Centre for Advanced Study
at the Norwegian Academy of Science and Letters

Hylleraas

Atoms, Molecules, and Materials in Extreme Environments

Programme

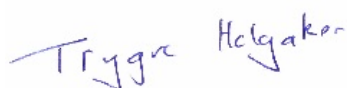4-6 June 2018
At the Norwegian Academy of Science and Letters

Oslo, 1st June 2018

Dear participants,

During the Academic Year 2017–2018, the project "Molecules in Extreme Environments" has taken place at the Centre for Advanced Study (CAS) at the Norwegian Academy of Science and Letters (https://cas.oslo.no) with twelve participants from Europe and New Zealand. At the CAS, we have studied theoretically how atoms, molecules and materials behave under extreme conditions, including high pressure and ultrastrong magnetic fields. An integral part of the project is the organization of the meeting "Atoms, Molecules and Materials in Extreme Environments", where top experts in this broad field can present and discuss their work. During three days, twenty-four talks and thirteen posters will be presented, covering topics such as molecules on white dwarf stars and neutron stars, synthesis of new compounds under high pressure, melting of neon under high pressure, modelling of hydrogen-rich planetary materials. The chemistry and physics of extreme environments is not only a fascinating topic in itself—it is also a stress test for our computational models, which have been developed and applied to the familiar chemistry and physics under Earth-like conditions. It is our hope that the meeting will provide a fruitful meeting ground for workers in the field and lead to new work in this exciting field.

We would like to thank Camilla Kottum Elmar at the CAS and Jan Ingar Johnsen and Simen Reine at the Hylleraas Centre for Quantum Molecular Sciences at the University of Oslo for much help with the organization of meeting. Finally, we would like to take the opportunity to thank CAS and its staff for providing us with a wonderful stay at CAS.

Trygve Helgaker, Trond Saue, and Peter Schwerdtfeger

Organizing Committee

Programme

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Monday June 4

08:00 - 08:30 Registration at the Academy

08:30 - 08:50 Opening:
Trygve Helgaker [Hylleraas Centre for Quantum Molecular Sciences]
Carl Fredrik Straumsheim [Communications adviser CAS]

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Session 1A: *Chairman:* Trygve Helgaker, Hylleraas Centre for Quantum Molecular Sciences

08:50 - 09:30 Anand Thirumalai, DigiPen Institute of Technology:
Glimpses of an alien chemistry: atoms in neutron star atmospheres

09:30 - 10:10 Stella Stopkowicz, Johannes Gutenberg – Universität Mainz:
Electronic structure in strong magnetic fields

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10:10 - 10:40 Coffee break

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Session 1B: *Chairman:* Alex Borgoo, Hylleraas Centre for Quantum Molecular Sciences

10:40 - 11:20 Bernie Schlegel, Wayne State University :
Computational simulation of molecules interacting with intense laser fields

11:20 - 12:00 Robin Santra, DESY and Universität Hamburg :
Molecules at high x-ray intensity: Challenges for theory

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12:00 - 14:00 Lunch

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Session 1C: *Chairman:* Wim Klopper, Karlsruhe Institute of Technology (KIT)

14:00 - 14:40 Wojciech Grochala, Center for New Technologies (CENT), University of Warsaw:
Alice in the High Pressure Wonderland --- or Learning How to Be a Humble Theoretician

14:40 - 15:20 Wojciech Bartkowiak, Wrocław University of Science and Technology:
Molecular electric properties upon spatial confinement

15:20 - 16:00 Roberto Cammi,University of Parma:
The eXtreme Pressure Polarizable Continuum Model

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16:00 - 16:30 Coffee break

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Session 1D: *Chairman:* Maria Dimitrova, University of Helsinki

16:30 - 17:10 Peter Schmelcher, Universität Hamburg:
   Ultralong-Range Molecules in External Fields

17:10 - 17:50 Raymond Ashoori, Center for Integrated Quantum Materials, MIT :
   A Method for Studying Tunnelling into Insulators:Discovery of a Sharp Tunnelling Resonance from Phonons of an Electronic Wigner Crystal

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17:50 - 19:00 Poster session

Tuesday June 5

Session 2A: *Chairman:* Trond Saue, Université Toulouse III – Paul Sabatier

08:30 - 09:10 Eugene Gregoryanz, School of Phyiscs and Astronomy, University of Edinburgh:
Solid hydrogen and its Isotopes at Extreme Conditions

09:10 - 09:50 Krzysztof Pachucki, University of Warsaw:
Precision physics with the hydrogen molecule

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09:50 - 10:20 Coffee break

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Session 2B: *Chairman:* Jürgen Gauss, Johannes Gutenberg – Universität Mainz

10:20 - 11:00 Agnes Dewaele, CEA, DAM, DIF, Arpajon:
Synthesis of new chemical compounds under pressure

11:00 - 11:40 Elke Pahl, Massey University Auckland:
Melting in Extreme Environments

11:40 - 12:20 Lukáš Félix Pašteka, Comenius University:
From atomic confinement to high pressure

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12:20 - 14:00 Lunch

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Session 2C: *Chairman:* Dage Sundholm, University of Helsinki

14:00 - 14:40 David Ceperly, University of Illinois at Urbana–Champaign:
Simulations of Dense Hydrogen

14:40 - 15:20 Eva Zurek, State University of New York at Buffalo:
Theoretical Predictions of Unique Hydride Phases Under Pressure

15:20 - 16:00 Andreas Hermann, School of Physics and Astronomy, University of Edinburgh:
Quantum modelling of hydrogen-rich planetary materials

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16:00 - 16:30 Coffee break

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Session 2D: *Chairman:* Hans-Joachim Werner, Universität Stuttgart

16:30 - 17:10 Carlo Rizzo, Laboratoire National des Champs Magnétiques Intenses (Toulouse):
Rubidium atoms in high magnetic field

17:10 - 17:50 Andy Teale, University of Nottingham:
Climbing Jacob's ladder under extreme conditions — density-functional approximations with non-local contributions for atoms and molecules in strong magnetic fields

17:50 - 18:30 Toru Shiozaki, Northwestern University (Chicago):
Open-shell molecules in strong magnetic fields

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20:00 - 23:00 Banquet at the Academy

Wednesday June 6

Session 3A: *Chairman:* Jan Linderberg, Aarhus University

08:30 - 09:10 Heiko Appel, Max Planck Institute for the Structure and Dynamics of Matter:
Real-time evolution of coupled Ehrenfest-Maxwell-Kohn-Sham equations for molecules exposed to strong magnetic fields and intense laser fields

09:10 - 09:50 Erik Tellgren, University of Oslo:
Quantum chemistry of molecules in strong magnetic fields

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09:50 - 10:20 Coffee break

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Session 3B: *Chairman:* Peter Schwerdtfeger, Massey University Auckland

10:20 - 11:00 Thomas Jagau, Ludwig Maximilian University of Munich:
Differences and similarities between autoionization and strong-field ionization

11:00 - 12:00 Lorenz Cederbaum, Universität Heidelberg:
On systems with and without excess energy in environment: ICD and other interatomic mechanisms

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12:00 - 12:10 Closing
Peter Schwerdtfeger, Massey University Auckland

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12:10 - 14:00 Lunch

Lecture Abstracts

Abstracts are listed alphabetically by the last names of the presenters

Real-time evolution of coupled Ehrenfest-Maxwell-Kohn-Sham equations for molecules exposed to strong magnetic fields and intense laser fields

Heiko Appel

Rene Jestädt, Johannes Flick, Christian Schäfer, Norah Hoffmann, Aaron Kelly, Michael Ruggenthaler, and Angel Rubio

Max Planck Institut für Struktur und Dynamik der Materie, Hamburg

This talk provides an overview of the recent work in our group on density functional theory (DFT) for quantum electrodynamics (QED)[1−8]. The first part of the presentation introduces the foundations of time-dependent DFT for QED. Compared to traditional density functional theory, our approach allows to explicitly include the quantized photon field in a density functional description. While this becomes important for small photon numbers and large field fluctuations, the limit of large photon numbers and small electromagnetic field fluctuations is well described by a Hartree level of approximation. For a real-time evolution, this corresponds to coupled Ehrenfest-Maxwell-Kohn-Sham equations. We illustrate this limit for molecules exposed to strong magnetic fields, as well as molecules exposed to strong femtosecond laser fields.

To describe larger electromagnetic field fluctuations, we introduce as further example how trajectory methods that have originally been developed for coupled electron-nuclear dynamics can be extended to describe light-matter coupling beyond the Maxwell-Schrödinger limit. In particular, we illustrate how to assess correlation functions of the quantized photon field as well as spontaneous emission processes with such trajectory approaches and discuss the significance for photo-stimulated processes.

In the remaining part of the presentation, we are focussing on atomic and molecular systems embedded in optical cavities or nanoplasmonic environments, where the matter-photon interaction is considered from the weak- to the strong-coupling limit and for individual photon modes as well as for the multimode case. We introduce a recently proposed cavity Born-Oppenheimer approximation and identify fundamental changes in Born-Oppenheimer surfaces, spectroscopic quantities, and conical intersections.

1. M. Ruggenthaler et. al. *Phys. Rev. A* **90**, 012508 (2014).
2. C. Pellegrini et. al. *Phys. Rev. Lett.* **115**, 093001 (2015).
3. J. Flick et. al. *PNAS* **112**, 15285 (2015).
4. J. Flick et. al. *J. Chem. Theory Comput.* **13**, 1616 (2017).
5. J. Flick et. al. *PNAS* **114**, 3026 (2017).
6. J. Flick et. al. *ACS Photonics* **5**, 992 (2018).
7. J. Flick et. al. *arXiv:1803.02519*
8. M. Ruggenthaler et. al. *Nature Reviews Chemistry* **2**, 0118 (2018).

