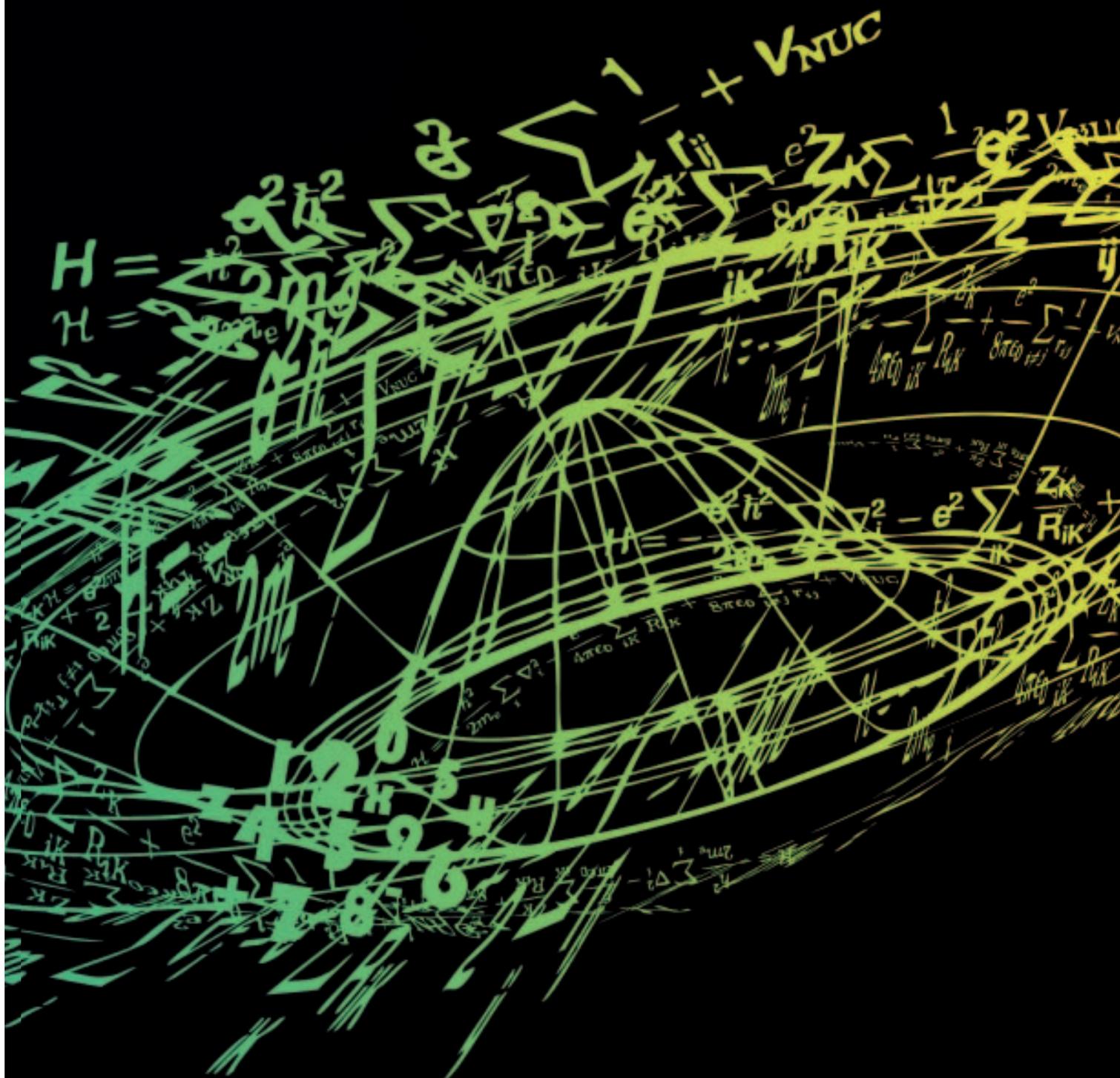


CTCC The Centre for Theoretical
and Computational Chemistry

annual report 2011





The Centre for Theoretical and Computational Chemistry (CTCC)

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

The CTCC is one of 21 national Centres of excellence in Norway and the only one in chemistry. The Centre has two nodes of equal size, hosted by the University of Oslo and the University of Tromsø. The CTCC receives an annual funding from the Research Council of Norway of about 9.5 MNOK for the period July 2007 – June 2017. The Centre also receives substantial support from the host institutions.

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 established an extensive visitors program for world-leading scientists, as well as for PhD students and postdocs from other research groups who wish to benefit from the expertise available at the Centre.

The CTCC is actively engaged in communicating the potentials offered by computational chemistry in all areas of chemistry, offering courses in the efficient utilization of quantum-chemistry programs on the computational infrastructure available in the Norwegian supercomputing program.

More information about the CTCC can be found at <http://www.ctcc.no>.



5 more years

Although much of the preparative work took place during 2010, a lot of attention was in 2011 directed towards the mid-term evaluation of the CTCC, and in particular whether the Research Council of Norway would grant us the last 5 years of operation. The international evaluation panel delivered their report in the spring of 2011, and we are happy that they confirmed our own assessment of the activity of the Centre, rating much of the activity as exceptionally good and the remainder as very good. As a consequence, the Research Council of Norway granted the CTCC a contract until 2017. We thank present and past staff at the CTCC for their excellent work leading to this very positive evaluation of the Centre.

Although very positive and a great inspiration for future work, the midterm evaluation showed that there are areas, scientifically as well as organizational, where we can improve further. Based on these recommendations, we will in the future focus our research in some areas, while at the same time bringing in new research dimensions that will help further integrate the theoretical and applied chemists in the Centre. Ensuring a good strategy for disseminating the programs and algorithms developed at the Centre will be given necessary attention, as this is an important forum for disseminating the results of the work at the CTCC that has a lot of impact in the scientific community while perhaps not being easily measurable. We will also use the advice and recommendation of the midterm evaluation to engage our host institutions in developing a long-term strategy for the center that reaches beyond the funding from the Research Council of Norway.

During 2010, the CTCC passed 200 publications and 1000 citations, and is very reassuring that we at the end of 2011 have reached new publication and citation milestones, with almost 300 publications and more than 2000 citations. The science produced at the CTCC thus has a noticeable impact in our community, and with almost 900 citations during 2011 alone, we believe that the scientific topics addressed at the Centre are at the core of the research front in theoretical and computational chemistry.

A major event at the CTCC in 2011 was the organi-

zation of the 15th European Seminar on Computational Methods in Quantum Chemistry at Oscarsborg fortress during four beautiful June days. Being one of the major meeting places for young researchers in quantum chemistry in Europe, the meeting gathered 89 participants from all over Europe (as well as a few non-European participants), providing a stimulating environment for discussing frontier research in the scientific domain that is at the core of the CTCC activities. We thank the members of the CTCC that helped in organizing this meeting for contributing to making it a great success.

As we now enter the second period of operation, some of our important colleagues at the Centre will take a less active role as they approach their retirement. However, they will continue their scientific work as affiliates at the Centre, and we use the opportunity to thank Prof. Claus Jørgen Nielsen and Prof. Inge Røeggen for their contributions to the success of the CTCC in the first five years. We also welcome our two new members, Prof. Bjørn-Olav Brandsdal, who will be extending our scientific focus to proteins and biomolecules, and Prof. Morten Hjort-Jensen, who will help create new insight into the correlation problem that is at the heart of computational chemistry.

We will use the momentum created by the CTCC during its first period of operation to secure the necessary funding for continuing research at the top international level also in the second period of operation. We are therefore looking forward to five more years of exciting science.



Kenneth Ruud



Trygve Helgaker

From the Board of Directors

We are happy to see that the strong scientific foundations on which the CTCC is based, has been both confirmed and recognized during 2011. A special conformation of the scientific qualities of the CTCC comes from the excellent mid-term evaluation of the Centre and the extension of the Center of Excellence contract by another 5 years. We congratulate all the CTCC members, past and present, on the excellent work they have done and that has led to this very favourable assessment of the activities at the Centre by an international panel of experts.

We are pleased to note that the CTCC in 2011, as it did in 2010, breaks new milestones in the scientific productivity and impact of the Centre, with a new record of almost 80 scientific publications in a single year and almost 900 citations in 2011 alone. This is a very clear illustration that the science at the CTCC is highly relevant and has a major impact on the international scientific community.

Following the award of a European Research Council (ERC) advanced grant to Centre director Trygve Helgaker in 2010, the Board of Directors are happy to be able to congratulate Centre director Kenneth Ruud and newly appointed adjunct professor Benedetta Mennucci from the University of Pisa with their awards of ERC starting grants for 2011. We are in particular happy to see that the CTCC is able to attract the best international researchers to take up positions at the CTCC.

We would also like to congratulate Centre director Trygve Helgaker with the award of the Research Prize

of the Research Council of Norway (Årets Møbius). This award attests to the high scientific standards of Prof. Helgaker's work and attests to his national as well as international recognition as a leader in his field.

2011 was the International Year of Chemistry (IYC2011), and provided a much needed arena for promoting chemical research in general, including the activity of the CTCC. Many CTCC researchers were engaged in outreach activities during the year, including writing popular scientific commentaries in newspapers. The work of organizing IYC2011 in Norway was led by Prof. Einar Uggerud of the CTCC, and we would like to congratulate him with a successful IYC2011 in Norway.

We would also like to thank and congratulate CTCC researcher Prof. Abhik Ghosh for his work on editing the popular scientific book "Letters to a Young Chemist" that was published during the IYC2011 and which was praised by Nature Chemistry as "a great source of chemical processes in real-world contexts for educators at a variety of levels". Such outreach activity is in part important for promoting the CTCC to a wider audience, but even more important in promoting chemistry and science in general.

We are confident, based on the excellent scientific achievements reached by the CTCC during 2011, and the boost in outreach activity that has resulted from the IYC2011, that CTCC will continue its excellent performance also in the second period of operation.



Professor Fred Godtlibsen
(Vice Dean at The Faculty of Science and Technology)
Chairman of the board



Professor AnneBritt Kolsto
(University of Oslo)
Vice-chairman of the board



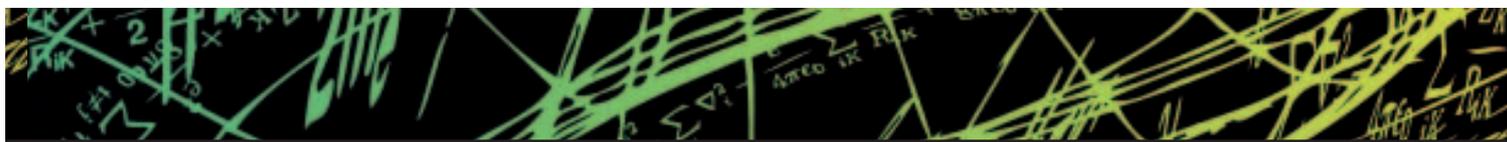
Dr. Nina Aas
(Statoil)



Professor Ragnar Winther
(Director of Centre of Mathematics for Applications, CMA)



Associate Professor Ole Swang
(Innovative Natural Gas Processes and Products, INGAP, and Senior Scientist at SINTEF Materials and Chemistry)



2011 in brief

Research focus: The scientific activities at the CTCC are concerned with the understanding of how the building blocks of the atoms, the nuclei and the electrons, interact with one another in creating molecules. The focus of the CTCC is thus on the fundamentals of chemistry. To obtain new insights in this area of research, the CTCC conducts research along two complementary but interlinked axes: first, the development of new computational methodologies and computer implementations of these algorithms; second, the use of such quantum-mechanical methodology to solve important chemical problems.

The scientific activities of the CTCC are organized into eight thematic work packages, each headed by a principal scientist, most of whom also contribute to one or more of the other work packages. Three packages are concerned with methodological developments: (1) large periodic and nonperiodic systems, (2) fragment approaches for large systems, and (3) multiscale methods with wavelets. Two packages contain significant elements of both methods development and applications: (4) properties and spectroscopy, and (5) dynamics and time development. Finally, three of our work packages are application oriented: (6) bioinorganic chemistry; (7) catalysis and organometallic chemistry; and (8) gas-phase reactions and photochemistry.

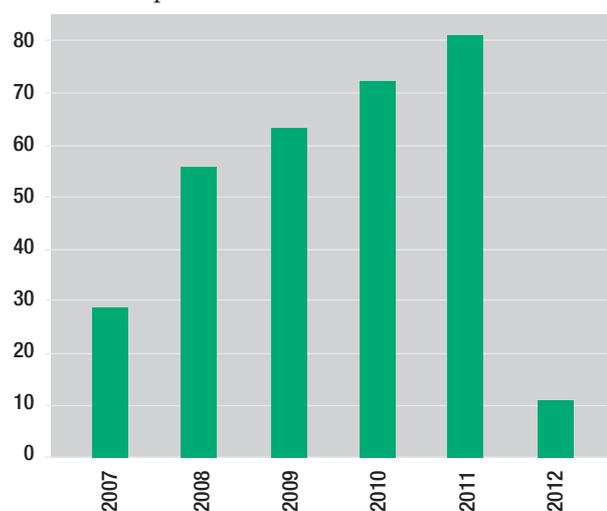
During 2011 and as part of the work connected to the midterm evaluation of the CTCC which took place in 2011, and the upcoming retirement of some of the CTCC senior researchers, an evaluation of the progress in the different work packages has been made, and plans for new research directions for the second period of operation have also been established. As a consequence of this analysis, we will for the next period of operation merge the activities in WP1 and WP2 into a single research activity on methods for describing large periodic and nonperiodic systems. The activities in WP5 and WP8 will also be merged into a single activity on dynamics and time-development of gas-phase reactions and photochemical processes.

