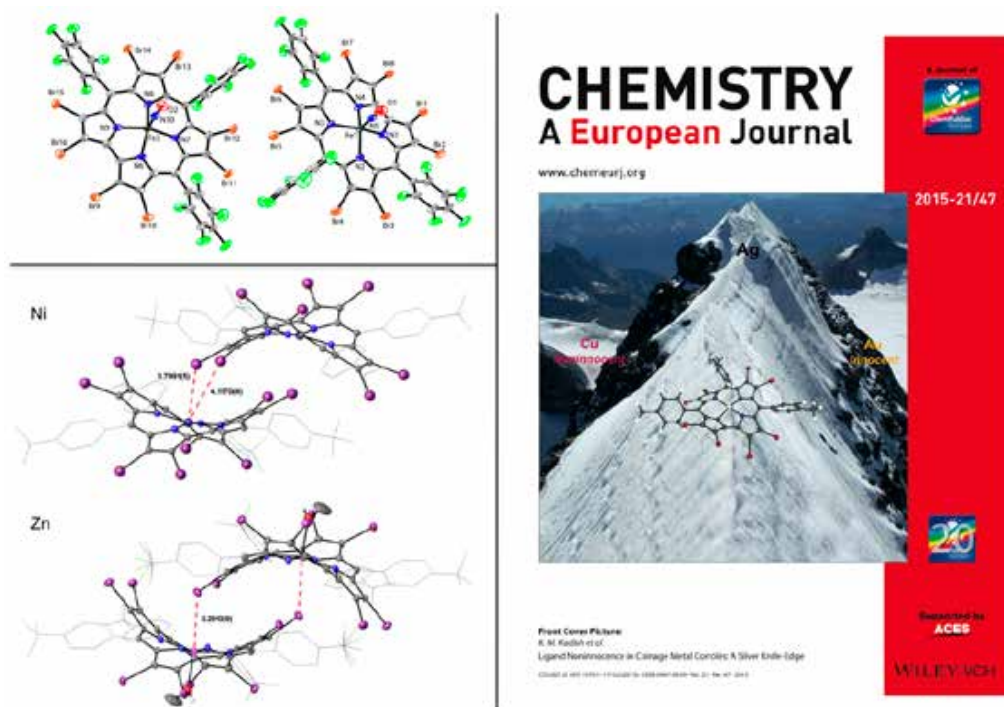


## WP6: Bioinorganic chemistry

Scientist in charge: Abhik Ghosh

The past year was a busy one for the Ghosh group, with a dozen or so published papers and a half-dozen major conference presentations (Figure 1). In the area of electronic structure and computational chemistry, our published work encompassed two broad areas, viz., heavy element corroles and the problem of ligand noninnocence (multideterminantal character) in transition metal complexes. In addition, several papers were published in the area of chemistry education (focusing on applications of quantum chemistry in teaching) as well as on purely experimental, synthetic research.

Heavy element corroles, the major target of our recent research, may be described as metal-ligand misfits, where a large, typically 5d element is coordinated by a sterically constrained corrole ligand. Gold, platinum, and osmium corroles are but a few of the unique complexes synthesized for the first time in our laboratory; key new complexes involving these and other 4d and 5d metals were synthesized



**Figure 1.** Top left: X-ray structure of a reactive FeNO octabromocorrole, with considerable significance with respect to ligand noninnocence. Bottom left: X-ray structures of Ni and Zn octaiodoporphyryns, with key metallophilic interactions indicated. Right: Journal cover depicting our work on 'Ligand Noninnocence in Coinage Metal Corroles: A Silver Knife-Edge'.

over the past year. In a somewhat unrelated development, octaiodoporphyryns were synthesized for the first time (Figure 1, bottom left) and their unique, saddled structures and highly redshifted optical spectra were analyzed in detail via DFT and TDDFT calculations.

In the area of ligand noninnocence, we uncovered two heretofore unsuspected cases of noninnocent systems. Thus, FeNO corroles, a thermodynamic sink of Fe-corrole-NO<sub>x</sub> chemistry and long assumed to consist of 'Fe(III) + NO• + corrole(3-)' were reformulated as 'Fe(II) + NO• + corrole(•2-)'. Second, silver corroles were found to be innocent or noninnocent, poised on a knife-edge, as it were, depending on the substitution pattern (Figure 1). Optical, infrared, and electrochemical studies, as well as DFT calculations, all played a critical role in providing the correct electronic-structural descriptions for these complexes.