A Method for Studying Tunnelling into Insulators:
Discovery of a Sharp Tunnelling Resonance from Phonons of an Electronic Wigner Crystal

Raymond Ashoori

Centre for Integrated Quantum Materials,
Massachusetts Institute of Technology, Cambridge, USA

In a system of free electrons, both the Coulomb repulsion and quantum kinetic energies diminish with decreased electron density. Since the kinetic energy diminishes faster than the Coulomb energy, it becomes energetically favorable for electrons to localize into a Wigner crystal, a phase transition predicted by Wigner more than 80 years ago. In the case of 2D systems, applying a quantizing magnetic field favors crystal formation by further freezing out the kinetic energy into Landau levels. For 2D electrons in a magnetic field, theory predicts that a Wigner crystal of quasiparticles in a Landau level exists near integer quantum Hall states as an insulating phase with an expected transition temperature in the range of a few hundred millikelvin or below. As the state in insulating, it is very difficult to probe it. Using a refined pulsed tunneling method[1], capable of probing insulating phases, we are able to measure tunneling current directly into the electronic crystal. I will present high-resolution tunneling measurements that reveal an previously unexpected and very sharp structure arising from the vibrational spectrum of the spatially ordered electronic structure[2]. The energy of this resonance depends on electron density and appears to diverge as the quasiparticle density is increased up to the transition at which the crystal melts and the resonance disappears. This observation conclusively demonstrates the existence of a WC with long correlation length, along with the long sought phase transition predicted by Wigner. The results also open door to using tunneling to probe and detect a wide variety of ordered electronic phases. I will also briefly show results from our extension of the pulsed tunneling method to perform full momentum and energy resolved tunneling spectroscopy (MERTS) to reveal the momentum resolved electronic spectral function of a 2DES embedded in a semiconductor[3]. In contrast to angle resolved photoemission spectroscopy, the technique remains operational in the presence of large externally applied magnetic fields and functions even for electronic systems with zero electrical conductivity or with zero electron density. MERTS provides a direct high-resolution and high-fidelity probe of the dispersion and dynamics of the interacting 2D electron system. Using this technique, we uncover signatures of many-body effects involving electron-phonon interactions, plasmons, polarons with unprecedented resolution.

[1] Dial, O. E., Ashoori, R. C., Pfeiffer, L. N., and West, K. W. "High Resolution Spectroscopy of Two-Dimensional Electron Systems" Nature 448, no. 7150 (2007): 176–179.
[2] Jang, J., Hunt, B. M., Pfeiffer, L. N., West, K. W., and Ashoori, R. C. "Sharp Tunnelling Resonance from the Vibrations of an Electronic Wigner Crystal" Nature Physics 13, (2017): 340–345.
[3] Jang, J., Yoo, H. M., Pfeiffer, L. N., West, K. W., Baldwin, K. W., and Ashoori, R. C. "Full Momentum and EnergyResolved Spectral Function of a 2D Electronic System" Science 358, no. 6365 (2017): 901–906.

Molecular electric properties upon spatial confinement

Wojciech Bartkowiak

Department of Physical and Quantum Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, PL-50370, Poland

The lecture is devoted to investigations of linear and nonlinear electric properties of spatially confined molecules. In general, the problem of a confined one- and two-electron atoms (H and He) and the smallest molecules (H_2^+ and H_2) in a sphere has a long history in quantum physics. Michels et al. (*Physica 4*, *1937*, 981–994). proposed a model of the centrally confined (compressed) hydrogen atom in order to study the variation of static dipole polarizability as a function of the effective pressure acting on the atom (confining potential: infinite potential barrier). Sommerfeld and Welker (*Ann. Phys. 32*, *1938*, 56–65) soon realized the significance of this model in interpreting the astrophysical data on the hydrogen atom spectra. Science then various theoretical approaches have been proposed to description of phenomena occurring in atomic and molecular matter in extreme conditions. It is important to emphasize that the complete quantum-mechanical description of the effects observed when a chemical object is placed inside a molecular cage (e.g., nanotube, fullerene, molecular container) or subjected to the high pressure is a difficult task. One of the simplest and effective approximation in this context based on the analytical external potentials (e.g. spherical and cylindrical harmonic oscillator potentials, penetrable, and impenetrable boxes) which, added in the form of one electron operator to the Hamiltonian of an isolated system, allow us to render the effect of orbital compression (directly connected with the spatial confinement). In the lecture this approximation will be subject of a critical examination in the context of description of the influence of spatial confinement on the linear and nonlinear electric properties of molecules. The several less or more general conclusions based on many years of investigations will be presented.

The eXtreme Pressure Polarizable Continuum Model

Roberto Cammi[1]

[1]Department of Chemical Science, Life Science, and Environmental Sustainability, University of Parma, Parma, Italy

Abstract

I review on a quantum chemical model [1-7] aimed to study the effects of very high pressures (p> 1GPa) on molecular properties and chemical reactions.

Originally developed for applications concerning the effect of extreme high pressures on the equilibrium geometries and vibrational frequencies of molecular systems [6-7], the XP-PCM method been recently extended to the study the effect of very high pressure on the electronic excitations [5], and on the potential energy profile of chemical reactions [2,3,4].

The talk will touch basics methodological aspects of the model as well as several of its applications.

References

[1] R. Cammi, in "Frontiers of Quantum Chemistry", M.J. Wojcik, H. Nakatsuji, B. Kirtman, Y. Ozaki, (Ed.s), Springer, 2018

[2] R. Cammi, Ann. Rep. Comp. Chem., 13, 117-135 (2017)

[3] B. Chen, R. Hoffmann, and R. Cammi, Angew. Chem. Int. Ed. 57, 11126 (2017)

[4] R. Cammi, J. Comp. Chem.36, 2246 (2015)

[5] R. Fukuda, M. Ehara, and R. Cammi, J. Chem. Theor. Comp.11, 2063(2015)

[6] M. Pagliai, G. Cardini, and R. Cammi, J. Phys. Chem. A 118, 5098(2014)

[7] R. Cammi, C. Cappelli, B. Mennucci, and J. Tomasi, J. Chem. Phys. 137, 154112 (2012)

On systems with and without excess energy in environment
ICD and other interatomic mechanisms.

Lorenz S. Cederbaum[1]

[1]Theoretical Chemistry Department/Institute of Physical Chemistry/University of Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

How does a microscopic system like an atom or a small molecule get rid of the excess electronic energy it has acquired, for instance, by absorbing a photon? If this microscopic system is isolated, the issue has been much investigated and the answer to this question is more or less well known. But what happens if our system has neighbors as is usually the case in nature or in the laboratory? In a human society, if our stress is large, we would like to pass it over to our neighbors.

Indeed, this is in brief what happens also to the sufficiently excited microscopic system. A new mechanism of energy transfer has been theoretically predicted and verified in several exciting experiments. This mechanism seems to prevail "everywhere" from the extreme quantum system of the He dimer to water and even to quantum dots. The transfer is ultrafast and typically dominates other relaxation pathways.

Can there be interatomic/intermolecular processes in environment when the system itself (again, an atom or small molecule) does not possess excess energy? The answer to this intriguing question is yes. The possible processes are introduced and discussed. Examples and arguments are presented which make clear that the processes in question play a substantial role in nature and laboratory.

Work on the interatomic processes discussed can be found in the Bibliography:
http://www.pci.uni-heidelberg.de/tc/usr/icd/ICD.refbase.html

Simulations of Dense Hydrogen

D M Ceperley   University of Illinois Urbana-Champaign

Hydrogen accounts for much of the visible mass in the universe. The properties of hydrogen and helium are important for understanding the giant planets, Jupiter and Saturn, but experiments under the relevant conditions are challenging. Even though hydrogen is the first element in the periodic table, calculating its properties is not simple since both the electronic and protonic correlations are quantum and correlated. It has long been an open question how hydrogen makes a transition from a molecular insulating state to an atomic metallic state[1]. We have developed new Quantum Monte Carlo simulation methods to treat such systems and using them, have studied molecular dissociation in liquid hydrogen and have observed clear evidence of an extra liquid-liquid phase transition[2]. During the past few years, several experiments[3,4] have reported observations of the transition we predicted, however, the observations do not agree with each other, differing in pressure by a factor of two.

We use a quantum Monte Carlo method (Coupled Electron Ion Monte Carlo) where we start with the true interaction between the electrons and protons and treat both fully quantum mechanically. In contrast to density functional calculations, all effects of electronic correlation are explicitly included. This is particularly important in hydrogen, because of possible self-interaction effects, difficulty in treating the hydrogen bond breaking and the large van der Waals interactions.   We model hydrogen with about 100 electrons and protons in a periodic cell. Special methods are used to extrapolate to the thermodynamic limit. With our method, we simulated hydrogen for temperatures in the range of 200K up to 5000K, and at relevant pressures, 100GPa to 500GPa. For temperatures below 2000K we observe[5] a first order transition between an insulating molecular liquid and a more dense metallic atomic liquid. Our predicted transition pressure are intermediate between the two experimental observations[3,4]. We have recently characterized this transition [6,8] and details of the molecular phase. [7]

1. McMahon, J. M., M. A. Morales, C. Pierleoni, and D. M. Ceperley, Rev. Mod. Phys. 84; 1607-1653 (2012).
2. Morales, M. A., C. Pierleoni, E. Schwegler, and D. M. Ceperley, Proc. Nat. Acad. of Sciences 107, 12799-12803 (2010).
3. Knudson, M. D. et al., Science 348, 1455 (2015).
4. Zaghoo, M. A. Salamat, and I. Silvera (2015), Phys. Rev. B 93, 155128 (2016).
5. C. Pierleoni, M. A. Morales, G. Rillo, M. Holzmann and D. M. Ceperley, Proc. Nat. Acad. Science (US), (2016).
6. C. Pierleoni, M. Holzmann, and D. M. Ceperley, Cont. Plasma Physics **58**, 99-106 (2018)
7. G. Rillo, M. A. Morales, D. M. Ceperley, and C. Pierleoni, J. Chem. Phys., **148**, 102314 (2018).
8. C. Pierleoni, G. Rillo, D. M. Ceperley and M. Holzmann, arXiv:1712.00392.

Synthesis of new chemical compounds under pressure

A. Dewaele

It is acknowledged for a long time that high pressure is a powerful tool to synthetize new materials with outstanding properties, such as diamond made in the laboratory some 65 years ago, followed by numerous other ultra-hard materials [1]. This kind of research has been accelerated in the 2000's by the spreading of the laser-heated diamond anvil cell tool, which allows to reach routinely pressures above 100 GPa (=1 Mar, 1 million of atmospheres) and temperatures above 3000 K, overcoming activation barriers for chemical reactions. In parallel, *ab initio* calculations have improved and they can now predict the ground state energy for many compounds and then find stable phases. The chemical affinities of elements are fundamentally altered in the Mbar range, and new compounds with unexpected stoichiometry and bonding are synthesized. I will illustrate, with the examples of xenon chemistry [2,3] and iron chemistry [4,5], the interest of joined theoretical-experimental research and the surprises on both sides.