The second period of operation will also see new activities at the CTCC, broadening the scientific scope and

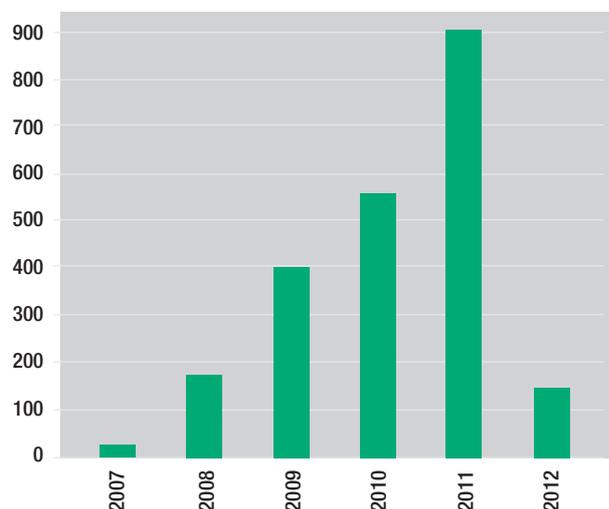
competence of the CTCC. Prof. Bjørn-Olav Brandsdal will join the CTCC as a full member in the second period of operation, increasing our activity in the field of biomolecular modelling. Many of the methodological developments made in recent years for extending quantum-chemical methods to large systems and to the time-domain will benefit from his expertise on biomolecular systems and these new computational methods may prove crucial in order to obtain accurate results for biomolecular properties and reactions.

Prof. Morten Hjort-Jensen will add strength to our activity in one of the core topics in computational chemistry, the description of the electron correlation problem. His research interests include a wide variety of problems in which electron correlation is essential and of a different nature than that encountered in molecules, hopefully including new insight that may improve the predictability of the methodologies developed at the CTCC.

Research: With a record number of 81 articles published in 2011, the CTCC is by the end of 2011 short by one article of its 300th publication. The activity thus remains high. Perhaps more important than the publication activity is the impact the scientific activities at the CTCC have on the community, and with close to 900 citations during 2011 to work produced at the Centre, the CTCC has now



Published Items in Each Year



Citations in Each Year

passed more than 2000 citations during the 4,5 years the Centre has been in operation.

At the beginning of 2012, 21 papers have been cited more than 21 times (the so-called h index), these articles originating from the work done in six different work packages. Almost all aspects of the scientific activities at the CTCC thus have a strong and immediate impact on the community. The article by CTCC director Prof. Trygve Helgaker in collaboration with the group of Prof. David J. Tozer at the University of Durham on a diagnostic test for the quality of Kohn–Sham excitation energies (*J. Chem. Phys.* **128**, 044118 (2008)) continues to have a major impact and is the most cited paper of the CTCC, with 75 citations in 2011 alone.

A major scientific recognition was in 2011 awarded to CTCC director Prof. Trygve Helgaker, who received the Research Prize of the Research Council of Norway (*Årets Møbius*). He received this award in recognition of his many significant contributions to simplify the quantum-mechanical equations that govern atoms and molecules, while at the same time increasing the accuracy of the calculations, and thus their predictive powers. *Årets Møbius* is awarded every year to an outstanding Norwegian scientist in any field of science, and Prof. Helgaker was presented with the prize at a ceremony in Oslo Concert Hall by Minister for Higher Education and Research,



Trygve Helgaker receives the award. Foto: Sverre Chr. Jarild

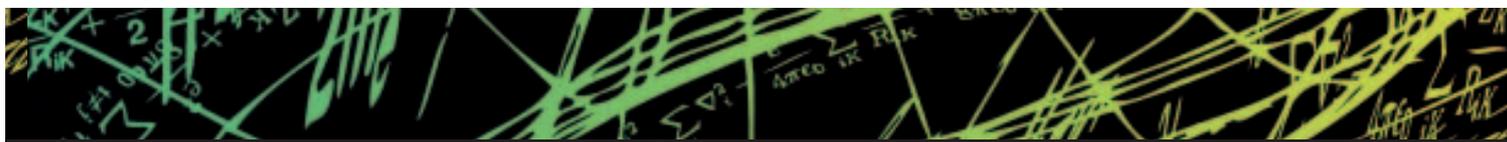
Tora Aasland.

This award follows the award in 2010 to Prof. Helgaker of an Advanced Investigator Grant by the European Research Council, which until 2011 was the only ERC granted in Norway in the domain of chemistry.

In 2011, however, two more ERC grants in chemistry were awarded to researchers working in part or in full in Norway, both recipients being members of the CTCC. CTCC director Kenneth Ruud was awarded a five-year ERC Starting Grant on a project entitled “Theoretical multiphoton spectroscopy for understanding surfaces and interfaces”. This project will utilize the tools developed as part of WP4 to create new insight into a complicated chemical problem by developing computational models that will help rationalize surface-specific spectroscopies.

In the same call, CTCC adjunct professor Benedetta Mennucci, who holds a permanent position at the University of Pisa (Italy), also received a five-year ERC Starting Grant for her project entitled “The interplay between quantum coherence and environment in the photosynthetic electronic energy transfer and light harvesting: a quantum chemical picture”. This project will complement well the activities of the CTCC in WP4 and the new work package on biomolecular modelling. As such, this project should benefit from her appointment at the CTCC, while the CTCC will benefit from the new insight that will arise from this project in terms of the Centre’s own research goals.

At the end of 2011, CTCC Director Kenneth Ruud was



awarded a research grant from the Research Council of Norway for the project “Relativistic two- and four-component density functional theory with periodic boundary conditions”. Together with CTCC director Trygve Helgaker and CTCC adjunct professor Trond Saue, he will build on the work done in WP1 and WP4 to develop a new code for studying heavy-element compounds in the solid state using four-component relativistic wave functions, creating a unique code for the study of molecular properties of compounds with elements from the entire periodic table.

CTCC director Prof. Trygve Helgaker is one of several principle investigators on a preparatory access grant awarded by the European PRACE project (Partnership for Advanced Computing in Europe) together with collaborators at the Royal School of Technology (KTH) in Stockholm. The grant will help deploy the linearly scaling version of the Dalton code (LSDalton) developed at the CTCC as part of WP1 onto the largest supercomputers in Europe.

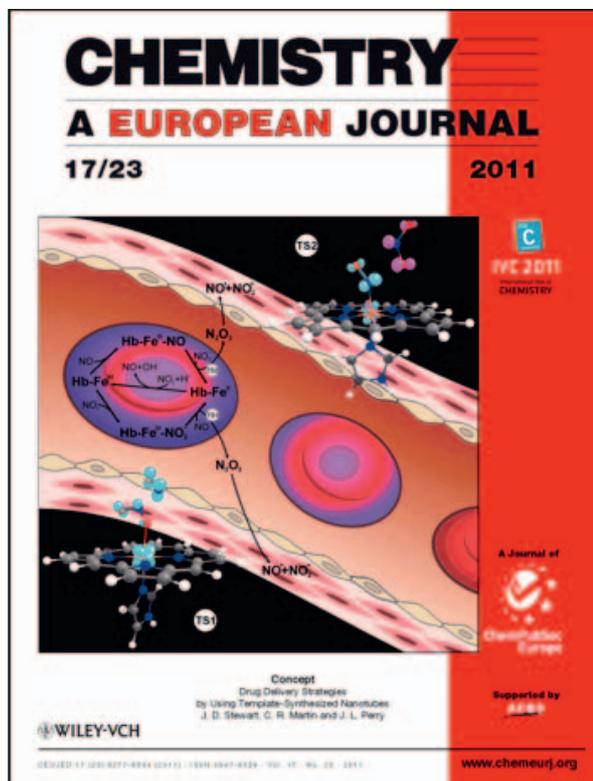
CTCC researcher Prof. Abhik Ghosh has received a

grant, together with CTCC directors Profs. Trygve Helgaker and Kenneth Ruud, from the Research Council of Norway entitled “In-silico design and understanding of the microscopic mechanism of new generations of clean energy materials”. In addition to gaining new insight into this very important area of research, the grant will also help the CTCC establish bilateral collaborations with the Indian Association for the Cultivation of Science and the University of Kolkata in India, strengthening the international profile of the Centre.

The research of CTCC researcher Prof. Abhik Ghosh have been featured on two occasions on the front cover over leading international journals. Together with researchers at the Department of Chemistry at the University of Tromsø and the University of the Free State in Bloemfontein in South Africa, his work on synthesizing and characterizing strongly saddled, chiral copper corroles was featured on the front cover of the april issue of the European Journal of Inorganic Chemistry.



Journal cover graphics: Copper corroles as a new class of nonplanar aromatics and of inherently chiral chromophores



Journal cover graphics: Schematic of the nitrite anhydrase process in a capillary



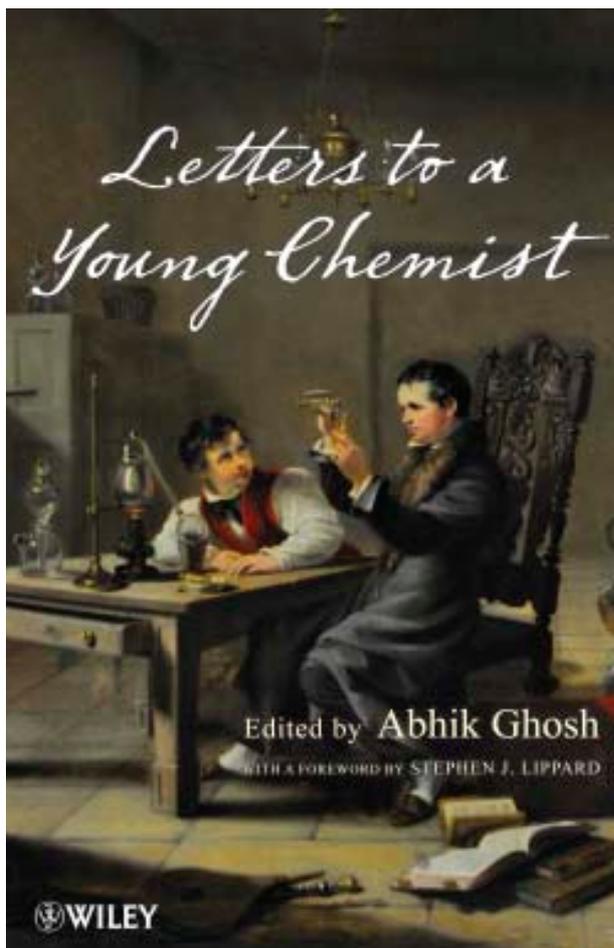
Prof. Abhik Ghosh, together with CTCC postdocs Bruno Cardey and Kathrin Hopmann also got the cover of the May issue of “Chemistry – A European Journal” for their paper discussing the role of nitrite as a hypoxia sensor. Fe(III)-nitrite-NO interactions inside red blood cells are proposed to lead to dinitrogen trioxide, an NO carrier that results in vasodilation under oxidative stress.

One of the former long-term visitors to the CTCC was Prof. Daniel Crawford from Virginia Tech in Blacksburg, who spent a 6 month sabbatical at the CTCC in the spring of 2009. Together with CTCC director Prof. Kenneth Ruud, he published a paper entitled “Coupled-Cluster Calculations of Vibrational Raman Optical Activity Spectra” in December 2011 in the journal ChemPhysChem, that was

designated a Very Important Paper by the journal.

Training: The CTCC continues to focus on the training of PhD students and postdocs in presentation skills. During May 10-11, the CTCC held its annual spring meeting at Malangen Brygger outside of Tromsø, where many of the Centre’s PhD students and postdocs gave oral presentations.

Members of the CTCC are also active in organizing international summer schools. CTCC adjunct Professor Trond Sæue from the University of Toulouse chairs the European Summer School in Quantum Chemistry, which was organized in the last two weeks of September in Sicily. In addition to Prof. Sæue, CTCC director Prof. Trygve Helgaker participated as a lecturer, and CTCC postdoc



Cover from Letters to a Young Chemist



Vladimir Rybkin at Forsker Grand Prix



Radovan Bast worked as a tutor at the summer school.

Outreach and dissemination: In the spring of 2011, the popular scientific book edited by CTCC researcher Prof. Abhik Ghosh entitled “Letters to a Young Chemist” was published, featuring popular scientific articles written by 17 internationally leading experts in chemistry. The articles are in the form of letters written to a young high-school student, “Angela”, describing their own fascination with chemistry in general and their own research topics in particular. The book has received a lot of media attention and has been very well received. Nature Chemistry praised the book for being “a great source of chemical processes in real-world context for educators at a variety of levels”.

A new concept for popularizing science that was introduced a few years back but which has quickly gained a lot of popularity is “Forsker Grand Prix”. In this competition, young scientists present their research in four minutes in a popular-scientific manner to an audience and to a panel of judges. In much the same manner as the Eurovision Song Contest, their performance are rated by the judges and the audience casts their votes. CTCC PhD student Vladimir Rybkin took on the challenge of presenting computational chemistry to the public, and did an excellent job presenting the work of the Centre to a large crowd in an engaging manner.

In June 2011, the CTCC hosted the 15th European Seminar on Computational Methods of Quantum Chemistry, gathering 89 researchers on a small island in the Oslo fjord, home to the historically important Oscarsborg fortress. The beautiful location, the weather and the high scientific quality of the invited lecturers all contributed to making this event a great success, as detailed elsewhere in this annual report.