In as yet unpublished work, we pursued a wide range of exciting topics with a somewhat applied focus. Highly promising results were obtained on new reagents for photodynamic therapy and dye-sensitized solar cells; substantial progress was also made toward developing corrole-based radiopharmaceuticals.

Among several invited talks at major conferences may be mentioned those at the 17th International Conference on Bioinorganic Chemistry (ICBIC17) in Beijing, P. R. China; 21st International Symposium on Fluorine Chem-

istry in Como, Italy; and two lectures at Pacificchem 2015 in Honolulu, Hawaii, USA.

## WP7: Catalysis and organometallic chemistry

**Scientist in charge: Mats Tilset**

Organometallic chemistry, which focuses on the properties of compounds containing metal-carbon bonds, is a fundamental pillar of homogeneous catalysis. Catalysts make chemical processes more eco-friendly by boosting selectivity and by allowing for milder reaction conditions. This work package is aimed at the development of new transition-metal catalysts for the synthesis of fine chemicals and the activation of small inert molecules, including carbon dioxide, water and simple hydrocarbons (e.g., ethylene and acetylene). Computational methods are used in collaboration with national and international experimental groups. These include the groups led by Erwan LeRoux (UiB), Richard Heyn (Oslo SINTEF), Nilay Hazari (Yale Univ., USA) and Robert Crabtree (Yale Univ., USA). Our joint theoretical-experimental efforts have been successful in several projects, since the drawbacks of one approach are often compensated by the advantages of the other.



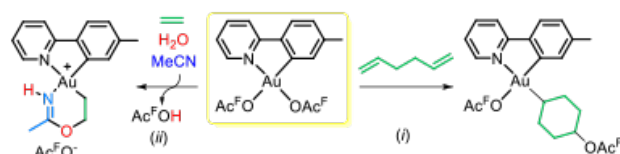


Further, the cutting-edge quantum chemistry software developed at the CTCC is opening new possibilities in the prediction and rationalization of complex molecular properties, including NMR and EPR parameters (see the Highlight by David Balcells and Michal Repisky in this report). In addition to journal publications, national and international conferences have been used to disseminate the results of these research projects. These included the CECAM conference organized by CTCC Prof. Cascella in France and the annual CTCC meeting at Sundvollen.

In order to support these research activities, the resources of the CTCC have been complemented with external funds provided by public agencies in competitive open calls. These include the FRIPRO-FRINATEK projects granted by the Research Council of Norway to Postdoc Ainara Nova (Young Research Talent) on carbon dioxide functionalization (see the Highlight by Nova in this report), Prof. Mats Tilset on gold(III) chemistry and catalysis, and Prof. LeRoux on carbon dioxide polymerization. Researcher Balcells has also his own independent project on catalytic water oxidation, which is supported by the EU Marie Skłodowska-Curie program. More recently, Tilset and Balcells, in collaboration with Hazari, obtained funding from the GROW program of the US NSF agency. This grant will support the three months research stay of Patrick Melvin (starting on February 2016), a PhD student from the Yale University, which will be trained in Computational Chemistry under the co-supervision of Postdoc Nova. We have previously hosted other students from the US, including Damian Hruszkewycz (NSF-GROW grant) and Alexandra Strom (Peder Sather grant from UC Berkeley). In Oslo, the PhD students doing the experimental work on the catalysis projects, including Marte Holmsen, Franziska Ihlefeldt and Jakob Wählender, are also being trained in the use of computational chemistry.