[1] RJ Hazen, The diamond makers, CUP, 1999

[2] A. Dewaele, N. Worth, C. J. Pickard, R. J. Needs, S. Pascarelli, O. Mathon, M. Mezouar and T. Irifune, Synthesis and stability of xenon oxides Xe_2O_5 and Xe_3O_2 under pressure, Nat. Chem. 8, 784, 2016

[3] A Dewaele, CM Pépin, G Geneste, G Garbarino, Reaction between nickel or iron and xenon under high pressure, High Pressure Research 37 (2), 137-146, 2017

[4] D. Laniel, A. Dewaele, G. Garbarino, High Pressure and High Temperature Synthesis of the Iron Pernitride FeN_2, Inorg. Chem., 2018 DOI: 10.1021/acs.inorgchem.7b03272

[5] D Laniel, A Dewaele, S Anzellini, N Guignot, Study of the iron nitride FeN into the megabar regime, J. Alloys Comp. 733, 53-58, 2017

Solid Hydrogen and its Isotopes at Extreme Conditions:
Raman studies at high pressures and low temperatures

Eugene Gregoryanz [1,2,3]

[1]*HPStar, Shanghai, China*
[2] *Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, China*
[3] *CSEC, The University of Edinburgh, Edinburgh, United Kingdom*

e.gregoryanz@ed.ac.uk

The discovery of phases IV [1,2] and V [3] has recently reignited interest in the studies of the dense hydrogen. As a result of these discoveries, the phase diagrams of hydrogen and deuterium above 180 GPa and at 300 K have been extensively studied experimentally by pushing the achievable *P-T* conditions and expanding the phase diagram to new limits. Despite the remarkable progress in our understanding of the behavior of both isotopes at very high density, there has been no attention given to the *P-T* conditions at medium compressions (*e.g.* *P-T* space around phases II). The behavior of $H_2(D_2)$ at these conditions is important to understand the evolution of the system during its transformation from the weak intermolecular state with strong intra-molecular forces (phases I, II, and III) to the layered phases (phases IV and V) with weaker intra-molecular bonding and stronger intermolecular interactions. At the same time, the rich and fascinating physics, which governs the behavior of dense hydrogens can still provide some unexpected and interesting results. In this presentation, I will revisit *P-T* phase diagrams of hydrogen and deuterium and present our resent Raman measurements on both isotopes in a wide pressure and temperature range.

[1] Eremets and Troyan, *Nature Materials* (2011).
[2] Howie *et al*. *Phys. Rev. Lett*. (2012).
[3] Dalladay-Simpson *et al*. *Nature* (2016)

Alice in the High Pressure Wonderland – or Learning How to Be a Humble Theoretician

Wojciech Grochala[1]

[1]Center of New Technologies, University of Warsaw, Żwirki i Wigury 93, 02089 Warsaw Poland

While chemistry alone offers much room for engineering of crystal structures, it is still useful to additionally take advantage of external parameters such as temperature and pressure, for achieving of the desired material topology and properties [1]. However, this is easier said than done, as application of very high pressures of the order of 100 GPa, or 1 mln atm, often has a surprising outcome, which does not necessarily fit the chemical intuition developed from analysis of reactivity and structures at 1 atm conditions. Moreover, theoretical tools used these days for large-scale structure prediction at elevated pressure conditions, often lack accuracy needed to correctly predict the outcome of experiments, and use of most common cheap DFT functionals may lead to entirely erroneous predictions [2].

The d^9 systems are notoriously difficult to study due to their strongly correlated nature, possibility of complex magnetism, and tendency for charge ordering for some of them [3]. In the talk I will discuss two distinct formally d^9 systems, *i.e.* AgF_2, AgO, which have been studied for some time by theory and only recently the experimental data become available [4,5,6]. I will describe structural complexity and interesting magnetic and electronic properties which have most recently been predicted for the structures found [7,8], as well as how theory ultimately met experiment.

If time allows the related but - as we will see - a very different case of AuO will be discussed [9].

[1]   Grochala, W.; et al.; *Angew. Chem. Int. Ed. Engl.* **2007**, *46* (20), 3620–3642.
[2]   Zurek, E.; Grochala, W.; *Phys. Chem. Chem. Phys.* **2015**, *17* (5), 2917–2934.
[3]   Grochala, W.; Hoffmann, R. *Angew. Chem. Int. Ed. Engl.* **2001**, *40* (15), 2742–278.
[4]   Grzelak, A.; et al.; *Inorg. Chem.* **2017**, *56* (10), 5804–5812.
[5]   Grzelak, A.; et al.; *Dalton. Trans.* **2017**, *46* (43), 14742–14745.
[6]   Grzelak, A.; et al.; *Inorg. Chem.* **2017**, *56* (23), 14651–14661.
[7]   Kurzydłowski, D.; Grochala, W.; *Angew. Chem. Int. Ed. Engl.* **2017**, *56* (34), 10114–10117.
[8]   Kurzydłowski, D.; et al.; *Chem. Commun.* **2018**, submitted.
[9]   Hermann, A.; et al.; *Inorg. Chem.* **2016**, *55* (3), 1278–1286.

Quantum modelling of hydrogen-rich planetary materials

Andreas Hermann
Centre for Science at Extreme Conditions and SUPA, School of Physics and Astronomy, The University of Edinburgh, EH9 3FD, United Kingdom.

Accurate models of the interior structure of planetary bodies, in our or other solar systems, are key to understanding their formation and many of their properties. For instance, the stratification (or lack thereof) of molecular mixtures inside icy planets' mantles influences their luminosity and cooling rates; and the presence (or not) of water stored inside rocky planets' mantles influences their convection rates, the magnitude of plate tectonics and presence of surface water.

But direct measurements of planetary interiors are virtually impossible and laboratory experiments are difficult, which is why first-principles calculations can make important contributions.

In my talk I will give an overview of our ongoing research aimed at a better understanding of planetary materials using electronic structure calculations, focussing on hydrogen-containing systems on several different pressure scales. I will show how wave-function based calculations allow us to describe clathrate hydrates stabilized in the kbar range, thereby overcoming density functionals' ambiguities in capturing weak host-guest interactions. I will also show how crystal structure prediction methodology can help develop a more complete picture of the formation of new hydrous minerals inside silicate-based rocky bodies, and discuss the phase evolution of mixtures of planetary ices relevant at pressures beyond 1 Mbar inside Neptune-like bodies. [1,2]

[1] Hermann A., Mookherjee M. (2016) High-pressure phase of brucite stable at Earth's mantle transition zone and lower mantle conditions. *Proc Natl Acad Sci* 113:13971–13976.
[2] Naden Robinson V., Wang Y., Ma Y., Hermann A. (2017) Stabilization of ammonia-rich hydrate inside icy planets. *Proc Natl Acad Sci* 114:9003–9008.

Differences and similarities between autoionization and strong-field ionization

Thomas-C. Jagau

Department of Chemistry, Ludwig Maximilian University of Munich
Butenandtstr. 5-13, D-81377 Munich, Germany

Electron-molecule collisions and non-perturbative light-matter interaction both involve the formation of resonances that belong to the continuum and are beyond the reach of electronic-structure methods for bound states. An elegant time-independent treatment of resonances is possible by means of complex-variable (CV) techniques from non-Hermitian quantum mechanics [1] where resonances are described as quasistationary states with complex energy.

This contribution will discuss differences and similarities between autoionizing resonances –which are formed in electron-molecule scattering– and Stark resonances –which are formed in electric fields and govern strong-field ionization. In particular, the consequences for a treatment in terms of electronic-structure theory will be considered and an implementation of molecular strong-field ionization rates at coupled-cluster levels of theory will be presented [2, 3].

Exemplary applications to small molecules such as CO, O_2, and H_2O indicate that an accurate treatment of electron correlation is of great importance even for a qualitatively correct description of the dependence of molecular strong-field ionization rates on the strength and orientation of the external field. The analysis of the second moments of the molecular charge distribution suggests a simple criterion for distinguishing tunnel and barrier suppression ionization in polyatomic molecules.

[1] N. Moiseyev, *Non-Hermitian Quantum Mechanics* (Cambridge University Press, Cambridge, UK, 2011).

[2] T.-C. Jagau, *J. Chem. Phys.* **145**, 204115 (2016).

[3] T.-C. Jagau, *J. Chem. Phys.* **148**, 204102 (2018).

Precision physics with the hydrogen molecule

Krzysztof Pachucki

Faculty of Physics, University of Warsaw

There is only one very narrow optical transition in the hydrogen atom, $1S - 2S$, and all the other transitions have much broader natural width. This is the reason of limited precision of the quantum electrodynamics tests on the hydrogen atom and limited accuracy of the Rydberg constant and of the proton charge radius. Moreover, the different value of the proton charge radius obtained from the measurement of the $2S - 2P$ transition in the muonic hydrogen indicates severe problems with interpretation of high precision spectroscopic results with the hydrogen atom. Currently, several projects are being pursued to measure the Rydberg constant by other means, for example from the 1S-2S transition in hydrogen-like helium ion, which is a very challenging task. In contrast to the atomic hydrogen, the transition frequencies between rotational and vibrational levels in hydrogen molecules can in principle be measured much more accurately, because their natural width is much smaller than that those of the hydrogenic excited states. This opens possibility for improved tests of quantum electrodynamic theory and for the accurate determination of the electron-proton (deuteron) mass ratio, of the Rydberg constant, and of the nuclear charge radius.

I will present a recent very accurate results for the dissociation energy of H_2, D_2, and HD molecules, which indicate significance of the nonadiabatic effects and resolve discrepancy of theoretical predictions with recent experimental values for H_2 and D_2. While theoretical accuracy is now significantly improved and is higher than experimental one, we still observe about 3σ discrepancy for the dissociation energy of HD, which requires further investigations. In addition I will present results for the shielding constant and spin-spin coupling in HD, which serve for the most accurate determination of the deuteron magnetic moment and for tests of Standard Model of fundamental interactions.

MELTING IN EXTREME ENVIRONMENTS

J. Wiebke[1], O. Smits[1], P. Jerabek[1], P. Schwerdtfeger [1,2], E. Florez[1,2], S. Stopkovich[2], A. Teale[2], W. Klopper[2], T. Helgaker[2] and E. Pahl[1,2]

[1]Centre for Theoretical Chemistry and Physics, INMS and NZIAS, Massey University Auckland
[2]Centre for Advanced Study (CAS) at the Norwegian Academy of Science and Letters, Department of Chemistry, University of Oslo, Norway

Melting results for rare gases under extremely high pressures as well as first results in strong magnetic fields are presented. Our approach to simulate phase transitions consists in exploring phase space with classical (parallel-tempering) Monte Carlo, MC, methods combined with a very accurate computation of the interaction energy of the sampled configurations. We employ many-body expansions in which the total interaction energy of the N-atom system is obtained by decomposing the total energy into two-, three- and higher-body fragments. For the two- and three-body contributions we use the highest level of quantum-mechanical treatment possible.