CTCC researchers have been giving talks at a large number of international conferences throughout 2011, and we do not list all of these here. We would, however, like to highlight that the CTCC was very well represented at the largest computational chemistry meeting of 2011, the congress of the World Association of Theoretical and Computational Chemists, which gathered more than 1300 researchers in Santiago de Compostela in Spain in the middle of July 2011. CTCC researchers Trygve Helgak-



*Einar Uggerud awarded by the Norwegian Chemical Society
Foto: Finn-Knut Hansen*

er, Benedetta Mennucci, Magdalena Pecul, Thomas Bondo Pedersen, Kenneth Ruud and Einar Uggerud all gave invited lectures, CTCC adjunct professor Sonia Coriani gave a contributed talk, and CTCC PhD student Krzysztof Mozgawa presented a poster.

2011 was designated by the United Nations as the International Year of Chemistry (IYC2011), and the members of the CTCC took an active part in these activities, and we highlight some of these activities elsewhere in this annual report. The work of organizing IYC2011 in Norway was lead by a national committee chaired by CTCC researcher Prof. Einar Uggerud, who tackled the challenge of organizing more than 20 large-scale events all over the country, as well as securing funding for these activities, in an excellent manner. His efforts were recognized by the Norwegian Chemical Society, who awarded him with a Honorary Membership of the society.

In the following, we present four highlights of recent CTCC research, giving a more detailed insight into some recent activities at the Centre.

Seeing the chemical bond

A key concept in chemistry is the notion of the chemical bond. Chemists' understanding of how atoms share electron pairs in molecules through the formation of chemical bonds is fundamental to a chemist in order to explain, understand and predict chemical reactions. The sharing of electron pairs in chemical bonds also forms the basis for molecular structure predictions, the repulsion between shared electron pairs leading to the geometrical arrangement of atoms in space.

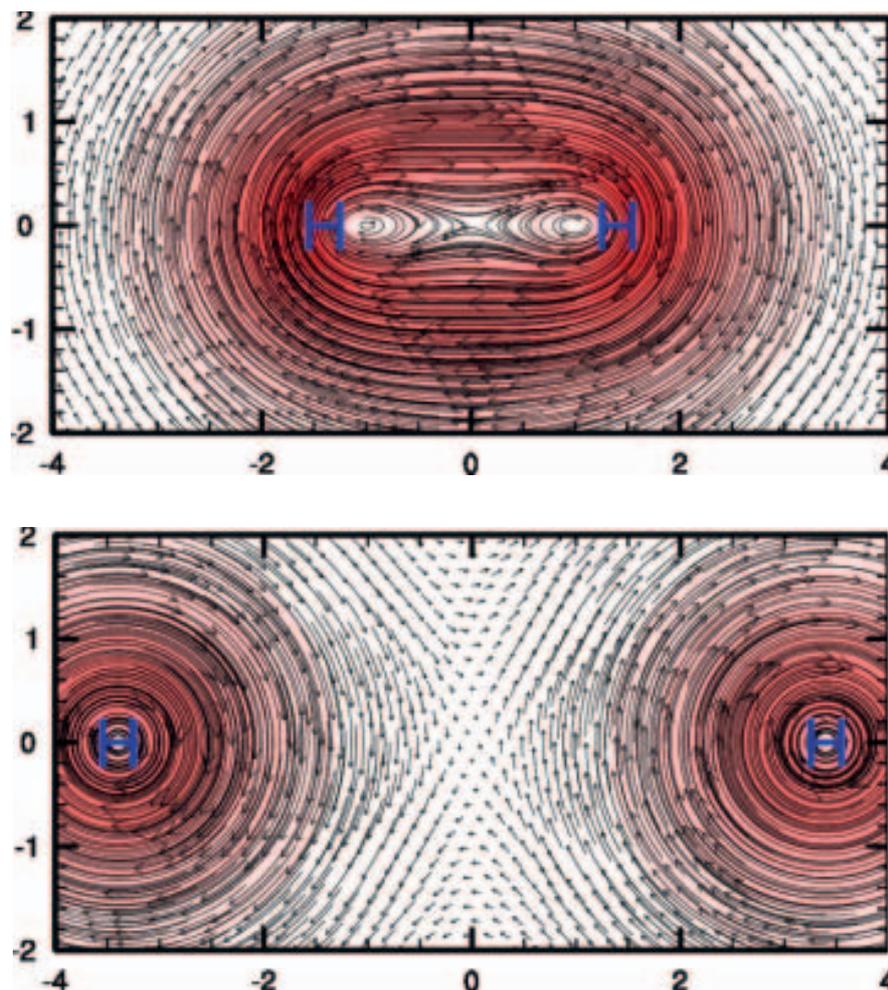
However, the chemical bond and the sharing of electron pairs are not quantum-mechanical observables, leaving a gap between what chemists would like to know

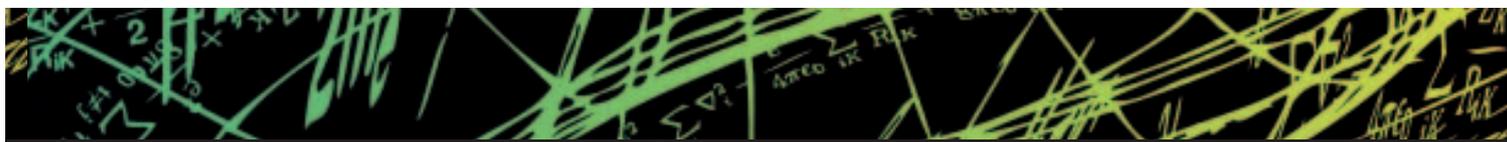
about a molecule in terms of bonding, and what can be extracted from a quantum-chemical calculation. Due to its usefulness as a concept, the literature is nevertheless full of models for partitioning molecular electron densities into localized quantities that could be said to correspond to chemical bonds. Although in many cases very useful, these definitions are always based on assumptions whose validity always remains uncertain, and whose correctness cannot be assessed from a comparison to experimental observations.

At the CTCC, we have taken a different route. Instead of focusing on the electron density itself, we consider the

density perturbed by an external magnetic field. This magnetic field induces a flow of the electrons in the molecule---that is, a magnetic-field-induced current which we from theoretical calculations can visualize. These currents have been studied for a long time in relation to aromatic systems, providing one definition of aromaticity in molecules.

What CTCC researchers discovered was that when studying these induced currents while a bond is being broken, we can not only see the chemical bond, but we can also visualize and see the sharing of electron pairs between atoms in a bond. This is illustrated in the figure at the left, where we show the induced current in the hydrogen molecule at two different bond lengths. At the equilibrium bond length of 0.74 Å, we clearly see the flow of electrons around the entire molecule, while at 1.8 Å, the electrons flow around its own atom





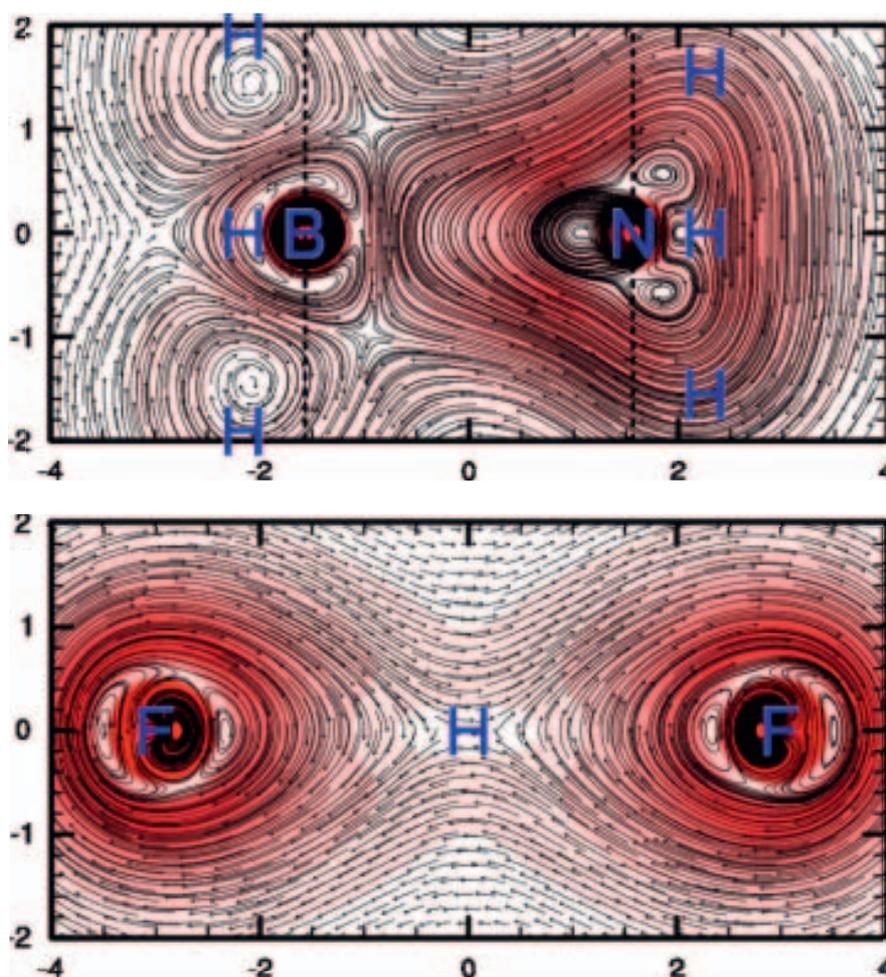
and are not shared, and thus no bond is present.

These models can also explain different kinds of bonding, and the figure below at the top shows a dative bond, in which one of the atoms donates both electrons in the bond, whereas at the bottom we see the prototypical three-center two-electron bond.

The magnetically induced currents are by themselves not observable, but they determine the local magnetic field experienced at a nucleus, and thus the nuclear magnetic shielding constants in a molecule. The model of chemical bonding through magnetic-field-induced

currents is therefore intimately connected to observable properties while allowing for a unique glimpse into the fascinating world of the chemical bond.

This work has been carried out by CTCC postdoc Radovan Bast and a visitor to the CTCC, Shubrodeep Pathak from Kolkata in India, in collaboration with CTCC director Kenneth Ruud.





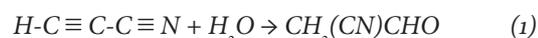
Quantum chemical and microwave investigations of cyanoacetaldehyde ($\text{CH}_2(\text{CN})\text{CHO}$), a potential prebiotic precursor of components of DNA and RNA

Where did the molecules that generated life come from and how were they formed? There are several potential molecular sources: Volcanic activities (especially underwater activities), interstellar “dust” (tiny silicate particles) covered with molecules, meteorites, and comets have all been suggested. A combination of compounds from all these sources is also a possibility.

It is now well established that “small” molecules containing up to about 20 atoms are generated in the gas phase in interstellar space at temperatures often slightly above 0 K and at very low pressures. Most of these molecules have been detected by means of their microwave rotational spectra. A majority of these compounds are believed to have been formed by reactions between a neutral compound and a cation, because such reactions often have near-zero activation energies, often a necessary requirement under these extreme conditions. The small interstellar molecules formed in this manner may condense out on dust and other particles forming an “ice”. The ice may be bombarded by ultraviolet radiation from nearby stars setting off a series of reactions and the formation of a wide variety of larger molecules. Analyses of carbonaceous meteorites provide strong support for this hypothesis. In a recent analysis of one such meteorite, tens of thousands, even millions, of different compounds were found. Comets are other celestial bodies where large amounts of interstellar molecules settle down. Early Earth was bombarded by comets and meteorites with their loads of a wide variety of molecules. A better starting point for life can hardly be envisaged.

Two of the compounds found in meteorites are the pyrimidines cytosine and uracil. The first of these two molecules is part of both DNA and RNA, while uracil is

found in RNA. Pyrimidines have been found in meteorites, and this shows that a prebiotic route to these molecules indeed exists. One mechanism for the formation of pyrimidines could be the following: Cyanoacetylene ($\text{H-C}\equiv\text{C-C}\equiv\text{N}$) is a prominent interstellar compound found in many sources in space and in the atmospheres of planets. Addition of water to cyanoacetylene could produce cyanoacetaldehyde



Urea and guanidine are two well-known and relatively prevalent prebiotic compounds. They could take part in the reaction sequence indicated in Figure 1, forming pyrimidines.

We have modeled the uncatalyzed gas-phase addition mechanism of eqn. (1) by ab initio quantum chemistry at the MP2/6-311++G** level of theory. A reaction mechanism consisting of several steps was found in these calculations, but the activation energy of the second crucial step is relatively high (216 kJ/mol), which makes it unlikely that cyanoacetaldehyde is formed in an uncatalyzed reaction. Similar calculations were performed for uncatalyzed reactions of water and protonated cyanoacetylene ($\text{H-N}\equiv\text{CCH}_2\text{CHO}^+$), which is known to exist in space. A significantly smaller activation energy was found for the second step (114 kJ/mol) in this case, as expected, but this activation energy is still so high that this reaction also seems unlikely. A catalyzed reaction therefore seems to be probable for the formation of cyanoacetaldehyde under interstellar conditions. This work has been published.



From Chemical education to Citizen science

The International Year of Chemistry provided a perfect motivation for increased community outreach for Professor Abhik Ghosh and Steffen Berg, M. Sc. student and an aspiring high school teacher. A broad palette of activities were chosen, which in terms of increasing popular appeal, may be listed as chemical education, citizen science, and popular science. Brief accounts of the first two are given below.