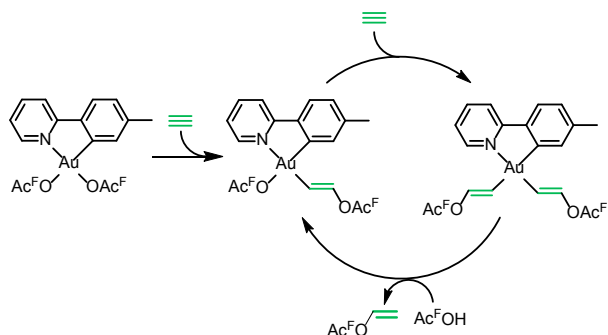
In the gold(III) project, we discovered interesting chemical transformations promoted by  $(\text{tpy})\text{Au}(\text{OAc}^{\text{F}})_2$ . In 2014, we reported the functionalization of ethylene by this complex (J. Am. Chem. Soc., 2014, 10104). The mechanistic study of this reaction showed that insertion of ethylene was only thermodynamically feasible in the position trans to the N of the tpy ligand. The same position is the only one active in the reaction with dienes (Figure 1 (i)). However, when the chain between the two double bonds is long enough, such in 1,6-heptadiene, instead of simple or double insertion, cyclization is observed. The computational study of this reaction suggests that nucleophilic

addition to the coordinated double bond involves the non-coordinated olefin rather than the  $\text{Ac}^{\text{F}}\text{O}^-$  anion.



**Figure 1.** Reactions promoted by  $(\text{tpy})\text{Au}(\text{OAc}^{\text{F}})_2$  ( $\text{OAc}^{\text{F}} = \text{OCOCF}_3$ ).

The  $(\text{tpy})\text{Au}(\text{OAc}^{\text{F}})_2$  complex is also able to activate ethylene, water and acetonitrile to yield a metallacycle in a one-pot reaction (Figure 1 (ii)). This means that both positions, trans-to-N and trans-to-C, are involved in this reactivity. This opens the door to more sophisticated transformations. We believe indeed that the ability of  $(\text{tpy})\text{Au}(\text{OAc}^{\text{F}})_2$  to activate multiple bonds in both positions makes possible the catalytic functionalization of acetylene with  $\text{Ac}^{\text{F}}\text{OH}$  (Figure 2). This hypothesis is based on the experimental and computational study of the mechanism of this reaction, which is almost completed. The decomposition pathways of Au(III) intermediates, a common problem in this chemistry, are also being explored.



**Figure 2.** Acetylene functionalization by  $(\text{tpy})\text{Au}(\text{OAc}^{\text{F}})_2$ .

Protonation of the tpy ligand has been investigated in species involved in the catalytic functionalization of acetylene. In addition, the insertion of ethylene and acetylene into the Au-X bond of  $\text{AuX}_3$  and  $\text{AuX}_2^+$  ( $\text{X} = \text{Cl}, \text{Me}, \text{and H}$ ) has been studied by combining DFT and CCSD(T) methods. The insight given by this joint theoretical-experimental studies will be used in the near future to design a new Au(III) complex able to perform these transformations in a catalytic fashion.

Since the PhD exchange of Hruszkewycz in 2013, we have been working on the design of an efficient Pd-catalyst for the Suzuki-Miyaura cross-coupling reaction.





This project was successfully completed in 2015 with the synthesis of one of the best Pd-catalysts known to date for this reaction. The catalyst has a high potential in the production of fine chemicals and is already commercialized by Sigma Aldrich, Strem Chemicals and Aspira Scientific. This work has been published in a series of articles (J. Am. Chem. Soc., 2014, 136, 7300; Organometallics, 2015, 34, 381; ACS Catal., 2015, 5, 3680; ACS Catal., 2015, 5, 5596) and was possible thanks to the collaboration between the Hazari group and Nova, Balcells and Tilset. The study started by exploring the dimerization step that was observed during the activation of allyl-type Pd pre-catalysts (blue path in Figure 3). This unproductive pathway can be in principle prevented by introducing functional groups at the R<sub>1</sub> position of the allyl ligand. However, the orientation of this group is not efficient enough to avoid the formation of Pd<sup>I</sup> μ-allyl dimers. This was solved by replacing the allyl moiety by indenyl-based ligands. This modification of the system is especially efficient with R<sub>3</sub> = tBu, since this group both prevents dimerization and accelerates the reduction step required to activate the pre-catalyst (red path in Figure 3).