For rare gases, we showed that this approach works well for melting under ambient conditions[1,3] and for Argon for pressures up to 100 GPa, 1 Million times the atmospheric pressure[2]. The many-body expansion, which yields already 90% of the interaction energy at ambient pressure, continues to work very well for high pressures although the three-body contributions gain in importance due to the strongly decreased interatomic distances. For the stochastic exploration of phase space, we work in the isobaric, isothermal ensemble, allowing for atom displacements as well as cell volume adjustments employing periodic boundary conditions. Excellent agreement with experimental data is found up to very high pressures. Deviations for pressures beyond 50 GPa are yet not understood and might also indicate challenges in the experimental set-up.[2]

First results for small Neon clusters are given for melting in strong homogeneous magnetic fields in the range of 0-0.3 a.u. The many-body expansion is augmented by including the orientation of the dimers (trimers) with respect to the direction of the magnetic field. The two-body contributions $E^{(2)}(B; R, \theta)$ now depend on the norm of the magnetic field B, the interatomic dimer distance R and the angle θ between the molecular axis with the magnetic field. These potential curves are presently computed on MP2 and coupled-cluster level. Interpolation of the data is performed to generate look-up tables which will allow to preserve the computational efficiency and high accuracy in the evaluation of the interaction energy needed for the MC melting simulations. We will be able to explore the melting of extended systems under high magnetic fields by using the results for small clusters and extrapolate to the infinite system as was successfully done before under ambient conditions.[1,3]

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From atomic confinement to high pressure

<u>L. F. Pašteka</u>,[1,2] M. Hasanbulli,[3] M. Wormit[†],[4] D. Sundholm,[1,5]
H.-J. Werner,[1,6] T. Saue,[1,7] T. Helgaker,[1,8] and P. Schwerdtfeger[1,3]

[1] *Centre for Advanced Study (CAS) at the Norwegian Academy of*
Science and Letters, Drammensveien 78, NO-0271 Oslo, Norway
[2] *Department of Physical and Theoretical Chemistry, Faculty of Natural*
Sciences, Comenius University, Mlynská dolina, 84104 Bratislava, Slovakia
[3] *Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced*
Study, Massey University Auckland, Private Bag 102904, 0745 Auckland, New Zealand
[4] *Theoretical and Computational Chemistry, Interdisciplinary Center for Scientific*
Computing (IWR), Im Neuenheimer Feld 368, 69120 Heidelberg, Germany
[5] *Department of Chemistry, University of Helsinki, P.O. Box 55 (A. I. Virtanens Plats 1), Finland*
[6] *Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*
[7] *Laboratoire de Chimie et Physique Quantiques, UMR 5626 CNRS –*
Universitè Toulouse III (Paul Sabatier), 31062 Toulouse Cedex 09, France
[8] *Department of Chemistry, The Centre for Theoretical and Computational*
Chemistry (CTCC), University of Oslo, Postbox 1033, Blindern 0315 Oslo, Norway

We present a detailed study of the non-relativistic atoms H, He, C and K as well as for the CH_4 molecule in the center of a spherical soft confinement potential of the form $V_s(r) = (r/r_0)^N$, which in the limit of $N \to \infty$ approaches the hard-wall confinement. Confined hydrogen is considered as a base model treated numerically to obtain ground and excited state energy shifts, and to analyze in detail the convergence toward the hard-wall potential. The use of Gaussian basis sets is analyzed in detail for confined hydrogen and helium for changing stiffness N and confinement radius r_0. This approach is further generalized for molecules with CH_4 as an example. A possible application of this field to atoms and molecules under high pressure is discussed.

Rubidium atoms in high magnetic field

Carlo Rizzo
Laboratoire National des Champs Magnétiques Intenses
Toulouse, France

I present a new technique to measure pulsed magnetic fields based on the use of rubidium in gas phase as a metrological standard.

In Toulouse, France, at the National Laboratory for high magnetic fields, we have therefore developed an instrument based on laser induced transitions at about 780 nm (D2 line) in rubidium gas contained in a mini-cell of 3 mm x 3 mm cross section.

To be able to insert such a cell in a standard high-field pulsed magnet, we have developed a fibred probe kept at a fixed temperature. Transitions are measured by a commercial wavemeter. One innovation of our sensor is that in addition to the usual monitoring of the light transmitted by the Rb cell, we also monitor the fluorescence emission of the gas sample from a volume of 0.13 mm^3.

We record optical spectra for fields from a few tesla up to 60 T investigating a wide range of magnetic interactions from the hyperfine Paschen-Back regime to the fine one and the transitions between them.

The magnetic field measurement is based on the rubidium absorption itself. The rubidium spectroscopic constants were previously measured with high precision, except the excited state Landé g-factor that we derive from the position of the absorption lines in the transition to the fine Paschen-Back regime.

Our spectroscopic investigation, even if limited by the Doppler broadening of the absorption lines, measures the field with a 20 ppm uncertainty at the explored high magnetic fields.

It also provides a determination of the excited state Landé g-factor equal to 1.33494(15) indicating that core and QED corrections are of the order of 6 10^{-4}, which appears higher than expected, although no published predictions exist for these corrections.

Molecules at high x-ray intensity: Challenges for theory

Robin Santra, DESY and Universität Hamburg

One of the key opportunities offered by the development of x-ray free-electron lasers is the determination, at atomic resolution, of the three-dimensional structure of biologically relevant macromolecules. The basic idea underlying molecular imaging using x-ray free-electron lasers is the "diffract-and-destroy" concept: If one uses an x-ray pulse that is sufficiently short (on the order of femtoseconds), then in a single shot an x-ray scattering pattern may be obtained that is practically unaffected by atomic displacements triggered by ionization events during the x-ray pulse. What cannot be eliminated in this way is the impact of the electronic damage on the x-ray scattering patterns. Theory, therefore, plays an important role in the development of this new imaging technique: A quantitative understanding is required of the damage processes occurring during the exposure of a molecule to an ultraintense, ultrafast x-ray pulse.

In this talk, I will present progress we have made in order to address this challenge. One tool we have developed, XMDYN [1], is a molecular-dynamics code that utilizes ab-initio atomic electronic-structure information, computed on the fly, within a Monte-Carlo framework. XMDYN has been successfully tested through experiments at LCLS [2] and SACLA [3]. XMDYN is part of a powerful start-to-end simulation framework for single-particle imaging at the European XFEL [4,5]. Recently, we have taken first steps towards a full ab-initio framework for simulating high-intensity x-ray–matter interactions [6,7]. Our new XMOLECULE software solves the polyatomic quantum-mechanical electronic-structure problem for every electronic state arising during the exposure of a molecule to a strong x-ray pulse. From this information, electronic transition rates (such as Auger decay rates) are computed on the fly, and the associated rate equations are integrated utilizing a Monte-Carlo method. XMOLECULE played a key role in a recent LCLS experiment on iodomethane, in which hard x-rays focused to a peak intensity exceeding 10^{19} W/cm^2 produced the highest charge states ever formed using light [8]. Not only did XMOLECULE correctly predict the charge-state distribution observed, but it also helped identify a new molecular ionization enhancement mechanism based on intramolecular charge transfer.

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Computational simulation of molecules interacting with intense laser fields

H. Bernhard Schlegel

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

The availability of short, intense laser pulses has opened up new frontiers in chemistry and physics. Attosecond laser pulses can directly explore electron dynamics, image molecular orbitals and probe bond making and breaking processes. Intense femtosecond laser pulses can act as photonic reagents by selectively altering the nuclear and electronic dynamics of molecules. The response of molecules to short, intense laser pulses cannot be treated by the perturbative methods used for ordinary spectroscopy. Direct simulation of the dynamics is needed to understand the behaviour of molecules under these extreme conditions.

Short, intense laser pulses in the optical range cause rapid ionization. We have used time-dependent configuration interaction with absorbing boundaries to simulate the ionization and find that strong field ionization rates depend markedly on the conjugation length of the molecule and the orientation of the molecule in the laser beam. The shapes of the ionization yield for linearly polarized light can be understood primarily in terms of the nodal structure of the highest occupied orbitals. Depending on the orbital energies, ionization from lower lying orbitals may also make significant contributions to the shapes. The shapes of the ionization yield for circularly polarized light can be readily explained in terms of the shapes for linearly polarized light.

In the mid IR range, short intense laser pulses can rapidly deposit substantial amounts of vibrational energy into specific parts of a molecule. Such highly energized molecules can undergo fast rearrangements and selective dissociations. We have used ab initio classical trajectory calculations in time-varying electric fields to examine the fragmentation of molecules in intense IR laser pulses.

Ultralong-Range Molecules in External Fields

Peter Schmelcher

Zentrum für Optische Quantentechnologien, Universität Hamburg
Luruper Chaussee 149, 22761 Hamburg, Germany
Hamburg Centre for Ultrafast Imaging, Universität Hamburg
Luruper Chaussee 149, 22761 Hamburg, Germany

Ultralong-Range Molecules provide a new type of highly excited Rydberg molecules with a novel binding mechanisms different from the 'traditional' covalent or ionic binding. They combine Rydberg atoms with ground state atoms in a single molecule thereby leading to molecular properties inherited from the Rydberg component. Huge bond lengths and corresponding dipole moments belong to the peculiar features of this species. They have been observed spectroscopically approximately a decade ago and are now under intense investigation in several ultracold atom groups worldwide. Due to their small binding energies they are extremely sensitive even to weak external electric and magnetic fields, as we shall demonstrate in this presentation [1,2,3]. Bond lengths, local equilibria, orientation and aligment can be controlled using fields and vary largely with the degree of excitation of the Rydberg atom(s). We compare experimental results with theory [2] and demonstrate isotropic as well as anisotropic interaction effects with a rich structure of the resulting vibrational dynamics and states. More recently high resolution spectroscopy has even seen the spin structure of those states - and we demonstrate what is necessary in order to describe the latter and combine it with the external field effects [4]. Moving from diatomic to triatomic systems [5,6] the first evidence for three-body interactions has been demonstrated in theory and experiment opening-up the possibility of a full control of chemical reaction dynamics in these highly excited Rydberg molecules.