Chemical education: Toward a rational approach to descriptive inorganic chemistry

Ever since molecular orbital theory and other theoretical concepts became an integral part of the undergraduate inorganic curriculum, there has been significant concern about the concomitant lack of emphasis on chemical facts, i.e. descriptive inorganic chemistry. The student who thought that silver chloride is a pale green gas has become part of the lore of chemical education. The problem, however, is more easily pointed out than fixed. Our solution at the CTCC, which has proven both popular and successful, has involved adopting a mechanistic, arrow-pushing approach to undergraduate inorganic chemistry, much as is done in organic chemistry. Although this may sound rather trivial, *not a single introductory inorganic text remotely attempts such an approach*. We described our approach in an article in the *Journal of Chemical Education* (Figure 1). A book-length exposition is also planned and a contract for such a text has been signed with John Wiley and Sons, Inc.

Why inorganic texts to date have completely eschewed arrow pushing, a tool that has been spectacularly successful in organic chemistry is an interesting point. One reason, we believe, is that in contrast to many common organic functional groups, simple p-block compounds such as hydrides, oxides, halides, etc. tend to be much more reactive and their reactions therefore have been far less thoroughly studied. Understandably, textbook writers have hesitated to emphasize an approach that has little grounding in experimental fact. On the other hand, mechanisms provide a logical framework which students can use to make sense of a large body of factual infor-

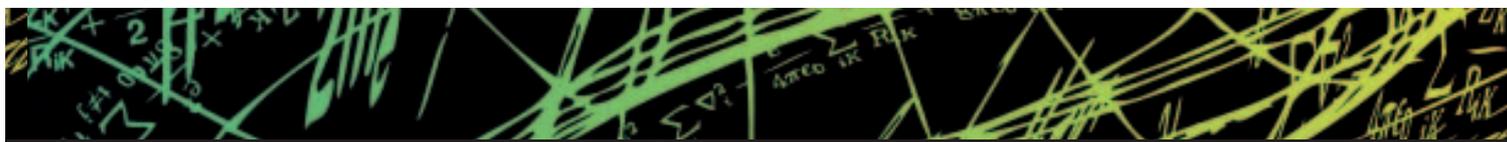
mation, no small thing in a field that is often perceived as amorphous and illogical. A mechanism may be unsubstantiated, but it provides a rationale for how a given reaction *might* occur, which in our view is enormously better than having no such rationale at all.

Computational Chemistry as Citizen Science

Much of main-group chemistry, in particular the chemistry of the p-block elements, as presented in standard inorganic texts, took shape before the present “DFT era” of computational chemistry. Accordingly, vast tracts of classic inorganic chemistry remain essentially untouched by modern quantum chemical methods. Fascinating structural and mechanistic questions abound, which can be profitably probed with DFT calculations. These provide vast opportunities for *citizen science*. The term may be defined as scientific contributions by private citizens, particularly amateurs, to projects of real scientific value. Such participation provides for wonderful hobbies for many adults and retirees. For high school and college students, citizen science can strongly complement formal schoolwork, wherein chemistry can often degenerate into rigid cookbook-style exercises. Citizen science is probably best developed in biology and, to a lesser extent, in other observational sciences such as astronomy and meteorology. Some of the best-known citizen science projects hail from the US and include a number of projects organized by the Cornell Laboratory of Ornithology, the public protein folding project Foldit, and the Whale Shark Photo-identification Library, to name just a few.

At first glance, a highly hardware-dependent science such as chemistry might not seem amenable to citizen science. Yet high school students *can* make significant contributions to chemistry research, a potential that Ghosh and Berg wish to tap at the CTCC. A wonderful example of citizen chemistry is provided by Professor Harry Gray’s “solar army” at Caltech, where high school students are enlisted to examine an endless variety of metal oxide materials as catalysts for solar water-splitting, one of the most important goals of contemporary energy research.

The Citizen Computational Chemistry (CCC) project,

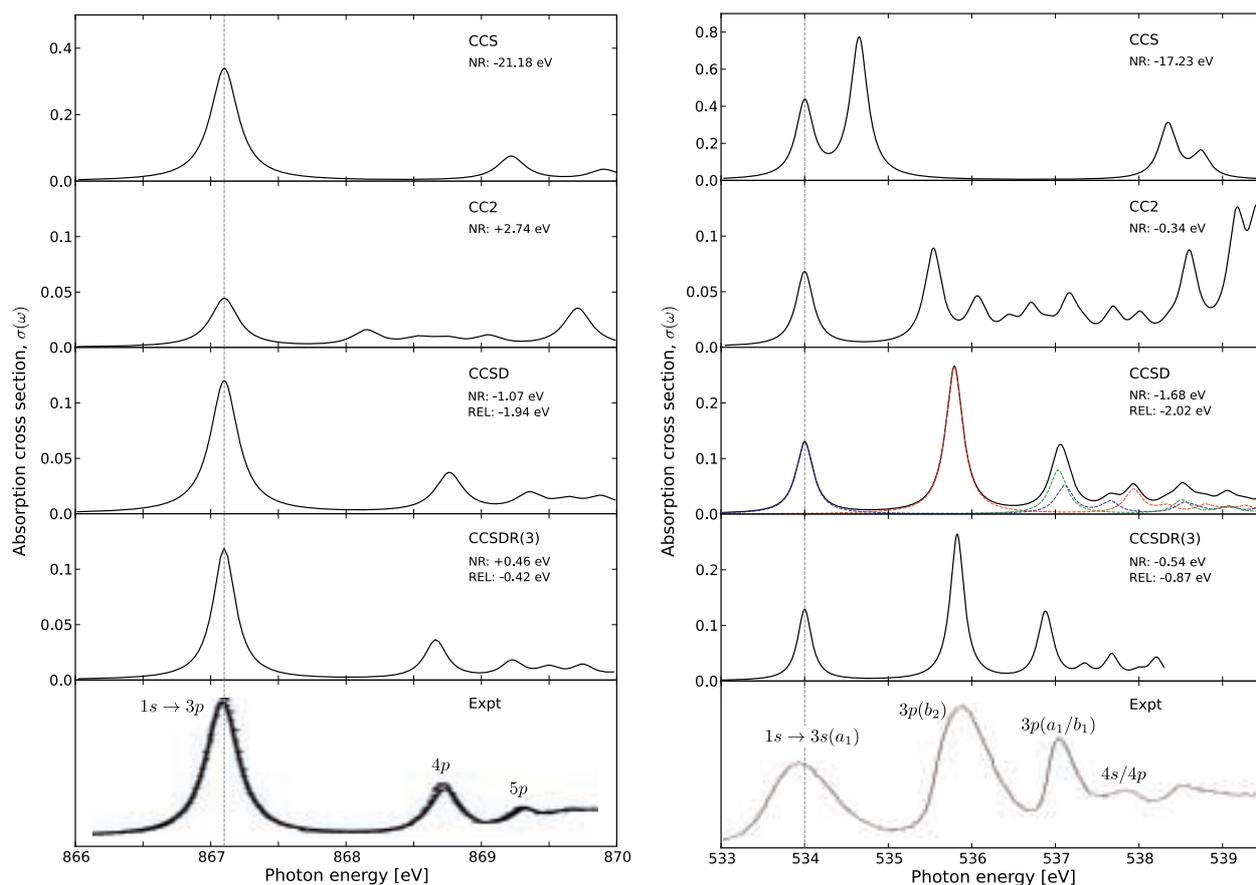


underway in the inorganic chemistry group at the CTCC, engages high school students and undergraduates to address important electronic-structural and mechanistic problems involving small inorganic molecules that can be easily simulated at home on a PC. At present, the questions fall into two broad categories: (a) Why does a given molecule have a given geometry (*say*, bent as opposed to linear)? (b) How can we choose between different mechanisms for a given process? So far, our CCC projects have focused on a variety of unusual metal nitrosyls and the somewhat exotic sulfur nitrides, a fascinating class of molecules often ignored in inorganic courses on account of their perceived complexity. The opportunity to participate in open-ended problems and real discovery, as opposed to cookbook-style exercises, is invariably exciting for young students. CCC also imparts valuable skills in, among others, molecular orbital arguments, geometry optimizations, and the assessment of proposed mechanisms. ‘Computational chemistry as citizen science’ clearly has vast potential, which Berg hopes to explore in coming years in the course of a PhD in chemical education.



Figure 1. (a) A *Journal of Chemical Education* article that presented a first exposition of Ghosh and Berg’s mechanistic approach to inorganic chemistry education; (b) Caltech’s Harry Gray, “five-star general of the solar army”; (c) Steffen Berg, an M. Sc. student with a strong interest in chemical education and outreach at the Tromsø Department of Chemistry.

Accurate coupled-cluster response methods for X-ray absorption spectroscopy

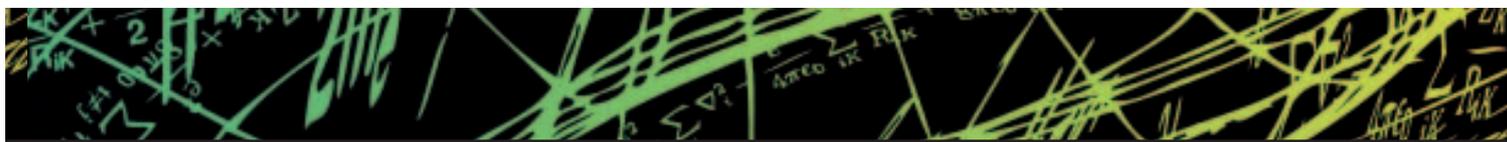


Comparison of computational and experimental near-edge absorption fine structure spectra of Neon (left) and Water (right).

Synchrotron radiation provides highly-focused, high-intensity light of well-defined characteristics with wavelengths from infrared to X-ray and is a widespread scientific tool in many areas of research including physics, chemistry, material science, and environmental sciences. A popular synchrotron radiation technique is X-ray absorption spectroscopy, where the photon energy is tuned to regions corresponding to the excitation of core electrons. Its successful application relies not only on the development of high-quality radiation sources and experimental techniques but also on theoretical methodologies. The analysis of core-level spectra in combination with

theoretical calculations reveals detailed electronic and structural information, such as the charge-transfer character of states, bonding nature, hybridization, chemical environment and site symmetry. Theoretical simulations are thus essential both in order to understand specific systems and for defining the information contents in the spectroscopic probes.

The quantum chemical description of core-excitation spectra is however not an easy task. The frequency region is very broad (20-50 eV) and requires the ability to treat a large number of excited states (~ 50 -500). Large relaxation effects occur upon excitation of a core electron, making



a balanced treatment of the core-excited state relative to the ground state difficult. Strong excitations of charge-transfer character may be induced. Relativistic effects are also important. All this poses stringent requirements on the quality and accuracy of the models employed to interpret the spectroscopic results. Even if a number of methodologies exist, often adapted to specific systems, elements or X-ray absorption edges, the development of a fully quantitative treatment remains challenging.

Coupled-cluster (cc) response theory has proven to be “the state-of-the-art method” for high-accuracy calculations of spectroscopic properties, with accuracy comparable, and sometimes even superior, to the one obtained in experimental studies. The hierarchy of cc levels enables systematic and rapid convergence of dynamic electron correlation, and, with inclusion of triple excitations, very high accuracy is reached in the description of electronic transitions in the UV/vis region of the spectrum. In X-ray spectroscopy, on the other hand, the use of cc response methods is almost unexplored, hampered mainly by the fact that the interesting semi-bound core-valence excited states are embedded in a continuum of valence-ionized states.

To overcome this problem, we have, as a first step towards the extension of cc theory to spectroscopic phenomena in the X-ray region, developed a new approach,

applicable to a hierarchy of cc approximations, where the absorption cross section is obtained not from the complete oscillator strength distribution, but from the imaginary part of the electric dipole polarizability. This is in the spirit of the “damped” formulations of response theory, where one explicitly takes into account the finite lifetimes of the excited states. The approach has the same qualities and virtues for X-ray spectroscopies that traditional response function approaches have shown for optical spectroscopies. It properly accounts for relaxation effects and is open-ended towards extensions to other spectroscopies in the X-ray region, such as X-ray circular dichroism or multiphoton X-ray absorption. Its accuracy in the description of electronic relaxation and differential correlation for the core-excited state depends only on the description of dynamic correlation and can be monitored by using the cc hierarchy, as typically done for UV/vis spectra. Another interesting future perspective is its combination with molecular mechanics methods for calculations on much larger systems, where the accuracy still can be maintained for a specific central core region.

This work has been published in *Phys. Rev. A* 85, 022507 (2012)

Outreach during the International Year of Chemistry

The United Nations declared 2011 as the International Year of Chemistry (IYC2011), with the goal of increasing public appreciation of chemistry as a solution to world needs, to encourage interest in chemistry among young people, and to generate enthusiasm for the creative future of chemistry. The responsibility for implementing IYC2011 was given to UNESCO and the International Union of Pure and Applied Chemistry (IUPAC). In Norway, the national adhering organization to IUPAC, the Norwegian Chemical Society (NKS), appointed a national committee to implement this event, chaired by CTCC researcher Prof. Einar Uggerud. In his capacity of president of the NKS, CTCC director Prof. Kenneth Ruud was also a member of this committee. A number of other CTCC researchers were engaged in IYC2011 activities, helping in promoting chemistry to the public, some highlights of which are given here.