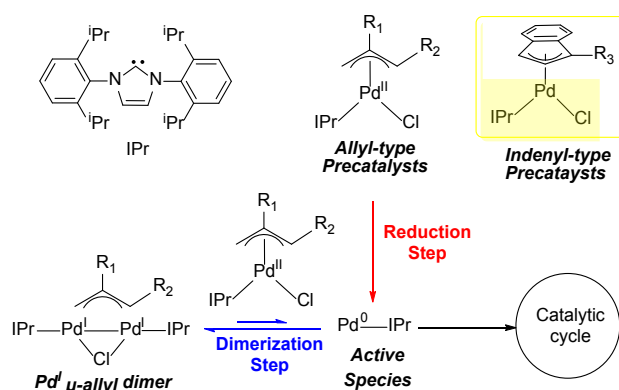


Figure 3. Key reactions in Pd-catalyzed cross-couplings.

PhD student Eirik Thoresen has started a project under the supervision of Prof. Tilset on the synthesis of new photosensitizers based on ruthenium complexes. The main goal is to synthesize aromatic N-donor ligands with pending carboxylate groups allowing for their integration into the metal organic frameworks (MOFs) developed at the inGAP research centre in Oslo. These ligands should also keep or improve the properties of the existing photosensitizers, which should absorb strongly in the near-IR region

of the visible spectrum. In the long term, the MOFs developed in this project will be tested in catalytic processes of high interest, including the photo-reduction of carbon dioxide. Researcher Balcells recently joined this project with the aim of interpreting the UV-VIS spectra recorded experimentally. This project required a thorough calibration of the method, including the functional and the solvation model used in the DFT calculations. The main insight given by these studies is the nature of the electronic transitions causing the absorption peaks (Figure 4). The good agreement observed between theory and experiment has been also used to guide the synthesis of new target photosensitizers.

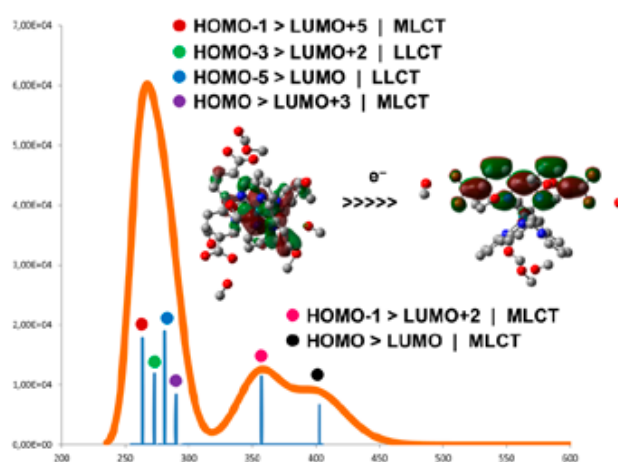


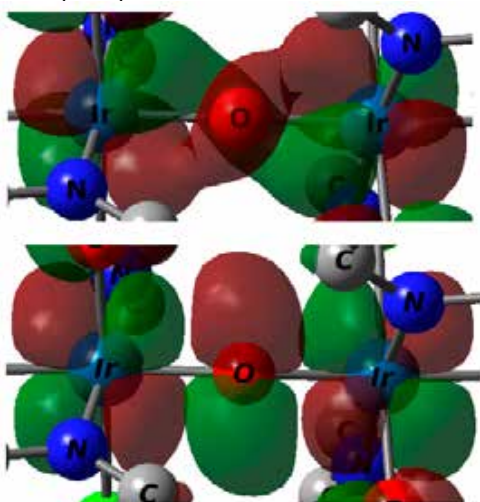
Figure 4. UV-VIS spectrum at the DFT( $\omega$ B97xd) level, with metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) electronic transitions. The orbital picture is given for the HOMO-LUMO transition.

PhD student Wähländer has been trained in the use of computational chemistry, which is being applied to the development of new organocatalysts for asymmetric Diels-Alder reactions. This work is co-supervised by Researcher Balcells on the theoretical part and by Profs. Gundersen and Amedjkouh (UiO Chemistry Dpt.) on the experimental part. The main objective of this project is to develop a chiral-on-phosphorous analogue of thiourea, which would be used in the synthesis of natural products with biological activity. Also at the UiO, Balcells has collaborated with Postdoc Burschowsky (Prof. Kregel group) in modeling the weak interactions responsible for catalysis in the chorismate mutase enzyme.