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Open-shell molecules in strong magnetic fields

Toru Shiozaki
Department of Chemistry, Northwestern University

In this talk, I will present our recent developments of computational tools for the electronic structures of open-shell molecules in strong magnetic fields. I will first illustrate an implementation of a GIAO extension of the four-component relativistic CASSCF method, which can handle external magnetic fields. This implementation allows for accurate and consistent discerption of interactions between spins and strong magnetic fields [1,2]. I will also show our efforts to extend these theories to anisotropic Gaussian basis functions to accelerate the basis-set convergence. Some results and remaining challenges will be presented.

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Electronic structure in strong magnetic fields: Closed-shell paramagnetism, paramagnetic bonding and White-Dwarf spectra

S. Stopkowicz[1,2], A. Borgoo[2,3], F. Hampe[1], E. I. Tellgren[2,3], W. Klopper[2,4], J. Gauss[1,2], A. M. Teale[2,5], T. Helgaker[2,3]

[1] Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Germany
[2] Centre for Advanced Study, Norwegian Academy of Science and Letters, Oslo, Norway
[3] Hylleraas Centre for Quantum Molecular Sciences, University of Olso, Norway
[4] Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Germany
[5] School of Chemistry, University of Nottingham, UK

Towards the end of their lives, most stars become White Dwarfs (WDs), i.e., stellar objects with sizes comparable to the Earth and densities comparable to the Sun. About 10-25% of these stars are magnetic and exhibit extreme field strengths of up to 100.000 Tesla. Rather little is known about the composition of their atmospheres and their chemistry in general. The reason for this is that such strong fields are not accessible through experiment. Observational spectra from such stars are, due to the strong-field effects, radically different from corresponding spectra from the lab which makes their assignment challenging. Therefore, the only way to study the composition of their atmospheres, or, more generally, the chemistry of atoms and molecules under these extreme conditions is through high-accuracy quantum-chemical calculations. The latter in turn have incorporate finite magnetic fields, thus requiring complex wave functions and the use of gauge-including atomic orbitals (London orbitals) to deal with the gauge-origin dependence of the Hamiltonian. In this talk, we will shed light on the mechanism of closed-shell paramagnetism in BH and present results on paramagnetic bonding [1] as well as the prediction of spectra in strong magnetic fields obtained with coupled-cluster (CC)[2,3] and equation-of-motion (EOM) CC[4] theories.

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Climbing Jacobs ladder under extreme conditions

A. M. Teale[1,2,3], S. Stopkowicz[2,4], T. Helgaker[2,3], C. Holzer[5], W. Klopper[2,5]

[1] School of Chemistry, University of Nottingham, UK

[2] Centre for Advanced Study, Norwegian Academy of Science and Letters, Oslo, Norway

[3] Hylleraas Centre for Quantum Molecular Sciences, University of Oslo, Norway

[4] Institut für Physikalische Chemie, Universität Mainz, Germany

[5] Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Germany

The generalization of density-functional methods to treat systems in the presence of strong magnetic fields is discussed in the context of current-density functional theory (CDFT) [1]. Generalizations of functionals on all 5 rungs of Jacob's ladder (see Fig. 1) are presented. Previous work [2] has shown that functionals at the meta-GGA level (rung 3), modified appropriately for use in the presence of a magnetic field, can provide a good compromise between computational cost and accuracy. In this presentation we discuss our recent development of methods corresponding to rungs 4 and 5 on Jacob's ladder [3, 4], allowing for practical application of CDFT to molecular systems with the gamut of density-functional methods. At the most complex level, rung 5, we consider functionals based on the correlation energy derived from the random-phase approximation (RPA).

The implementation of RPA functionals provides a natural stepping stone to a range of beyond-DFT approaches; we have recently constructed generalizations of GW methods (G_0W_0 and linearized G_0W_0) for the study of atoms and molecules in magnetic fields. The quasi-particle energies from these theories provide direct access to approximate ionization energies and electron affinities in the presence of strong magnetic fields. Furthermore, excitation energies in strong fields may be calculated utilizing these quasi-particle energies and the Bethe-Salpeter equation.

This suite of current-density-functional based methods provides a new toolbox for low cost simulation of atomic and molecular systems in strong magnetic fields.
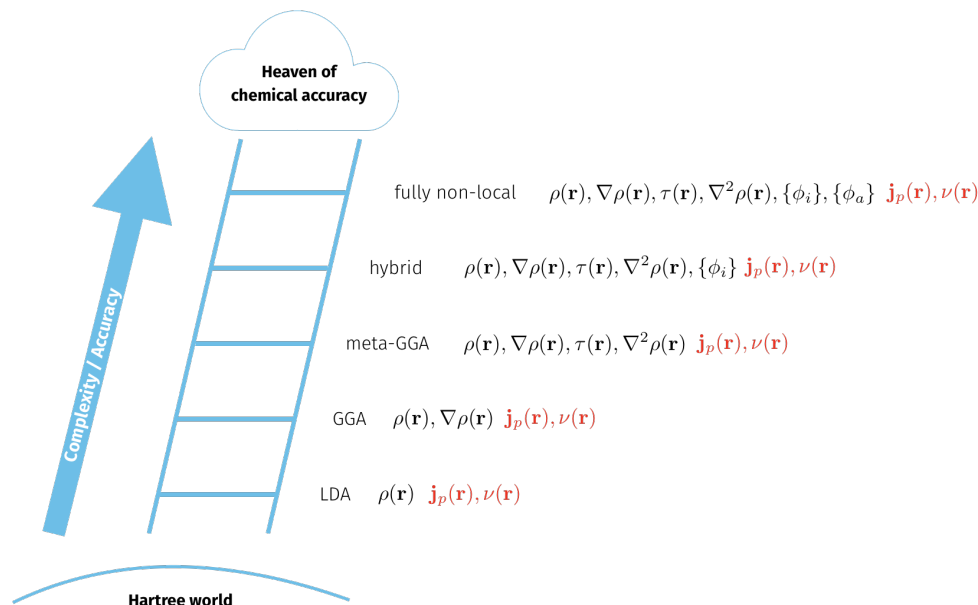

Figure 1: Schematic categorisation of density-functionals according to the complexity / non-locality of their components. Extra contributions arising in CDFT generalizations are shown in red.

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Quantum chemistry in strong magnetic fields

E. Tellgren, K. K. Lange, A. M. Teale, U. Ekström,
E. Sagvolden, S. Kvaal, J. Austad, S. Reimann, A. Borgoo,
H. Fliegl, S. Sen, and T. H. Helgaker

Department of Chemistry, University of Oslo,
P.O. Box N-1033 Blindern, Oslo, Norway

Terrestrial magnetic fields are weak compared to the energy scale of a small molecule. Perturbative approaches treating magnetic field effects as small corrections to zero-field calculations are therefore almost exclusively used in quantum chemistry. Over several years, we have developed the LONDON quantum chemistry package for non-perturbative quantum chemistry in strong magnetic fields [9]. This talk summarizes these developments. The LONDON has been used to uncover effects beyond the reach of perturbation theory, such as transitions from paramagnetism to diamagnetism [7], a novel type of chemical bond [8, 2], and effects of non-uniform magnetic fields that break spin symmetry [6, 4]. The implementaion has also been used to learn about computational methods that aim at magnetic properties. By comparing more accurate correlated calculations to density-functional and current-density-functional approximations, we have gained insight into the performance and limitations of presently available approximations [5, 1, 3].

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Glimpses of an alien chemistry: atoms in neutron star atmospheres

Anand Thirumalai

DigiPen Institute of Technology, Redmond, Washington, USA

It is a matter of great theoretical and practical concern that as of 2018, we only really know the structure of the most basic atoms, hydrogen and helium, in intense magnetic fields such as those found in white dwarfs and neutron stars (B > 100,000 T). These are the most highly magnetised objects in the observable universe. The energy levels, transition wavelengths, oscillator strengths and electric and magnetic properties of virtually the entire periodic table is almost completely unknown in such field strengths. Such atomic data is crucial for correctly interpreting the emergent spectra from magnetised compact objects, particularly since evidence is now mounting for the presence of atoms such as carbon being present in their atmospheres. In white dwarfs, there are also other species such as phosphorus, silicon and sulphur present in appreciable quantities, even in cooler and therefore older white dwarfs. This is strange due to the very short timescales (< 100 years) for the heavier atoms to submerge in the atmospheres of white dwarfs. Thus, the older the white dwarf, the less the contaminants, and the chemistry is expected to be predominantly H or He. In neutron stars on the other the hand story is the reverse, only the younger neutron stars are expected to have H and He which are the remnants from supernova fallback material during collapse. The older neutron stars are expected to have purely heavier elements; the products of nuclear burning of lighter elements. Therefore it is now understood that the presence of low- and mid-Z elements such as carbon (and for that matter Si, P, S etc) in older varieties of both white dwarfs and neutron stars is probably due to accretion of ambient material -- material from erstwhile exoplanets for example. This also raises the unique question regarding molecular chemistry and magnetic properties in such field strengths, which is a nearly completely unexplored domain. Recent evidence has emerged for the presence of molecular hydrogen in regular non-magnetised white dwarfs, further motivating the search for simple molecules in the atmospheres of the magnetised counterparts. This also requires a considerable theoretical input from the quantum chemistry side for careful spectral analysis. In this talk I shall summarize the state-of-the-art in the field of strong field atomic and molecular structure, relevant to white dwarfs and neutron stars and also describe my recent efforts in developing fast atomic structure software that computes the energy landscape of low-Z atoms in intense magnetic fields.

Theoretical Predictions of Unique Hydride Phases Under Pressure

Eva Zurek

State University of New York at Buffalo, New York, USA

The pressure variable opens the door towards the synthesis of materials with unique properties and electronic structures. Under pressure elements that would not normally combine may form stable compounds or they may mix in novel proportions. As a result, we cannot use our chemical intuition developed at 1 atm to predict phases that become stable when they are compressed. To enable our search for novel hydride phases that can be synthesized under pressure we have developed XtalOpt, an open-source evolutionary algorithm for crystal structure prediction. XtalOpt has been employed to find the most stable structures of hydrides with unique stoichiometries. Some of these are superconducting at high temperatures. Herein, we describe our predictions of the binary hydrides of scandium, and iron as well as ternary hydrides at pressures that can be achieved in diamond anvil cells. The electronic structure and bonding of the predicted phases is analysed by detailed first-principles calculations.