On the opening day of IYC2011 in Norway, Profs. Uggerud and Ruud published a commentary in the major Norwegian newspaper *Aftenposten* on the importance of chemistry for our modern society and the future of our planet. Profs. Abhik Ghosh and Kenneth Ruud also wrote a commentary on nanotechnology that was featured during the science days in the local newspaper in Tromsø, *Nordlys*.

An issue of the Norwegian supercomputing magazine *Meta* also highlighted the IYC with a special issue on supercomputing in chemistry, featuring popular scientific articles from all research groups in this field in Norway. CTCC director Prof. Trygve Helgaker together with CTCC postdoc Erik Tellgren and CTCC PhD student Kai Lange presented an article entitled “Molecules in Strong Magnetic Fields”, and CTCC affiliate Prof. Bjørn-Olav Brandsdal presented an article entitled “Antimicrobial peptides emerge as a

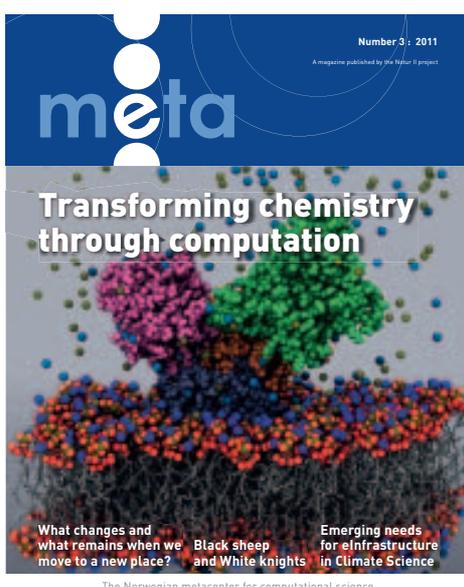
new class of drugs”. CTCC director Prof. Kenneth wrote an introductory comment to this special thematic issue titled “Transforming chemistry through computation”.

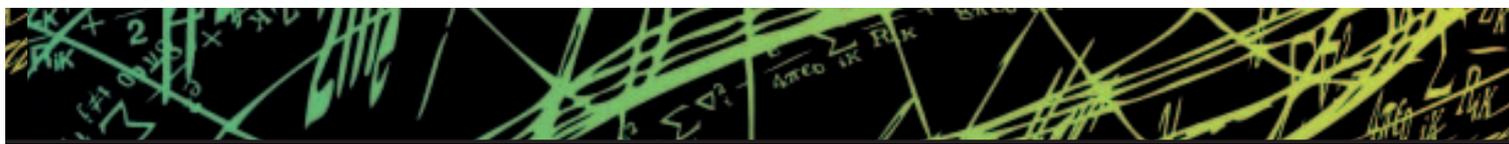
CTCC postdoc Kathrin Hopmann, together with Prof. Ruud, also wrote a popular article for *Kjemi*, the news magazine of the Norwegian Chemical Society, on the use of theoretical spectroscopy, in combination with experiment, to elucidate the absolute configuration of chiral molecules. In the same issue, CTCC director Prof. Helgaker also presented an article entitled “Chemistry and materials”, focusing on the potential of computing in addressing important questions in chemistry and materials research.

The same issue of *Kjemi* also included an article by master’s student Steffen Berg and Prof. Ghosh on their new approach to teaching inorganic chemistry, a formal exposition of which was published in the *Journal of Chemical Education* under the title “Arrow Pushing: A Rational, Participatory Approach To Teaching Descriptive Inorganic Chemistry”.

Besides writing popular science articles, CTCC members were strongly involved in a number of other outreach activities related to IYC2011, including, among other things, organizing a one-week chemistry festival at the Technical Museum in Oslo, giving popular scientific lectures at schools, and a major role in the Science Week during September 2011, the theme for the Science Week in 2011 being chemistry.

The IYC2011 has boosted the outreach activities of the entire chemistry community as well as the CTCC. The challenge will now be for the CTCC to build on this momentum and maintain an equally visible outreach profile in the years ahead.





Midterm evaluation of the CTCC

A much anticipated event in 2011 was the publication of the midterm evaluation of the activities at the CTCC .

The overall assessment of the Centre was that much of the activity is exceptionally good with the remainder very good, and that the Centre had established Oslo and Tromsø as internationally recognized Centres for research in theoretical chemistry. On the basis of this assessment, the Research Council of Norway granted the Centre a second period of operation.

The international evaluation found that the CTCC had been responsible for a substantial body of innovative research at an internationally leading level. Although one of the major goals of the Centre, an increased use of new computational methodology in support of experimental studies has not yet materialized to a significant extent, the committee found that the Centre has taken the necessary measures to allow this to happen in the second phase.

The CTCC was praised for its excellent environment for researcher training, despite the challenges sometimes faced in recruiting PhD students, combining high-level research activity with well-selected topics, and encouraging a productive ethos. The extensive international visitor program contributes to this excellent research training environment, creating an open atmosphere of interaction and exchange of ideas.

The CTCC was also complemented for tackling the gender issue, identified as a particular challenge for the area of research of the Centre, in highly imaginative ways, including the appointment of female adjunct professors and focussed workshops and visitor programs, leading to some small successes in this area.

The evaluation committee recommended that the Centre continues its research plan in its

current form. However, the committee considered the exit strategy weak, and strongly recommended the host universities to recognize the benefits of the networking arrangements for the Centre's international profile and future recruitment, and to commit themselves to support this activity after the funding from the Research Council of Norway ends. The committee also advised the Centre to focus on fostering the nascent collaborations between theoreticians and experimentalists, as these collaborations is expected by the evaluation committee to be crucial in securing future funding after 2017, when "relevance" may have to have a stronger focus, in order to be able to prepare competitive proposals in a wide range of funding instruments.

The CTCC was encouraged to explore the possibility of appointing a suitably trained expert to help get the codes developed at the Centre (Dalton and Dirac) into a form where they can be disseminated in a self-sustaining way.

The CTCC is very happy with the positive evaluation of our activity so far, and also that the committee supports our plans for addressing some of the concerns identified both by us and by the evaluation committee. We feel,

however, that some of the activities and work that has been done at the Centre was not been duly recognized by the international evaluation committee, despite being noted in the background material and scientific assessments prepared by experts in our field and by our own scientific advisory board.

Based on the evaluation, we will work together with our board and our scientific advisory board to further improve the quality of our work and to lay a good foundation for our activity beyond the lifetime of the Centre.



Midterm Evaluation
of Eight Centres of Excellence
(SFF-II)





European Seminar on Computational Methods in Quantum Chemistry 2011

Since the first such seminar in Strasbourg in 1969, the European Seminars on Computational Methods in Quantum Chemistry (ESCMQC) or “Strasbourg Seminars” have been organized every third year in different European locations. From Thursday June 16 until Sunday June 19 2011, the 15th ESCMQC was held at Oscarsborg Fortress, on a small island just outside Drøbak, a seaside town 40 km south of Oslo, sponsored by the CTCC. Like previous seminars in this series, the Oscarsborg meeting highlighted new developments in computational quantum chemistry but with a stronger emphasis on density-functional theory than at the previous seminars. The Oscarsborg meeting attracted about 90 participants from 20 countries who gave a total of 38 oral presentations and 25 poster presentations.

The Strasbourg seminars have traditionally been a venue for young workers in the field to present their work. The Oscarsborg meeting continued this important tradition—with two exceptions, all speakers were less than 50 years old. The quality of the presentations were

unusually high, covering the very latest developments in areas such as coupled-cluster theory, explicit correlation, multireference theory, density-functional theory, range-separation techniques, density-matrix renormalization techniques, linear-scaling and condensed-phase techniques and molecular properties.

The organizing committee, consisting of Prof. Jürgen Gauss (University of Karlsruhe, Germany), Prof. Trygve Helgaker (CTCC, chair) and Prof. Fred Manby (University of Bristol, UK) initially made a selection of 21 invited speakers, nearly all of whom accepted the invitation. The remaining 17 speakers were subsequently selected among the participants of the meeting, based on the abstracts submitted for the meeting. Important for the success of the meeting was the administrative support and help with many practicalities provided by Anne Marie Øveraa, John Vedde and Simen Reine at the CTCC and the Department of Chemistry in Oslo, all of whom contributed greatly to the success of the meeting.





Almlöf–Gropen lecture 2011: Prof. Pekka Pyykkö, University of Helsinki, Finland



The 2011 Almlöf–Gropen lecture was given by Prof. Pekka Pyykkö from the Department of Chemistry, University of Helsinki, Finland. His lecture was presented on October 5 in Oslo and October 6 in Tromsø.

Prof. Pyykkö was born in Hinnerjoki in Finland in 1941 and graduated from the University of Turku in 1967. Following a postdoc period abroad, he became an Associate Professor of Quantum Chemistry at Åbo Academy in 1974. Since 1984 Prof. Pyykkö has been a Professor in Chemistry at the University of Helsinki, as an emeritus since 2009. Prof. Pyykkö has received many honours and rewards in recognition of his contributions to chemistry and science—most recently he was the recipient of the Schrödinger Medal for 2012 of the World Association of Theoretical and Computational Chemists. He has published over 300 scientific papers and the bibliography “Relativistic Theory of Atoms and Molecules I–III”.

Prof. Pyykkö began his scientific activity as a solid-state NMR spectroscopist but soon turned his attention to quantum chemistry and, in particular, to the role of

relativity in chemistry. According to Prof. Pyykkö, the study of relativity in chemistry “has been a scientific gold mine, still far from empty”. Most recently, for example, he explained why the lead batteries work rather than tin batteries: Relativity makes lead battery efficient by increasing the electronegativity of lead dioxide—with relativity excluded, the battery loses about 80% of its voltage. As a result, “cars start because of relativity”. This insight caught the attention not only of chemists but a much wider audience through articles on his work in journals such as the *Economist*. In his talk “Relativity and Chemistry; some recent results” given in Oslo and Tromsø, these and other effects of relativity were discussed, to large audiences of interested chemists and physicists.

Another long-term interest of Prof. Pyykkö has been the use of quantum chemistry to predict new inorganic species—indeed, in the course of his career he has predicted a number of species that have subsequently been synthesized.



CTCC members

Principal scientists



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UiT



Abhik Ghosh
Professor
UiT



Kenneth Ruud
Professor
UiT



Mats Tilset
Professor
UiO



Luca Frediani
Associate
Professor
UiT



Trygve Helgaker
Professor
UiO



Inge Røeggen
Professor
UiT



Einar Uggerud
Professor
UiO



Knut Fægri
Professor
UiO



**Claus Jørgen
Nielsen**
Professor
UiO

Researchers



**Vebjørn
Bakken**
UiO



**Thomas Bondo
Pedersen**
UiO



Simen S. Reine
UiO



**Clemens
Woywod**
UiT



Dan Jonsson
UiT



Michael Przybytek
UiO



Andrew Teale
UiO

Postdocs



**Niels H.
Andersen**
UiO



John Earles
UiT



Thomas Kjærgaard
UiO



**Mauritz
Ryding**
UiO



Radovan Bast
UiT



Ulf Egil Ekström
UiO



Na Lin
UiT



**Hans Sverre
Smalø**
UiO



Bruno Cardey
UiT



Bin Gao
UiT



Ying-Chan Lin
UiT



Yizhen Tang
UiO



Adam Chamberlin
UiT



Kathrin Hopmann
UiT



Michal Repisky
UiT



Erik Tellgren
UiO



Andreas Thorvaldsen
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Ville Weijo
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Li-Ming Yang
UiO

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Marco Anelli
UiT



Stig Rune Jensen
UiT



Mihayo Musabila Maguta
UiO



Vladimir Rybkin
UiO



Arne J. C. Bunkan
UiO



Kai K. Lange
UiO



Xiaojun Li
UiT



Anton Simakov
UiO



Antoine Durdek
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Patrick Merlot
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Johannes Rekkedal
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Arnfinn Hykkerud Steindal
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Geir Isaksen
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Krzysztof Mozgawa
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Magnus Ringholm
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Alexyz Zatula
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Harald Møllendal
Professor
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Svein Samdal
Professor
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Professor II
UiT

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Professor AnneBritt Kolstø
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Vice-chairman of the board

Dr. Nina Aas
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Associate Professor Ole Swang
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Professor Kersti Hermansson
(Uppsala University, Sweden)

Professor Mike Robb
(Imperial College London, UK)

Professor Per-Olof Åstrand
(Norwegian University of Science and Technology, Norway)



Visiting scientists

Name	From	Period (from - to)
Taye B. Demissie	Poland	160111-180411
Anna Młodzianowska	Poland	230211-290311
Penny Brothers	New Zealand	040311-100311
Heike Fliegl	Finland	110311-210311
Marcel Swart	Spain	130311-150311
Stefano Corini	Italia	280311-080411
Petr Bour	Czech Republic	040411-280411
Jana Hudecova	Czech Republic	070411-180411
Agnes Vibok	Hungary	270411-070511
Gabor Halasz	Hungary	270411-070511
Andras Csehi	Hungary	270411-070511
Alessandro Biancardi	Italia	060511-060711
Franklin Ferraro	Italia	090511-200511
Jeanet Conradie	South-Africa	140511-010611
Marek Wojcik	Poland	170511-280511
Carl Wamser	USA	220511-300511
Luis Alvarez-Thon	Chile	270511-050611
Karina Kornobis	USA	310511-300811
Jógvan Magnus Haugaard Olsen	Denmark	040611-300811
Daniel Friese	Germany	270611-010711
Per-Olof Åstrand	Norway	300611-020711
Patrick Norman	Sweden	300611-020711
Emmanuel Fromager	France	070711-170711
Alexandrina Stoyanova	France	070711-170711
Yann Cornaton	France	070711-170711
Artur Wodynski	Poland	090811-090911
Maciej Kaminski	Poland	010911-180911
Maciej Kaminski	Poland	011011-131211
Artur Wodynski	Poland	021011-151011
Malgorzata Kauch	Poland	021011-151011
Alexey Arbuznikov	Germany	290911-161011
Pekka Pyykko	Finland	061011-071011
Agnes Vibok	Hungary	121011-221011
Gabor Halasz	Hungary	121011-221011
Andras Csehi	Hungary	121011-221011
Name	From	Period (from - to)