In the context of his Marie Curie grant, Balcells has also started a new project on catalytic water oxidation in collaboration with the experimental group of Prof.



Crabtree. The goal is to design a new catalyst based on an iridium-oxo-iridium bridge generating a set of  $d(\text{Ir})-p(\text{O})-\pi$ ,  $n$  and  $\pi^*$  molecular orbitals (Figure 5). By carefully tuning the ancillary ligands, the  $\pi^*$  orbital yields a low-lying LUMO (lowest unoccupied molecular orbital), which causes strong absorption in the near-IR region of the visible spectrum. This can be used to drive the catalytic process by means of sunlight. Further, this electronic structure induces strong coupling between the two metal centers, which facilitates the oxidation of the metal centers to the high Ir(V) state required for catalysis. DFT and TDDFT have been used to explore the structure, reactivity and spectroscopy properties of this hypothetical catalytic system.



**Figure 5.** Non-bonding  $n$  (top) and antibonding  $\pi^*$  (bottom) orbitals in a bridging Ir-O-Ir moiety.

A few years ago, theoretical-experimental collaborations were started after puzzling experiments were completed, aiming for a rational interpretation. Nowadays calculations and experiments are performed in a parallel and synergic manner. Fostering and spreading this new approach has been the main goal and success of 2015. New research projects with external cofunding have been started on the basis of an expanding network of national and international collaborations. The training activities have also grown and are locally spreading over the Chemistry Department in Oslo. In this regard, Prof. II Odile Eisenstein kept playing a key role by building bridges between the CTCC and the experimental groups.

[WP8: defunct]

[WP9: defunct]

## WP10: Biomolecular modeling

**Scientists in charge:** Bjørn-Olav Brandsdal and Michele Cascella

Much of the effort in the CTCC-Tromsø node has been devoted to the graphical user interface Qgui and the development of the software (J Mol Graph Mod, 60, 15-23, 2015). Qgui enables rapid setup and analysis of free-energy calculations and empirical valence bond simulations, including automatic parameter assignments. Users of the Qgui program already include groups in North- and South-America, Asia and Europe.

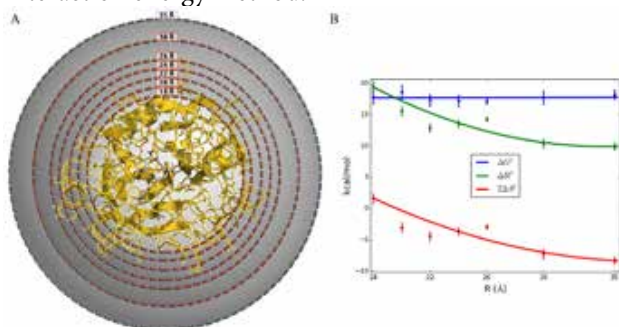
In parallel with developing Qgui, we have continued the investigation of the hypothesis that surface rigidity can be used to tune the thermodynamic activation parameters of enzymes. We have continued our studies of cold- and warm-active enzymes, focusing on the thermodynamic activation parameters the enzyme catalyzed reactions. Cold-active enzymes are able to catalyze reactions at low to moderate temperatures much more efficiently compared with their warm-active counterparts, mainly due to lowering of the activation enthalpy. The enzymatic reactions are studied using the EVB method, and calculating Arrhenius plots from brute force simulations. Remarkably, we find that, when the enzyme surface is gradually restrained from the outside and inwards, the activation enthalpy-entropy balance changes significantly, but the activation free energy remains essentially invariant (Figure 1).