Poster Abstracts

Abstracts are listed alphabetically by the last names of the presenters

1. Magnar Bjørve: *Periodic systems in a multiwavelets framework*

2. Maria Dimitrova: *Halomethanes in strong magnetic fields*

3. Fabian K. Faulstich: *Analysis of the coupled-cluster method tailored by tensor-network states in quantum chemistry*

4. Heike Fliegl: *The effect of strong magnetic fields on the ring currents of tetraoxaisophlorin*

5. Florian Hampe: *Highly accurate treatment of atoms and molecules in strong magnetic fields with CC & EOM-CC methods*

6. Julie Héron: *Magnetic properties of* $[NpO_2(dpc)_2]^{2-}$: *in solid state and in solution*

7. Christof Holzer: *Two-component quasirelativistic GW/BSE methods in molecular quantum chemistry*

8. T. Lankau: *Molecular dynamics study of lignin degradation under high pressure and temperature*

9. Benedicte Ofstad: *Non-orthogonal orbital optimized coupled-cluster, numerical results*

10. Morten Piibeleht: *Updates to many-particle quantum electrodynamics in GRASP2K*

11. Sangita Sen: *A local tensor that unifies kinetic energy density and vorticity dependent exchange-correlation functionals*

12. Odile R. Smits: *Oganesson, the noble solid. Ab-initio Monte Carlo melting simulations of the heavy noble gases*

13. De-Yin Wu: *Theoretical studies of plasmon-enhanced Raman spectroscopy and chemical reactions in noble metal nanogaps*

Periodic systems in a multiwavelets framework

Magnar Bjørgve*, Stig Rune Jensen and Luca Frediani

Department of Chemistry, UiT The Arctic University of Norway
Hylleraas Centre for Quantum Molecular Sciences

The MRChem group has shown how MultiWavelets (MWs) have proven extremely efficient in describing the nuclear cusps, combined with extremely useful mathematical properties leading to results with unprecedented accuracy in molecular (non-periodic) calculations. In this project do we expand the MRChem code to solve the Kohn-Sham equations for periodic systems in order to achieve high accuracy calculation in the modeling of material and their properties

Halomethanes in strong magnetic fields

Maria Dimitrova,[1,2] **Dage Sundholm,**[1,2] **Trygve Helgaker,**[1,3] **Trond Saue,** [1,4] **Stella Stopkowicz,** [1,5] **Andrew Teale,** [1,6] **Wim Klopper,**[1,7] **Peter Schwerdtfeger.**[1,8]

[1]CAS, Norwegian Academy of Sciences and Letters, [2]University of Helsinki, Finland,
[3]University of Oslo, Norway, [4]Université Toulouse III – Paul Sabatier, France,
[5]Johannes Gutenberg – Universität Mainz, Germany, [6]University of Nottingham, UK,
[7]Karlsruhe Institute of Technology, Germany, [8]Massey University, Auckland, New Zealand

The electrons in a molecule interact with an external magnetic field, affecting the electronic structure, energy and geometry. The Schrödinger equation involves an additional term, where the angular momentum operator appears, thus requiring that atomic and molecular orbitals are complex functions. This requires new quantum chemistry programs to be employed. We are investigating the electronic states and geometries of methane, halogenated methanes and their building blocks: H, C, H_2, H_3, H_4, HF, HCl, CH, CH_2, and CH_3. We study their behaviour in magnetic fields up to 1 a.u. and compare the energies, geometries and the character of the excited states of the molecules. We use the LONDON program[1] to perform geometry optimisation at the Restricted and Unrestricted Hartree-Fock levels of theory using uncontracted Dunning basis sets: cc-pVDZ, aug-cc-pVDZ, and aug-cc-pVTZ with London orbitals. The magnetic field strength is increased in steps of 0.1 a.u.

The CH molecule is stabilised by a magnetic field perpendicularly oriented to the C – H bond. It was found to be bound until 0.25 a.u. in its quartet state. The methane molecule becomes elongated along the magnetic field direction. All bond lengths are equal at field strengths between 0 and 1 a.u. The alignment of the molecule with respect to the magnetic field vector changes with the multiplicity. When $B \parallel C_2$ symmetry axis, the symmetry point group of the optimised structure changes from T_d at zero field to C_{2v}. The bond lengths remain equal to each other at all magnetic field strengths. The energies of the triplet states cross the singlet-state curve at about 0.3 a.u. and thus the triplet becomes the ground state. However the energy of the molecule is higher than the sum of the energies of its constituting atoms, and it dissociates. In the investigated halometanes, as the field strength grows, the C – X bond becomes almost perpendicular to the magnetic field. Their length remains practically constant. The molecules keep the C_{2v} symmetry point group at all investigated field strengths. The bond lengths initially become shorter but then start elongating, until eventually the molecule dissociates.

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ANALYSIS OF THE COUPLED-CLUSTER METHOD TAILORED BY TENSOR-NETWORK STATES IN QUANTUM CHEMISTRY

FABIAN M. FAULSTICH*, ANDRE LAESTADIUS*, SIMEN KVAAL*, ÖRS LEGEZA†, AND REINHOLD SCHNEIDER‡

We analyze mathematical properties of tailored coupled-cluster (TCC) methods as finite dimensional non-linear Galerkin schemes [1]. This multi-reference formalism combines the single-reference coupled-cluster (CC) approach with a full configuration interaction solution covering the static correlation [2]. This keeps the computational costs low as the full configuration interaction solution is calculated for a subsystem and guarantees the high accuracy of the CC method for the dynamical correlation.

Based on Zarantonello's Theorem, we prove that TCC schemes attain locally unique solutions fulfilling a quasi-optimal error bound. To meet that end, we formally characterize the TCC function and show local strongly monotonicity and Lipschitz continuity. We introduce the novel CAS-EXT-gap assumption for multi-reference problems replacing the HOMO-LUMO gap, which is unreasonable for statically correlated systems. From this assumption, results from previous analyses [5, 3, 4] are adaptable to the TCC formalism presented here.

Further we perform a first error analysis revealing the mathematical complexity of the TCC-methods. Due to the basis-splitting nature of the TCC formalism, the error decomposes into several parts. Using the Aubin-Nitsche-duality method we derive a quadratic error bound. However, as TCC-methods do not converge to the Full-CI solution a methodological error enters this bound, which can be qualitatively and quantitatively explained by the basis-splitting.

The motivation and importance of our work is i.a. based on the recent approach in which the Full-CI solution was approximated by the density matrix renormalization group (DMRG) method [6]. The computational results presented in [6] for the chromium dimer Cr_2 show that the precession of the DMRG-TCC method outruns traditional high accuracy CC methods like CCSD(T) and even CCSDTQ. The outstanding performance of the young DMRG-TCC method makes it an extremely promising candidate for the computation of strongly correlated systems.

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*Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway (f.m.faulstich@kjemi.uio.no).

†Strongly Correlated Systems "Lendület" Research Group, Wigner Research Center for Physics, H-1525, Budapest, Hungary.

‡Modeling, Simulation and Optimization in Science, Department of Mathematics, Technische Universität Berlin, Sekretariat MA 5-3, Straße des 17. Juni 136, 10623 Berlin,Germany

The effect of strong magnetic fields on the ring currents of tetraoxaisophlorin

Heike Fliegl[1], **Trygve Helgaker**[1], **Erik Tellgren**[1]

[1]*Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, P.O.Box 1033 Blindern, 0315 Oslo, Norway.*

When aiming at systematically synthesizing porphyrinoids with distinct properties knowledge about electron mobility pathways is essential. Experimentally, these pathways are not easily accessible, which makes complementary theoretical studies necessary. It is possible to determine reliable aromatic pathways in porphyrinoid macrocycles by studying magnetically induced current densities for weak magnetic fields.[1, 2] However, little is known about the effect of strong magnetic fields on the current density and current pathways of porphyrinoids, which is the topic of the present work. We investigate tetraoxaisophlorin, which is a strongly antiaromatic and air stable molecule that can be expected to show interesting effects upon placement into a strong magnetic field.[3] For our study of magnetically induced currents we employed gauge-including atomic orbitals and different field strengths as implemented in the London program.[5]

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Highly accurate treatment of atoms and molecules in strong magnetic fields with CC & EOM-CC methods

Florian Hampe, Simon Blaschke, Stella Stopkowicz

Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

In strong magnetic fields of around 1 a.u. (with 1 $B_0 \approx 235\,000$ T), Coulomb and magnetic forces in atoms and molecules become equally important. Such fields occur, e.g., on magnetic white dwarf stars. Their observable spectra differ substantially from those of non-magnetic white dwarfs. However, such field strengths cannot be produced in laboratories on Earth, such that theory has to provide reliable data to investigate the drastically altered electronic structure which these strong fields cause.

As this field of research is rather unknown territory, accurate wave function methods are essential. In order to extend the applicability to more than just the simplest systems, coupled cluster (CC) and equation-of-motion (EOM) CC methods can be employed. [1,2]

In this work, we discuss the behavior of selected systems as a function of the magnetic field. First, BH and CH^+ serve as examples to explain the phenomenon of closed-shell paramagnetism: While the paramagnetic response can be observed on Earth, its explanation cannot be given without taking strong field effects into account. Second, the interaction energy for noble gas dimers obtained on the CCSD(T) level of theory is discussed, presenting examples for systems stabilized by paramagnetic bonding. [3] Furthermore, first steps towards the prediction of magnetic white dwarfs' observational spectra are presented by EOM-CCSD calculations for the transition moments for low excited states of the carbon atom and LiH.

[1] S. Stopkowicz, J. Gauss, K. K. Lange, E. I. Tellgren, and T. Helgaker, *J. Chem. Phys.* **143**, 074110 (2015).

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Magnetic properties of [NpO$_2$(dpc)$_2$]$^{2-}$:
in solid state and in solution.

Julie Héron, Hélène Bolvin
Hylleraas Centre for Quantum Molecular Sciences
Universitetet i Oslo, Norway.
Laboratoire de Chimie et de Physique Quantiques
Université Toulouse 3, France
Email address: bolvin@irsamc.ups-tlse.fr

Magnetic properties of the [NpO$_2$(dpc)$_2$]$^{2-}$ (see Figure 1) have been characterized both in solid state and in solution. In solid state, experiments have been performed in the team of E. Colineau using a SQUID (ITU in Karlsruhe) and in solution, they have been performed in the team of C. Berthon using p-NMR and the Evans method (CEA Marcoule). The susceptibility differ by 20 % between the two states.