Name	From	Period (from - to)
Pawel Siuda	Poland	171011-291011
Jeanet Conradie	South-Africa	300911-161011
Hugo Vasquez	Mexico	040911-181111
Patrick Norman	Sweden	071111-111111
Ludwik Adamovicz	USA	150611-110711
Taku Onishi	Japan	310711-010911
Taku Onishi	Japan	190611-200611
Alexandrina Stoyanova	France	190611-230611
Pekka Pyykko	Finland	051011-061011
Alexander Tkalych	Canada	300811-301111
Alex Borgoo	Great Britain	130911-220911
Bickelhaupt	Nederland	101111-121111
Charles Perrin	USA	290911-300911
Jean-Claude Guillemain	France	200811-270811
Klavs Hansen	Sweden	170811-190811
Klavs Hansen	Sweden	111211-171211
Olof Echt	USA	170811-190811
Tobias Redder	Germany	010911-311211
Bertil Dynefors	Sweden	111211-171211
Kaveh Najafian	Sweden	111211-171211
Thorsten Rohwedder	Germany	211011-211011
Odile Eisenstein	France	221111-231111
Jürgen Gauss	Germany	051211-061211
Michal Repisky	Norway (UiT)	110211-110211
Nils Middendorf	Germany	240211-250211
Patrick Ettenhuber	Germany	110511-120511



Bringing the world to Tromsø and Tromsø to the world: Prof. Penny Brothers (The University of Auckland, New Zealand) on Tromsø island. Penny, Dr. Anna Młodzianowska and Dr. Adam Chamberlin on a northern lights watch.

Interview with visiting scientist Wim Klopper (Karlsruhe Institute of Technology, Germany)



Why did you choose to visit the CTCC, and how did you learn about the CTCC and its visitors program?

I have been aware of the CTCC since its foundation in July 2007. In the past five years, this Centre of Excellence (CoE) dedicated to theoretical and computational chemistry has achieved a spectacular international visibility and has already made a remarkable scientific impact. Today, it seems very hard to overlook the CTCC in the community of theoretical and computational chemists. I have known Trygve Helgaker and Kenneth Ruud since I worked as a post-doctoral research assistant (*førsteamanuensis*) in Trygve's research group at Oslo University in 1996-1998. I have kept in contact with Trygve and Kenneth ever since, and scientific collaborations have continued. On one occasion during the last few years (I have forgotten which one), Trygve mentioned the possibility of spending some time at the CTCC. Knowing the people and the research carried out at the CTCC, this seemed a very appealing prospect to me. I felt that a visit to the

CTCC would provide me with great opportunities to look into (for me) completely new areas of research in fundamental theoretical chemistry, and method development in particular. I chose the winter term from September 2010 until March 2011 for the visit, since for me in Karlsruhe, this term was free of teaching duties and administrative work and the like. At home, such a term is called "Forschungssemester", which simply translates into time for doing research. The short distance and frequent connections between Gardermoen and Frankfurt Airports allowed for short trips back to Karlsruhe to look after matters at home.

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

Concerning method development in the field of theoretical chemistry, my research at the Karlsruhe Institute of Technology (KIT) focuses on high-level wave function based methods such as coupled-cluster theory, using Slater-type geminals as two-particle basis functions (as opposed to one-particle functions such as orbitals, which most other people use). These methods have been developed for small to medium-sized molecules (up to 20 atoms). At the CTCC, basic research is being carried out in the area of density functional theory on the one hand, and methods are being developed for systems with periodic boundary conditions (polymers, surfaces, solids) on the other hand. Much more other work is done as well, of course, but these two activities seemed particularly interesting to me. It looked very exciting to connect the Slater-type geminals of my Karlsruhe research group with the perturbation theories for systems with periodic boundary conditions in Oslo. Furthermore, I had since long be intrigued by the random phase approximation, which is currently being studied intensively by the density functional community, also in Oslo. Indeed, it turned out to be extremely valuable to learn more about the random phase approximation in Oslo (we jointly published a paper entitled "Spin flipping in ring-coupled-cluster-doubles theory" in *Chem. Phys. Lett.* **2011**, 510, 147 on the subject), and since early this year in Karlsruhe, a Ph.D. research project has started on implementing the corre-



sponding random phase approximations with Slater-type geminals. Concerning the work for systems with periodic boundary conditions, I managed, with the help of Simen S. Reine (tusen takk!), to implement all of the two-particle integrals needed for Slater-type geminals, and work in this area is still ongoing. Furthermore, the visit at CTCC gave me enough time to develop an interference-corrected explicitly correlated second-order perturbation theory (*Chem. Phys. Lett.* **2011**, 503, 157), and when my Ph.D. student Nils Middendorf visited the CTCC for some time early 2011, Trygve and I looked at the basis set convergence of coupled-cluster and perturbation theory computations of the two-electron Darwin term. Our paper on this topic will soon appear in *Chem. Phys.*

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

Conditions were excellent for the work that I wanted to do. I very much enjoyed the long discussions with Trygve on density functional theory, the random phase approximation, and other things. Also talking science to Sonia Coriani, who was a frequent visitor to Oslo because of her position as an adjunct professor at the CTCC, and Andrew Teale and Thomas Bondo Pedersen was very valuable. It was great fun to learn about new methods,

to discover similarities between seemingly different computational models, to exchange and analyse computed data, and so forth. The scientific environment was very stimulating and motivating. Understanding, discoveries, and inventions are among the things that make science a very satisfying occupation, and I got plenty of it at the CTCC. Certainly, the lunchroom was at the heart of the very warm and friendly social environment.

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

I very much enjoyed my time in Oslo. The flat in Duehaugveien was excellent and very convenient. My wife Sonja and our two children (Tanja, 15, and Sven, 13) visited Oslo a couple of times during the stay. Since we all had lived at Vindern very close to the University of Oslo in 1996-1998 (Sven was born in Oslo!), we all enjoyed very much reviving the good old times we had 13-15 years ago. Now, we hiked in Nordmarka and enjoyed cross-country skiing when there was snow, for example during the Nordic World Ski Championships in February/March. Norway is a great country with great people, and Oslo is a good place to feel home.

Total revenue and expenditure figures

FINANSIERING i tusen kroner	Reell finans 2007	Reell finans 2008	Reell finans 2009	Reell finans 2010	Reell finans 2011	Planlagt finans 2012	Planlagt finans 2013-2017	Totalt finans
REGNSKAPSFØRTE INNTEKTER PÅ SFF ved vertsinstitusjonen								
Vertsinstitusjonen	3 300	8 099	7 900	8 000	8 200	8 200	32 100	75 799
Norges forskningsråd - SFF	3 900	6 400	11 137	10 932	12 552	11 923	34 800	91 644
Samarbeidspartner (navngis)								0
Internasjonale midler								0
Andre offentlige								0
Andre NFR-prosjekter								0
Andre offentlige enn NFR								0
Andre private								0
Sum regnskapsførte inntekter	7 200	14 499	19 037	18 932	20 752	20 123	66 900	167 443
ANDRE INNTEKTER = Ikke regnskapsførte midler på SFF ved vertsinstitusjonen								
Samarbeidspartner A								0
Samarbeidspartner B								0
Vertsinstitusjonen								0
Andre								0
Sum ikke regnskapsførte midler	0	0	0	0	0	0	0	0
Sum årets finansiering	7 200	14 499	19 037	18 932	20 752	20 123	66 900	167 443
Finansieringsplanens beløp								
Avvik fra finansieringsplanen	7 200	14 499	19 037	18 932	20 752	20 123	66 900	167 443
Overført (+/-)		5 006	4 148	4 083	1 598	110	110	
Sum finansiering og overføring	7 200	19 505	23 185	23 015	22 350	20 233	67 010	182 498
KOSTNADER i tusen kroner								
REGNSKAPSFØRTE KOSTNADER PÅ SFF ved vertsinstitusjonen								
Personell og lokaler	632	13 139	16 397	19 229	18 936	17 408	62 375	148 116
(Lønn og sosiale kostnader)								0
(Lokaler - husleie og drift)								0
Innkjøpte FoU tjenester								0
Utstyr								0
Andre driftskostnader	1 562	2 218	2 705	2 188	3 304	2 715	4 635	19 327
Sum regnskapsførte utgifter	2 194	15 357	19 102	21 417	22 240	20 123	67 010	167 443
ANDRE KOSTNADER = Ikke regnskapsførte kostnader på SFF ved vertsinstitusjonen								
Personell og lokaler	0	0	0	0	0	0	0	0
(Lønn og sosiale kostnader)								0
(Lokaler - husleie og drift)								0
Innkjøpte FoU tjenester								0
Utstyr								0
Andre driftskostnader								0
Sum ikke regnskapsført	0	0	0	0	0	0	0	0
Sum utgifter	2 194	15 357	19 102	21 417	22 240	20 123	67 010	167 443
Til overføring (+/-)	5 006	4 148	4 083	1 598	110	110	0	15 055

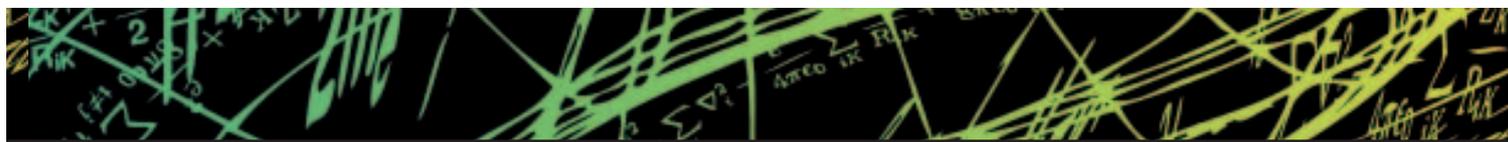


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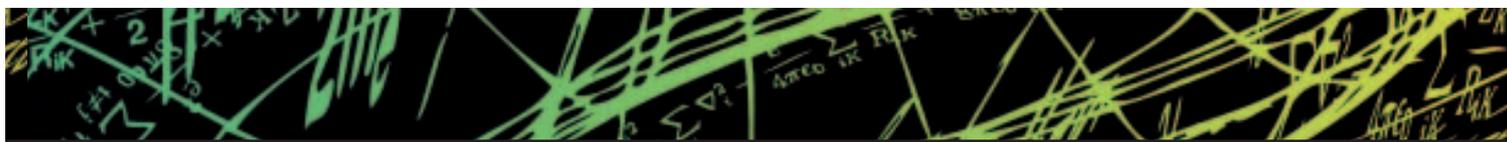
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Appendix B: Activity reports

WP1: Large periodic and nonperiodic systems

Scientist in charge: Trygve Helgaker

In 2011 we made several important contributions to WP1: the functionality of the newly developed LSDALTON code has been made available to users around the world through the release of the DALTON 2011 suite, we have greatly improved both the code performance and its range of applicability, and we have enhanced important technical aspects related to code testing and version control. Moreover, we have continued our efforts into the development of new tools, like the new Gaussian-based PBC code, linear-scaling correlated treatments, molecules in strong magnetic fields, and the development of efficient evaluation of the exchange contribution appearing in hybrid DFT. Importantly, work was begun to parallelize LSDALTON in 2011, with the aim of efficiently utilizing several thousand cores by the end of 2012. In the following, we briefly describe the above points.

The Dalton2011 suite consists of two powerful molecular electronic-structure programs, DALTON and LSDALTON. Of the two, the LSDALTON program is aimed at large molecular systems, comprising hundreds to thousands of atoms. The released LSDALTON program is comprised of a highly efficient, linear-scaling Kohn–Sham and Hartree–Fock code, with robust and efficient wave-function optimization procedures and highly efficient first-order methods for geometry optimizations. LSDALTON includes functionality for a range of molecular properties: excitation energies, polarizabilities and first hyperpolarizabilities, damped and undamped two-photon absorption, permanent dipole moments of ground and excited states, regular and excited-state molecular gradients and second hyperpolarizabilities.

During 2011, a significant effort was directed at code optimization. We have greatly improved the computational performance by intensive code optimizations, typically resulting in a speed-up of a factor two or more on a single processor. The multi-threaded version of the code has also seen significant improvements, with good

scalability up to 16 nodes. We have moreover greatly reduced the memory requirements for LSDALTON, allowing for better utilization of computational resources and for calculations on larger systems.

New features added to LSDALTON during 2011 include a new grid partitioning for the numerical treatment of the exchange–correlation contribution in Kohn–Sham density-functional theory (DFT) better suited for large systems, a new one-electron integral-evaluation framework for magnetic properties (nuclear magnetic shielding constants, magnetic circular dichroism, Verdet constants, magnetizabilities) and the implementation of an improved integral screening technique (MBIE). A continued effort has been directed at the new Gaussian-based periodic code.