As noted in the annual report for 2014, the purine nucleotide phosphorylase (PNP) was chosen as a new model system to challenge our approach, focusing on enthalpy and entropy compensations in enzymatic reactions. Unfortunately, this turned out to be a problematic system to work with. Nonetheless, we have been able to resolve the mechanistic issues and produced Arrhenius plots in agreement with experimental data (Figure 2). The high specificity for 6-oxopurines over 6-aminopurines is attributed to the preorganization of the active site towards the former substrate. Long-range mutations have experimentally been shown to give rise to enthalpy-entropy compensations, which is fully captured by our EVB simulations. Most interestingly, these mutations seem to change the rigidity of the protein surface distant to the active site in a similar fashion as observed for tempera-

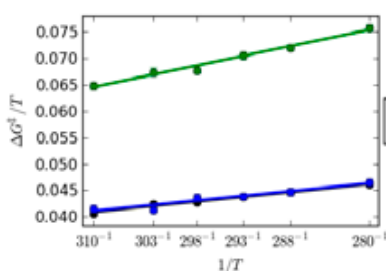


ture adaptation of enzymes.

Inspired by the success in modeling temperature dependence of the chemical reaction rates, we are now working on extending the concept to include ligand-binding van't Hoff plots. This work involves modifications of existing methodologies to cope with different temperatures, as the dielectric constant varies as a function of temperature, yielding different screening factors for the electrostatic interactions. In parallel, the theoretically exact free-energy perturbation method is used for benchmarking and tuning of the more simplified linear-interaction energy method.



**Figure 1.** Restraining solute atoms and its effects on calculated thermodynamic activation parameters. (A) Radius (Å) of simulation sphere without restraints. Solute atoms between R (18, 20, 22, 24, 26 and 30 Å) and 35 Å are restrained with a force constant of 100 kcal/mol/Å<sup>2</sup>. (B) Thermodynamic activation parameters for the systems restrained in (A), showing that the parameters for cold-active trypsin is gradually converted to those of warm-adapted trypsin.



**Figure 2.** Calculated Arrhenius plots for guanosine (black), inosine (blue) and adenosine (green) for the glycosidic bond cleavage step in purine nucleoside phosphorylase.

The Oslo node of CTCC employed two new collaborators in the course of 2015: Dr. Hima Bindu Kolli with a one-year researcher contract, and Sigbjørn Loland Bore as PhD student. They are working under the supervision of Michele Cascella on development of hybrid particle-field (hPF) methods for biological systems.

The hPF method, originally proposed in soft-matter and polymer sciences, is similar in spirit to DFT for electronic structure calculations, as it models a system of several interacting particles as a system of independent particles subject to an external potential that is a functional of the particle density:

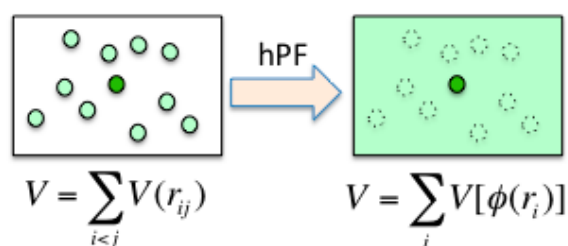
$$H(\Gamma) = H_0(\Gamma) + W(\Gamma)$$

where  $H_0(\Gamma)$  is the independent particle Hamiltonian, and  $W(\Gamma)$  is the external potential

$$W(\Gamma) = W[\phi(\mathbf{r}; \Gamma)]$$

and  $\phi$  is the density.

This method does not require direct calculation of particle-particle distance potentials, and therefore it scales like  $N \ln N$ . Moreover, integration of the equations of motion is done independently for the various particles. This leads to very efficient parallelization schemes, producing significant acceleration of computation times with respect to standard molecular dynamics.



**Figure 3.** The hPF method: particle present in the system interact with a potential dependent on the density

To establish this research line, CTCC hosted Prof. Giuseppe Milano, from the university of Salerno, Italy, for the month of August. Prof. Milano is a leading scientist in the hPF simulations, who devised the first extension of the method to molecular dynamics. The team of Prof. Cascella joined the team of developers of the OCCAM code, the hPF code written by Prof. Milano, and is now working on development and implementation of the tools and routines required to extend the method to biological systems. The work concentrates on extension of hPF to charged systems, definition of hPF-consistent coarse-grained Hamiltonians for biopolymers, and establishment of multi-resolution all-atom/coarse-grained/hPF models.

Recently, the Partnership for Advanced Computing in Europe (PRACE) consortium funded a joint application between the two groups with Preparatory Access (Type C) grant of 500 000 CPU hours for the optimization of the OCCAM code.