The calculation of properties of open-shell 5f molecules is a challenge for the methods of quantum chemistry: these complexes have many low-lying configurations, spin-orbit effects are important and correlation effects must be taken into account. The SO-CASPT2 method gives results that compare well to experimental data: it is a two-step wave function based method. The multiconfigurational nature of the wave functions is described by starting with a CASSCF calculation, correlation effects are calculated by second order theory and spin-orbit effects are introduced in the very last step by a state interaction procedure.

NpO$_2$$^{2+}$ is in the *5f^1* configuration and it has been already shown that the equatorial ligands play an important role for the determination of the nature of the ground state [1]. We performed quantum chemical calculation with the SO-CASPT2 method in order to analyze these differences. For the present complex, our calculations are in good agreement with the experimental data and we show that the Li$^+$ counter cation present in the solid phase plays the key difference.

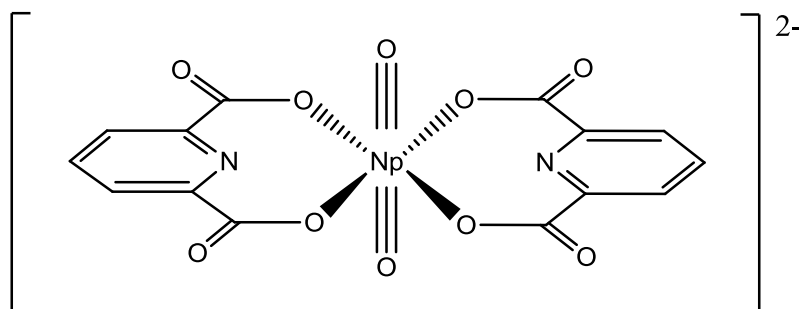Figure 1: Structure of the complex [NpO$_2$(dpc)$_2$]$^{2-}$.

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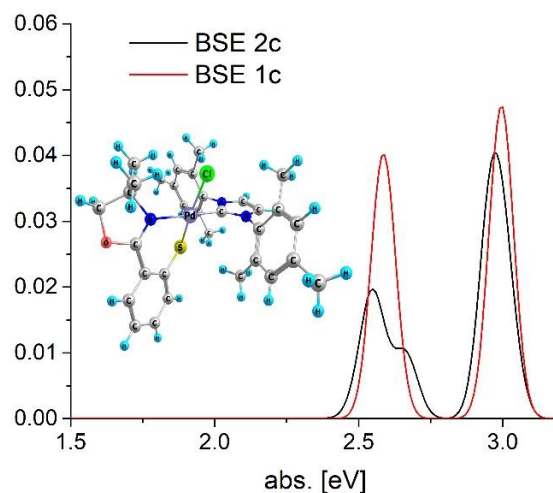# TWO-COMPONENT QUASIRELATIVISTIC GW/BSE METHODS IN MOLECULAR QUANTUM CHEMISTRY

Christof Holzer[1], Wim Klopper[1,2]

[1]Institut für Physikalische Chemie, Karlsruher Institut für Technologie,
Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany
[2]Centre for Advanced Study (CAS) at The Norwegian Academy of Science and Letters,
Drammensveien 78, N-0271 Oslo, Norway

The two-component (2c) GW/BSE ansatz is a promising method for applications in molecular quantum chemistry. Starting from DFT or Hartree-Fock references the central object, the Green's function, is evaluated and used to significantly improve upon various molecular properties. The simplest GW method is G_0W_0 with screening from the random-phase-approximation, i.e. non-interacting electron-hole pairs (RPA). This yields an improved set of quasi-particle (QP) energies (resembling IPs) from the starting orbital energies. These QP energies can then be used as starting point for several further calculations, e.g. solving the Bethe-Salpeter equation (BSE) to obtain optical excitation spectra, circular dichroism or interaction energies of van der Waals bound systems.[1,2]

We aim at extending the formalism for 2c GW to open shell systems, as well as to systems in strong magnetic fields. Based on these 2c QP corrections the Bethe-Salpeter equation can be solved iteratively to obtain e.g. UV/Vis absorption spectra including scalar-relativistic and spin-orbit effects.

Figure 1. 1c and 2c absorption spectra of a metal complex calculated at G_0W_0-BSE@PBE0/dhf-TZVP(P)-2c level of theory. Calculation done on a local compute node (Intel(R) Xeon(R) Gold 6154; 256 GB RAM, 85 hours).

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[2] X. Gui, C. Holzer, W. Klopper, J. Chem. Theory. Comput. 14 (2018) 2127

Molecular Dynamics Study of Lignin Degradation under High Pressure and Temperature

T. Lankau, C.H. Yu

Department of Chemistry, National Tsing Hua University,
101 KuangFu Road Sec.2, HsinChu 30013, Taiwan

The base catalysed depolymerisation (BCD) of lignin into small molecules as an alternative feedstock for chemical industries becomes increasingly important in times of dwindling resources. A recent computational study [1] of the hydrolysis of 2-phenoxy-1-phenylethanol (**1**) as a model for the βO4' linkage in lignin showed that the cleavage of the βO4' link can proceed *via* the corresponding alkoxide (**2**) yielding an oxirane (**3**) and a phenolate anion (**4**).

$$(1)$$
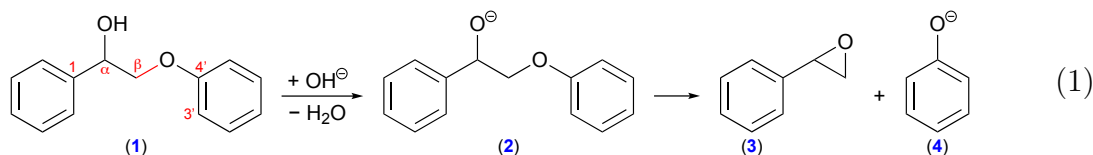
The intermediate oxiranes (**3**) partake in the formation of undesired byproducts, which reduce the overall yields of the BCD reaction below economical feasability.

To understand the critical formation of the oxiranes (**3**) on an atomistic level, QM/MM molecular dynamics simulations are used to study reaction 1 in aqueous solution under standard and reactor conditions (T = 573.15 K, ϱ = 0.743 kg/l). The density ϱ of the reactor setup was chosen to match the experimental value of pure water at 573.15 K and 250 bar. [2] The simulations show that the reaction changes from and internal S_N2 reaction to a S_N1 type mechanism involving a contact ion pair as the $C^\beta O$ bond breaks. These intermediate carbocations can explain the wide range of byproducts in the BCD reaction.

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Non-orthogonal orbital optimized coupled-cluster, numerical results

Benedicte Ofstad[1], Rolf H. Myhre[1], and Simen Kvaal[1]

1. *Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, 0315 Oslo, Norway*

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Non-orthogonal orbital optimized coupled-cluster (NOCC) was originally developed in order to solve the problem of gauge dependence in coupled cluster linear response theory. The model is relatively complicated, and there were doubts of whether untruncated NOCC was equivalent to the full configuration interaction (FCI), the method has therefore received limited interest. One of the authors has recently demonstrated the equivalence between the NOCC and FCI equations. We have developed a pilot implementation for NOCCD and present ground state energies and potential energy surfaces for various small molecules. These are compared to coupled-cluster singles and doubles (CCSD) and orbital optimized coupled-cluster (OCC). For two-electron systems, NOCCD and OCC doubles is identical to FCI up to machine precision.

Updates to many-particle quantum electrodynamics in GRASP2K

Morten Piibeleht, Lukáš Félix Pašteka, Kai Wang, Per Jönsson, Peter Schwerdtfeger

Abstract: GRASP2K [Jönsson et al., 2013] is a software for performing atomic structure calculations in the full four component Dirac equation formalism. It is also able to include effects that go beyond the Dirac-Coulomb Hamiltonian, such as the Breit interaction, vacuum polarization and self-energy — all of which can be considered to be approximations a fully quantum electrodynamic (QED) treatment of an atom.

In particular, the QED self-energy corrections are currently estimated by extrapolating the exact self-energy corrections of hydrogenic (single-electron) orbitals to many-electron orbitals and using those values to estimate the self-energy correction of the whole atomic wave function. Since the original implementation of QED in GRASP, several other effective operators have been proposed in the literature for including self-energy effects in many-electron calculations, such as those by [Pyykkö & Zhao, 2003; Flambaum & Ginges, 2005; Shabaev et.al., 2013].

Here we report the progress on the implementation the additional self-energy methods in the GRASP2K code and on the investigation of their performace. Our aim is to make state of the art QED corrections easily available to the community.

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# A local tensor that unifies kinetic energy density and vorticity dependent exchange-correlation functionals

Sangita Sen and Erik I. Tellgren[*]

Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo

We present a kinetic energy tensor that unifies a scalar kinetic energy density commonly used in meta-Generalized Gradient Approximation (mGGA) functionals and the vorticity density that appears in paramagnetic current-density-functional theory (CDFT). Both types of functionals can thus be subsumed as special cases of a novel functional form that is naturally placed on the third rung of Jacob's ladder. Moreover, the kinetic energy tensor is related to the exchange hole curvature, is gauge invariant, and has very clearcut N-representability conditions. The latter conditions enable the definition of effective number of non-negligible orbitals. Whereas quantities such as the Electron Localization Function (ELF) can discriminate effective one-orbital regions from other regions, the present kinetic energy tensor can discriminate between one-, two-, three-, and four-or- more orbital regions.
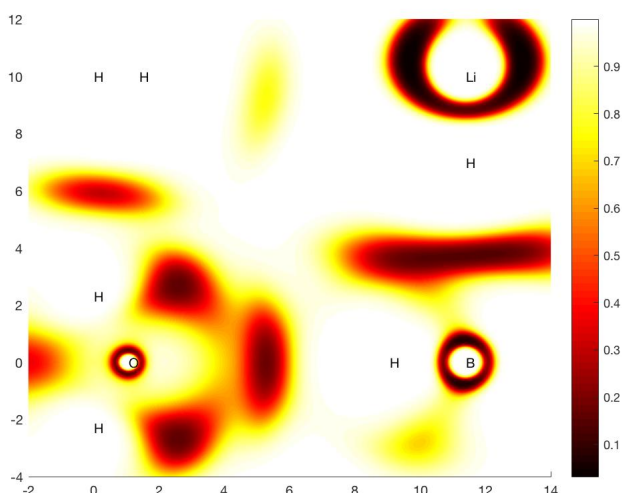
ELF plot for the H_2–LiH–BH–H_2O system.
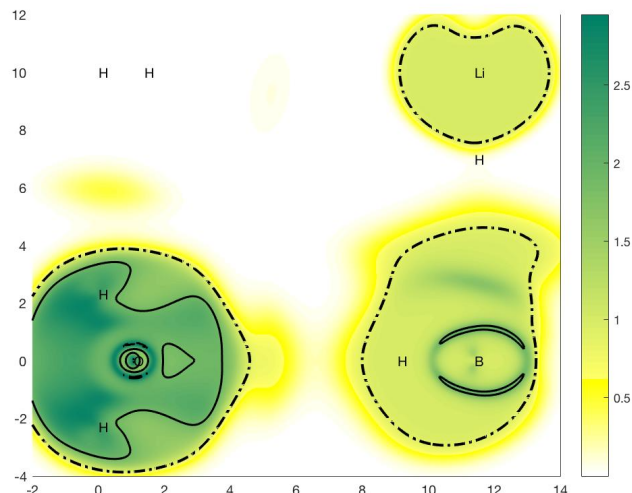
Effective rank estimates for the H_2–LiH–BH–H_2O system from our kinetic energy tensor, **Q**. Contour lines are displayed for visual support at the levels 0.9 (dash-dot), 1.9 (solid), and 2.9 (dashed).