Extensive work has also been carried out on our novel density-fitting method for exact exchange (PARI). The PARI method has shown both the expected accuracy and speed-up for smaller systems, but unfortunately erratic behaviour for certain larger molecules. The reason for this behaviour has been identified and we are currently investigating how it can be remedied for the reliable and fast inclusion of exact exchange for very large systems.

On the technical side, we have greatly simplified and extended the testing of code functionality and have also added performance testing - all of which are carried out automatically on a daily basis on different platforms and with different compilers and libraries. The above technical improvements allow for a more stable coding environment, resulting in a much more efficient code development in the long run.

As part of the European PRACE partnership, LSDALTON is undergoing a major transition towards massive parallelization, aiming at scalability up to several thousand processors. The initial foundation for the new hybrid OpenMP/MPI scheme was laid down in 2011. This project will be finished in 2012, with an LSDALTON code where integral contributions are calculated in a fully distributed fashion and interfaced with ScaLapack for linear-algebra operations.

During 2012, significant progress has also been made



towards the efficient linear-scaling calculations at the second-order Møller–Plesset (MP2) and coupled-cluster-single-doubles (CCSD) levels of theory, within the divide-expand-and-consolidate (DEC) framework, in collaboration with the group of Prof. Poul Jørgensen at Aarhus University. The CTCC has made important contributions, relating to the efficient and flexible evaluation of integrals. DEC-MP2 molecular energies and gradients and DEC-CCSD energies are currently available.

Finally, much work has been devoted to developing our LONDON code, which originally arose from a theoretical formulation of magnetic periodic boundary conditions for periodic systems subject to finite magnetic fields. Such a formulation gives rise to the same type of Gaussian/plane-wave hybrid integrals as molecular finite-field calculations using London atomic orbitals to ensure gauge-origin independence. Recent work on this code includes an implementation of full configuration-interaction (FCI) and complete-active-space self-consistent-field (CASSCF) modules, a very general framework for computing differentiated integrals including the implementation of Hartree–Fock geometrical gradients and a geometry optimization script, and a pilot code for the computation of excitation energies in the random-phase approximation (RPA). A numerical grid-based integrator for DFT and current-DFT (CDFT) functionals and an MP2 code are planned for 2012.

Further developments concern three-center integrals and optimization tools for the calculation of adiabatic-connection (AC) curves and the study of CDFT functionals within the mathematically rigorous convex analysis approach to DFT due to Lieb. Initial pilot versions of these tools were put in place at the end of 2011.

WP 2: Fragment approach for large systems

Scientist in charge: Inge Røeggen

The PATMOS model – “Perturbed ATOMS in MOlecules and Solids” – is a new computational model for the study of the electronic structure of molecules and solids. The key

idea in this approach is to consider a complex as a system of interacting perturbed atoms. In defining the model, each valence electron is described by a separate spatial orbital. However, the determination of these spatial orbitals is a nontrivial problem. Several approaches have been explored. The presently adopted solution is unrestricted Hartree-Fock (UHF) with a particular localization of the UHF orbitals. The UHF orbitals are localized by projecting a set of target orbitals onto the UHF orbitals, and followed by a symmetric orthonormalization of the projected orbitals in the UHF orbital space. The target orbitals are derived from a modified high-spin restricted Hartree-Fock functional – the PATMOS functional. The modification implies that only Coulomb terms are included for singly occupied orbitals belonging to different atoms. A localization of the singly occupied target orbitals to the vicinity of a nucleus is obtained by restricting the basis set expansion of these orbitals to a set of atomic functions all centered on the same nucleus.

Hence, the localized UHF orbitals define the atoms in the complex.

Energy corrections with respect to the UHF energy are calculated within the energy incremental framework. The total energy can then be written as a sum of intra- and interatomic terms. A general, full configuration interaction code using the UHF orbitals as reference orbitals has been implemented by CTCC researcher Bin Gao.

In a forthcoming publication, the character of the perturbed atoms is illustrated by calculations on the hydrogen molecule, methane and benzene. Furthermore, two classical interpretative problems in chemistry are discussed: the change of equilibrium bond angle in the series H_2O , H_2S , H_2Se and H_2Te ; and the rotational barrier in ethane.

The idea of perturbed atoms is at the heart of a new approach for the calculation of the UHF wave function for large systems. Work is under way to implement this new approach.



WP 3: Multiwavelets

Scientist in charge: Tor Flå

The work in WP3 was in 2011 concentrated on further development of a program for solving the Poisson, Helmholtz and Kohn-Sham equations, with the goal of linear scaling calculations of molecular electronic orbitals, realized in the quantum-chemistry program MRChem. Our approach is based on an integral reformulation of the Kohn-Sham (KS) equations. This reformulation makes it possible 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. This reformulation also makes it possible to do an expansion in Alpert's multiwavelets using the non-standard representation of the operators in such a way that elementary operations like convolution of separated integral kernels and multiplication of linear and nonlinear potentials can be done with linear complexity.

The main activities of 2011 can be summarized as follows:

CTCC PhD student Antoine Durdek, in collaboration with Jensen, Juselius, Frediani, and Flå has formulated and implemented a generalized multiwavelets basis and multiresolution, both in one and three dimensions, and tested it successfully with respect to reduced complexity on Gaussian- and Slater-type orbitals. An exponential approximation theorem has been proposed for this representation based on the numerical results. A report on this work is currently being written.

Jensen, Durdek, Juselius, and Frediani have developed and implemented a scheme to order nodes in an adaptive tree structure by means of space-filling paths called Hilbert curves. Such an ordering has much better localization properties than the original Lebesgue ordering. This work proved essential to achieve good performance in the subsequent parallelization of the code: the locality of the Hilbert curve guarantees minimal communication overhead with a pattern which is highly focussed on nearest-neighbour communication.

The application of integral operators in the NS form, which is the kernel of the code, has been efficiently paral-

lelized (Juselius and Jensen). A report has been written about parallelization and complexity tests for adaptive tree representations of orbitals and KS operators, including Hilbert curves in the multiwavelet program.

Jensen, Durdek, Frediani and Flå have worked on optimizers for the KS orbitals. Several strategies have been attempted: (1) the straightforward iteration of the integral equations, (2) a DIIS-like procedure and (3) a direct SCF iteration method for N orbitals. The third and most efficient method is based on a stepwise direct orthonormalization of the N occupied orbitals and the Fock matrix space spanned by the occupied orbitals. A Krylov scheme based on both the history of orbital variations and diagonalized Fock matrix variations is employed in the iterations. Orbital variations are corrected for the history of orthonormalization matrices. The method has been tested for some molecules such as water and benzene, and found to yield robust convergence for a wide range of initial values of N orbitals and eigenvalues. We have a paper in progress with the description of the method. We also intend to initiate a collaboration with Prof. R. Schneider on the theoretical basis and convergence of this method and other improved optimizers to test their efficiency and applicability. In particular one such improved version is based on the exponential reformulation of the iteration procedure, which guarantees orthonormality, by construction.

WP4: Molecular properties and spectroscopy

Scientist in charge: Luca Frediani

On the methodological side, there has in 2011 been five major lines of development. The largest of these activities in terms of resources used is the so-called OpenRSP project, in which we aim at building a highly flexible, open-ended program for calculating molecular properties of arbitrary order for density-functional theory for both one-, two- and four-component Kohn-Sham wave functions. This project is reaching the end of the most essential development stages with the completion of a fully



analytic implementation of quartic force fields, essential for determining fundamental vibrational frequencies, and also for the determination of nonlinear vibrational spectroscopies of various kinds. The work has involved the development of programs for the open-ended calculation of one- and two-electron integral derivatives and derivatives of exchange-correlation kernels. All these programs have been designed as stand-alone modules/libraries, allowing for easy integration into any existing quantum chemistry program.

Another line of development has been the development of methods for polarizable embedding as a means of partitioning large systems into an essential part that needs to be treated quantum mechanically, and a part which can be treated more approximately. In 2011 we have for instance performed a study of the one- and two-photon absorption properties of the Green Fluorescent Protein using this polarizable embedding approach. The chromophore, consisting of three amino acids, were in this study treated quantum mechanically, and the rest of the structure by a polarizable force field. Our results do not support the proposal that the differences between the one- and two-photon spectra are due to states that are one-photon inactive. This work has been done in collaboration with the research group of Dr. Jacob Kongsted at the University of Southern Denmark.

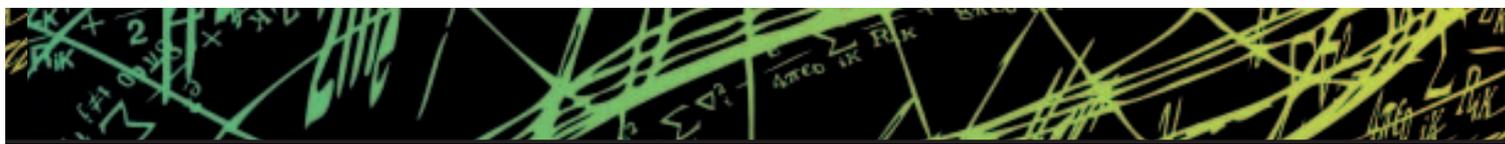
Following the same modularity ideas which inspire the OpenRSP project, we have also developed an external module for continuum solvation calculations. The main goal is to provide this functionality to any quantum chemistry code in an efficient and reliable way with a minimal coding effort. The module implements the traditional Polarizable Continuum Model (PCM) in the Integral Equation Formalism (IEF) and also the newer wavelet PCM code that takes advantage of the wavelet formalism (this activity is closely related to WP3). The modularity is also within the module itself: besides the choice of solver (traditional/wavelet) one can also choose among different cavity generators and choose freely the Green's function to describe different environments (traditional solvents, ionic solutions, liquid crystals, dielectric and metal

surfaces in planar and spherical symmetry). This work is done in collaboration with CTCC adjunct Prof. Benedetta Mennucci (University of Pisa, Italy) and Prof. Helmut Harbrecht (Univ. of Basel, Switzerland). The module has been interfaced with the Dalton program and work is in progress on interfacing it with the Dirac program.

We have also initiated a collaboration with the research group of Prof. Dovesi at the University of Torino on the implementation of nonlinear optical properties of molecular solids, where we have combined our own expertise on the evaluation of higher-order response functions and exchange-correlation kernels with the expertise of our Italian collaborators on the description of molecular solids. The code developed have among other applications been used to study the nonlinear optical properties of nanotubes.

In 2011 we have reached a consistent derivation of the material constants from microscopic theory. Despite the importance of these material constants in for instance the design of so-called metamaterials, no rigid first-principles theory for the fundamental properties of matter in the part of the electromagnetic spectrum corresponding to visible light has been available. Such a theory is therefore important in the design of metamaterials that could display novel properties that would allow for the construction of perfect lenses or invisibility cloaks. Starting from the absorption coefficients defined in terms of the induced current density, we have been able to rigorously derive such an expression for the permittivity, and in this manner also provide an indirect proof for the validity of one of two proposed expressions for the inverse permeability.

Finally, we have developed, together with collaborators at the CNR in Pisa, novel methods for the study of vibronic properties of different absorption properties such as magnetic circular dichroism. The formalism has also been used to study the induced circular dichroism spectrum of a molecule which is chiral only through isotopic substitution, showing that the vibronic problem in this case is complicated, but that accurate results can be obtained. We have also extended this formalism to the



study of resonance Raman spectra.

A very encouraging development in the activity of WP4 is the increased interaction with experimental chemists, and not only with calculations as a contributor to experimental studies, but rather to studies in which an experimental analysis would not be possible in a secure manner without simultaneous theoretical calculations. We would in particular like to highlight the collaboration with MabCent, a Norwegian Centre for Research-based innovation, and the pharmaceutical company LyTiX, on the use of calculation of chiroptical spectroscopy, Nuclear Magnetic Resonance and vibrational spectroscopic parameters for determining the absolute stereochemistry of natural products identified as possible new drug candidates from marine bioprospection studies. These natural products are often chiral and their absolute configuration is often important for their activity as a drug. The absolute configuration of a chiral compound can only be determined, when crystal structures cannot be obtained, by combining theoretical calculations and experimental measurements of chiroptical properties such as vibrational circular dichroism and Raman Optical Activity. The experimentally recorded spectra have been obtained by collaborators in Poland and in the Czech republic. CTCC researcher Kathrin Hopman has been driving force in this activity at the CTCC.

Another area of application that has been of interest in 2011 is the understanding of the electronic excited states of vitamin B12, a topic that has some overlap with the activity in WP6. Vitamin B12 is essential to the functioning of the brain and the nervous system in humans, and an understanding of the electronic excited states of these molecules is therefore important. In collaboration CTCC visitors Prof. Pawel Kozlowski and PhD student Karina Kornobis, we have been studying the excited states of these molecules by analysing and comparing calculations of magnetic circular dichroism spectra with experimental observations. The size of the systems, and the complexity of the problem, have also spurred benchmark studies of the accuracy of different exchange-correlation functions for studies of excited states in these systems.

WP5: Dynamics and time-development

Scientist in charge: Einar Uggerud

During 2011, the emphasis has been on developing and implementing efficient methods for Born-Oppenheimer dynamics (BOD), and to apply these to chemical problems coupled to our experimental activities, in particular in gas phase ion chemistry. Significant progress has been made in improving the computer codes for more accurate and faster integration of the equations of motion, and to interface the dynamics code with a development version of Dalton giving access to linearly scaling methods for electronic structure calculations. This work, closely connected to activities central to WP1 and the group of Prof. Helgaker, is now seen to be fruitful in a number of applications, including the study of large water clusters and the mechanochemistry of biological and industrial polymers.

Two co-workers, one postdoctoral fellow (H.S. Smalø, from May 2011) and one Ph.D. student (V. Rybkin, from August 2008), are involved in the work package. Rybkin has worked on the methodological aspects of the project, and has been successful in both implementing and applying a new predictor-corrector method, as well as a Fock matrix update scheme — leading to reduced computational times. It is noteworthy that Rybkin recently was able to take advantage of these major methodological developments and the local availability of efficient linear scaling electronic structure methods to demonstrate that trajectories now can be integrated into the picosecond time range for clusters containing 21 water molecules. In this manner, it has become possible for the first time to study proton migration and evaporation dynamics of nanosized water droplets for extended periods of time. We expect this development of *ab initio* direct dynamics to have impact in many fields of chemistry.

Dr. Smalø has been active in the theoretical modelling of force-induced chemical processes. He is continuing the work of his predecessor, Dr. Iozzi, and has been able to address a number of important issues in mechanochemistry. During his first year of employment of the CTCC, he intends to publish two papers, one on the mechanism



of sonochemically-induced ring opening of triazole containing linear polymers and one more generic paper on the effects of applying a variable external force to the ends of polyethylene chains and peptide molecules. The latter paper will contain in-depth analyses on chain-length dependence on local responses to the applied force, evaluation of simple analytical potential energy functions, and a critical assessment of the popular Bell formula for estimating bond activation energies.

In addition, students and collaborators have been active in a number of experimental investigations, for which quantum chemical models are essential for interpretation of the experimental results. The experimental activities include reaction dynamics of carbon-carbon bond-breaking and bond-forming reactions of relevance to the photosynthetic dark reaction and to interstellar chemistry, and the physical and chemical properties of hydrogen-bonded clusters of importance to atmospheric science.

WP6: Bioinorganic chemistry

Scientist in charge: Abhik Ghosh

Two broad themes were pursued in 2011, the chemistry of porphyrin analogues, particularly corroles, and transition-metal-small-molecule interactions. A highlight of our contributions to corrole chemistry, which is still a young field compared with porphyrin chemistry, was the solution of a series of metallocorrole crystal structures. In conjunction with DFT and multiconfigurational ab initio studies, the crystallographic studies in many ways mapped out the limits of corrole structural chemistry. A key conclusion is that, compared with porphyrins, metallocorroles are much stiffer with respect to nonplanar deformations. Copper corroles are an important exception to this generalization. A specific metal-ligand orbital interaction (which may be viewed as ligand noninnocence) drives a saddling deformation in copper corroles, which may be strongly accentuated by sterically hindered peripheral substituents. By contrast, other metallocorroles, even if sterically hindered, are as a rule planar. These

structural studies were published by and large in a series of papers in *Inorganic Chemistry* and the *European Journal of Inorganic Chemistry*; a review of our overall contributions is currently in press in *Accounts of Chemical Research*.

The first synthesis of gold corroles by Ghosh group postdocs Kolle E. Thomas and Abraham Alemayehu, including crystallographic studies in collaboration with the Advanced Light Source (Dr. Christine Beavers) in Berkeley, CA, was another highlight of the Ghosh group's contributions to corrole chemistry. Electrochemical, optical and DFT studies strongly suggested that gold corroles, unlike their copper analogues are innocent. The subject of ligand noninnocence, a ubiquitous theme in corrole chemistry, was further explored in collaboration with Prof. Kristine Pierloot of the Catholic University of Leuven, Belgium. Gold corroles are phosphorescent. A variety of photophysical measurements are underway, providing valuable raw material for detailed theoretical studies in collaboration with Professor Kenneth Ruud. Dr. Adam Chamberlin, a postdoc working jointly with Profs. Ghosh and Ruud, completed an intriguing project on resonant two-photon absorption by porphyrins and corroles. Mention should also be made of Dr. Hugo Vasquez Lima, a CTCC visitor from Mexico who made theoretical contributions on the effects of extended conjugation on metallocorrole optical spectra. Corroles were also studied for their potential as dye-sensitized solar cells, in collaborations with Professor Carl Wamser (Portland State University, OR) and Michael Walter (University of North Carolina, Charlotte), both of whom visited the CTCC recently. Last but not least are boron corroles, fascinating from a coordination chemistry perspective in that these complexes feature corroles as binucleating ligands, and a key crystal structure structure was solved in a collaborative project involving CTCC visitor Dr. Anna Młodzianowska and Prof. Penny Brothers (The University of Auckland, New Zealand, Figure 2).

Transition-metal-NO_x interactions was another major theme pursued under this work package. Long an area of collaboration with Prof. Jeanet Conradie of the



University of the Free State, South Africa, this area saw expert contributions from CTCC postdocs Dr. Kathrin Hopmann and Dr. Bruno Cardey. A major DFT modeling study of hemoglobin's role as a nitrite anhydrase, including the role of nitrite in hypoxic vasodilation, was completed and published in *Chemistry – A European Journal*. A unique stable, reduced FeNO complex ($\{FeNO\}^8$ in the Enemark-Feltham notation) was studied in collaboration with Prof. Todd Harrop's group at the University of Georgia, Athens. Pursuing a longstanding interest in "the weird and the wonderful", we continued to study a variety of rather "exotic" heme and nonheme complexes with DFT methods, partly in collaboration with Prof. Mikio Nakamura (Toho University, Japan) and Prof. Stephen J. Lippard (MIT, USA). Of somewhat limited interest individually, these studies nonetheless have a major cumulative effect and expand our appreciation of the electronic structures of important bioinorganic "functional groups" such as hemes and FeNO units.

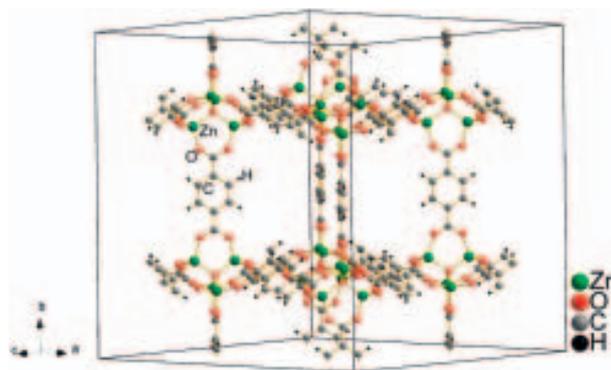
WP7: Catalysis and organometallic chemistry

Scientist in charge: Mats Tilset

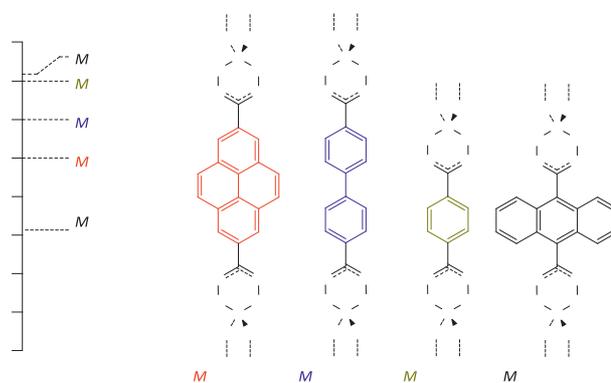
Catalysis is of paramount importance for the development of efficient, selective, and environmentally benign processes in the production of bulk and fine chemicals and materials. Any rational approach to catalyst design requires an in-depth understanding of the underlying reaction mechanisms and catalyst structure. Currently, the most fruitful way to gain this insight is to combine experimental and computational approaches. In this work package, coworkers have in 2011 focused on systems of relevance to heterogeneous as well as homogeneous catalysis. Li-Ming Yang served his final year as a postdoc at CTCC. In addition, coworkers who are primarily experimentalists working on University- or Research Council-funded projects have dedicated parts of their PhD periods to supplement their experimental activities with computational approaches to better understand experiments. In 2011, this has included Marianne Lenes

Rosenberg (who has successfully defended her thesis, with a significant computational chapter), Eirin Langseth (current PhD student), and Margaret Scheuermann (visiting experimentalist PhD student from University of Washington). Our ongoing efforts in computational organometallic chemistry and catalysis primarily utilize DFT methodologies.

Li-Ming Yang has focused his computational efforts on MOFs using periodic DFT methods. MOFs are crystalline, nanoporous materials that are constructed from inorganic cornerstones that are connected by polyfunctional organic ligands (linkers) to form three-dimensional networks. The MOF series M -IRMOF- n (where n is a number denoting in a non-systematic way the identity of



Schematic depiction of Zn-IRMOF-1 (also called MOF-5).



Approximate bandgaps of M -IRMOF- n materials. The M -IRMOF-993 compounds are predicted to be intermediate band (IB) materials.



the linker and the cornerstone metal $M = \text{Zn, Cd, Be, Mg, Ca, Sr, Ba}$) have been systematically studied. These so-called isorecticular MOFs have the same topologies, insofar as the tetranuclear M_4O cornerstones are bridged by aromatic dicarboxylic acids resulting in a cubic superstructure (see top figure). So far, only the $M = \text{Zn}$ structures have been experimentally prepared, but our calculations suggest that the other members should have similar stabilities. In a series of papers (4 published, 1 submitted so far), the structures and formation enthalpies as well as important bonding, electronic, and optical properties of these MOFs have been investigated. Experimentalists have recently reported that some MOFs act as semiconductors and exhibit photocatalytic behavior. In this regard, electronic and optical properties are of interest, and in particular data concerning the bandgaps of the materials. The following summarizes some highlights of our findings for the M -IRMOF- n series (bottom figure): For a given linker (symbolized by n), the bandgap is rather independent of the identity of the cornerstone metal M . On the other hand, the bandgap is highly dependent on the identity of the linker, a long linker resulting in a decrease in the bandgap – although the linker size is not the only parameter that matters. Interestingly, the M -IRMOF-993 materials are predicted by us to be possible intermediate band (IB) materials even without prior doping, and might be relevant for the design of multiple-photon-harvesting materials in solar cells. The prediction remains to be experimentally verified. The MOF work has been done in collaboration with members of the Centre for Materials Science and Nanotechnology at UiO.

A second major project last year involved a very fruitful interaction between experimental and computational approaches in homogeneous catalysis. We have developed a highly unusual cis-selective cyclopropanation reaction catalyzed by a Rh(I) system with a chelating N-heterocyclic iminocarbene ligand. Computational studies with DFT methods have helped establish a possible reaction mechanism that can account for the observed high cis selectivity. The computational results helped us with the design of an improved catalyst. The computational

results have been published in *Organometallics*. This collaborative effort between an experimental PhD student (Marianne Lenés Rosenberg) with separate funding and CTCC postdoc Andreas Krapp gave the PhD student good training in computational chemistry and demonstrates a successful approach towards one of the goals of CTCC, namely to propagate the use of computational modeling to a broader scientific community.

Another project, which is still ongoing and which also benefits from the integration of experiment and computational work deals with reactions and dynamic behavior of organogold complexes. Eirin Langseth, a University-funded PhD student, examines experimentally as well as computationally, reactions between electrophiles, and in particular the proton, and Au(III) complexes. Preliminary results suggest that the Au(III) complexes behave distinctly different from closely related isoelectronic Pt(II) species. Finally, visiting PhD student Margaret Scheuermann investigates an interesting O_2 -mediated, intramolecular C-H activation reaction in an organometallic Pd complex.

wp 8: Gas-phase reactions and photochemistry

Scientist in charge: Claus Nielsen

We have continued systematic studies of the potential energy surfaces of reactions relevant to the atmospheric photo-oxidation of amines. The focus has been on gas-phase degradation reactions of amines used in Carbon Capture and Storage, and on the chemistry of the primary photo-oxidation products.

1. Studies of OH radical reactions with 2-aminoethanol, monoethanolamin (MEA), N-Methyl ethanolamine (NMEA) and 2-amino-2-methyl-1-propanol (AMP) have been completed.
2. Studies of formation and photolysis reactions of simple N-nitrosamines and N-nitramines such as CH_3NHNO , CH_3NHNO_2 , $(\text{CH}_3)_2\text{NNO}$, $(\text{CH}_3)_2\text{NNO}_2$, $\text{CH}_3\text{CH}_2\text{NHNO}$, $\text{CH}_3\text{CH}_2\text{NHNO}_2$, $(\text{CH}_3\text{CH}_2)_2\text{NNO}$ and $(\text{CH}_3\text{CH}_2)_2\text{NNO}_2$ are complete. Results from



kinetic studies of the OH radical and Cl atom reactions with the abovementioned nitramines have been reported. Results from kinetic studies of NO_3 radical reactions with the abovementioned nitrosamines have been reported.

3. Amides and imines are major products in atmospheric photo-oxidation of amines. Calculations of the OH radical reaction with NH_2CHO are complete and experimental studies of kinetic isotope effects are ongoing. The OH radical reactions with two imines, $\text{CH}_2=\text{NH}$ and $\text{CH}_2=\text{NCH}_3$, are complete.
4. Amines are bases and will to some degree neutralise acids in the gas phase and in an aerosol. The thermochemistry of aminium salt formation has been studied by quantum chemistry calculations and experimentally by a volatility tandem differential mobility analyser in combination with time-of-flight aerosol mass spectrometry. The results have been communicated.

The systematic theoretical studies combined with experimental work on atmospheric amine chemistry have produced a comprehensive understanding of all environmentally relevant processes involving amines.