Oganesson, the noble solid.
Ab-initio Monte Carlo melting simulations of the heavy noble gases.

O. R. Smits, P. Jerabek, E. Pahl, P. Schwerdtfeger

Centre for Theoretical Chemistry and Physics (CTCP), Institute for Natural and Mathematical Sciences (INMS) and The New Zealand Institute for Advanced Study (NZIAS), New Zealand
smits.odile.rosette@gmail.com

The elements in the last column of the periodic table owe their name to their common property: by cause of their full valence electron shell these elements are inert and are therefore in a gaseous phase at ambient conditions. The heaviest of all, Oganesson, might be an exception: due to its incredible large nuclear mass, relativistic contributions increase the binding energy, hinting Oganesson to be a solid at room temperature. So far, only three single Oganesson atoms have been synthesized and with a half-life of 0.89 ms it is not possible to study this element experimentally. Therefore, ab-initio methods are our only possibility on learning about the properties of this exotic element.

Here we present our study on the melting temperatures of the heavy noble gases by means of Parallel Tempering Monte Carlo (PTMC), through either direct sampling of the bulk and from a finite cluster approach. This method allows us to obtain the interaction energy E(N) of an N atomic system numerically by repeated random sampling. The melting temperatures are determined from the equilibrium heat capacity as the maximum of the heat capacity curves. The PTMC simulations are conducted for ab-initio two and three body potentials which have been obtained by state-of-the-art relativistic coupled-cluster theory.

Theoretical Studies of Plasmon-Enhanced Raman Spectroscopy and Chemical Reactions in Noble Metal Nanogaps

De-Yin Wu[1], Jian-Zhang Zhou[1], Zhong-Qun Tian[1]*

[1] State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[*]Email address:dywu@xmu.edu.cn

Surface plasmon resonance (SPR) not only enhances extremely giant spectral signals but also induces chemical reactions of molecules adsorbed on noble metals of nanostructures. The former is contributed from the radiation process while the latter is closely related radiationless process. Recently, the SPR effects can be thought as three kinds of the SPR effects (the field enhanced mode, the hot carrier mode, and the photothermal mode) [1]. Among the three modes, we will analyze the hot carrier effect from the SPR effect when the probing molecules adsorb into the metal nanogaps, as shown in Figure 1. They are consisted of symmetric biosphere, asymmetric biosphere, and sphere-plane configurations, which can form the hot spot of SPR and extremely enhance the local optical field and optical absorption [2,3]. First, we built up the metal-molecule-metal cluster model and carried out the density functional theoretical calculations [4]. The different functional approaches were used to calculate the optimized geometries and electronic structures. On the basis of these theoretical calculations, we further obtain the energy level alignment and the low-lying states. They will be matched to the light scattering processes due to the SPR effect. Meanwhile, we also calculated the vibrational frequencies of the probing molecules in the metal-molecule-metal nanogaps. These properties were used to analyze the surface-enhanced Raman spectra of the probing molecules. Second, we further constructed the metal-molecule-metal nanogap and to calculate the field enhancement and light adsorption in the configurations. We considered the SPR effect of the nanogap on the optical absorption and the SPR induced chemical reactions. Finally, the calculated results are used to explain the probability of the interfacial charge transfer, which is often the determined step in the consecutive chemical reactions.

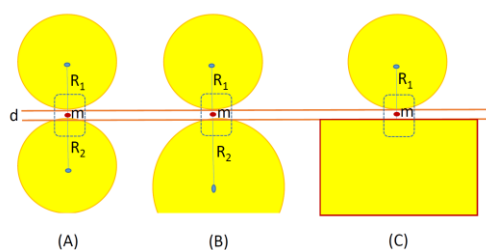Figure 1. Configurations of nanogaps dependent on the size of spheres

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List of participants

Last name:	First name:	E-mail:	Institution:
Appel	Heiko	heiko.appel@mpsd.mpg.de	Max-Planck-Institut fuer Struktur und Dynamik der Materie
Ashoori	Raymond	ashoori@mit.edu	Massachusetts Institute of Technology
Bartkowiak	Wojciech	wojciech.bartkowiak@pwr.edu.pl	Wroclaw University of Science and Technology
Bjørgve	Magnar	magnbjor@gmail.com	UiT – The Arctic University of Norway
Bolvin	Hélène	bolvin@irsamc.ups-tlse.fr	CNRS DR14
Bondo Pedersen	Thomas	t.b.pedersen@kjemi.uio.no	University of Oslo
Borgoo	Alex	ajborgoo@gmail.com	University of Oslo
Cammi	Roberto	roberto.cammi@unipr.it	University of Parma
Cederbaum	Lorenz	lorenz.cederbaum@pci.uni-heidelberg.de	University of Heidelberg
Ceperley	David	david@ceperley.com	University of Illinois Urbana-Champaign
Dewaele	Agnès	agnes.dewaele@cea.fr	Commissariat à l'Energie Atomique
Dimitrova	Maria	maria.dimitrova@helsinki.fi	University of Helsinki CAS
Faulstich	Fabian	f.m.faulstich@kjemi.uio.no	University of Oslo
Fliegl	Heike	heike.fliegl@kjemi.uio.no	University of Oslo
Florez	Edison	edisonffh@gmail.com	Institute of Natural and Mathematical Sciences
Gauss	Jürgen	gauss@uni-mainz.de	Johannes Gutenberg-Universität Mainz
Gregoryanz	Eugene	e.gregoryanz@ed.ac.uk	The University of Edinburgh
Grochala	Wojciech	w.grochala@cent.uw.edu.pl	Univ. Warsaw
Hampe	Florian	hampe@uni-mainz.de	Johannes Gutenberg - Universität Mainz
Heilemann Myhre	Rolf	r.h.myhre@kjemi.uio.no	University of Oslo
Helgaker	Trygve	t.u.helgaker@kjemi.uio.no	University of Oslo
Hermann	Andreas	a.hermann@ed.ac.uk	The University of Edinburgh
Héron	Julie	julie.heron@kjemi.uio.no	Universitetet i Oslo
Holzer	Christof	christof.holzer@kit.edu	Karlsruhe Institute of Technology
Jagau	Thomas	th.jagau@lmu.de	University of Munich
Jensen	Stig Rune	stig.r.jensen@uit.no	UiT – The Arctic University of Norway
Klopper	Willem	klopper@kit.edu	Karlsruhe Institute of Technology
Kvaal	Simen	simen.kvaal@kjemi.uio.no	University of Oslo
Lankau	Timm	lankau@oxygen.chem.nthu.edu.tw	National Tsing Hua University
Linderberg	Jan	boforsarn@mail.dk	Aarhus Universitet
Ofstad	Benedicte	benediof@gmail.com	University of Oslo
Pachucki	Krzysztof	Krzysztof.Pachucki@fuw.edu.pl	University of Warsaw

List of participants

Surname	First name	Email	Affiliation
Pahl	Elke	E.Pahl@massey.ac.nz	Massey University. Albany
Pasteka	Lukas F.	lukas.f.pasteka@gmail.com	Faculty of Natural Sciences. Comenius University
Piibeleht	Morten	morten.piibeleht@gmail.com	Massey University
Reimann	Sarah	sarah.reimann@kjemi.uio.no	University of Oslo
Reine	Simen Sommerfelt	simen.reine@kjemi.uio.no	University of Oslo
Rizzo	Carlo	carlo.rizzo@lncmi.cnrs.fr	Université de Toulouse. Paul Sabatier
Ryley	Matthew	Matthew.Ryley@nottingham.ac.uk	University of Nottingham
Santra	Robin	robin.santra@cfel.de	DESY and Universität Hamburg
Saue	Trond	trond.saue@irsamc.ups-tlse.fr	UMR 5626 CNRS -–- Université Toulouse III-Paul Sabatier
Schlegel	H. Bernhard	hbs@chem.wayne.edu	Wayne State University
Schmelcher	Peter	pschmelc@physnet.uni-hamburg.de	University of Hamburg
Schwerdtfeger	Peter	p.a.schwerdtfeger@massey.ac.nz	Massey University
Sen	Sangita	sangita.sen310187@gmail.com	University of Oslo
Shiozaki	Toru	shiozaki@northwestern.edu	Northwestern University
Skau Hansen	Audun	a.s.hansen@kjemi.uio.no	University of Oslo
Smits	Odile	odilersmits@live.nl	Massey University
Stopkowicz	Stella	stella.stopkowicz@uni-mainz.de	Johannes Gutenberg - Universität Mainz
Sundholm	Dage	sundholm@chem.helsinki.fi	University of Helsinki
Teale	Andy	andrew.teale@nottingham.ac.uk	University of Nottingham
Tellgren	Erik	erik.tellgren@kjemi.uio.no	Department of Chemistry. University of Oslo
Thirumalai	Anand	anand.thirumalai@gmail.com	Digipen Institute of Technology
Werner	Hans-Joachim	werner@theochem.uni-stuttgart.de	University of Stuttgart
Wirz	Lukas	lukas.wirz@helsinki.fi	University of Helsinki
Wu	Deyin	dywu@xmu.edu.cn	Xiamen University
Zurek	Eva	ezurek@buffalo.edu	University at Buffalo