

Annual meeting in Computational Chemistry
Norwegian Chemical Society
Trondheim, November 22-23, 2010



Cover Art:

Chemographic picture by Prof. Em. Reidar E. Stølevik, Department of Chemistry, NTNU

NORWEGIAN CHEMICAL SOCIETY

Annual meeting in Computational Chemistry

The workshop will take place November 22-23 2010 at [Britannia Hotel](#) in Trondheim, Norway and is organized by the Computational Chemistry group in the Norwegian Chemical Society.

NB! If you have special dietary requests, please send a note by email to the contact person.

PARTICIPATION

The participation fee is 1200 NOK for NKS members (and 1600 NOK for non-members). Lunch and dinner on Monday and lunch on Tuesday are included in the workshop fee.

Not a member in the Norwegian Chemical Society (NKS)? You can register [here](#) for an annual fee of 300 NOK.

Registration is done by sending an email to the Contact person (see below) stating Name, Affiliation and NKS membership number (to get the reduced fee). Each "group leader" will be billed for the participation fee so an accurate statement of the affiliation is required.

[List of participants](#)

HOTEL

Participants have to make their own hotel arrangements. We have made an agreement with Britannia Hotel (1070 NOK for a single room and 1270 NOK for a double room) for a limited number of rooms and for reservations made before October 26.

PROGRAM

The workshop will start at 10 am on November 22 and end at 5.30 pm on November 23. Please, make your travel arrangements accordingly. The meeting schedule is planned so that participants from Norway can arrive on Monday morning and leave with a flight around 7 pm on Tuesday evening.

The meeting is regarded as an opportunity for young scientists to present their work in an informal environment. Please, submit a title for a presentation. We expect that all suggested contributions will be accepted for a short presentation (20 minutes including questions and discussion).

[Final program](#)

ABSTRACTS

Contributors are requested to submit a one-page abstract as a **pdf-file**. As last year, we adopt the layout and templates of [13th ICQC – International congress of quantum chemistry](#). A book of abstracts will be provided on-line three days before the workshop (a printed version will not be available).

TRAVEL DETAILS

Trondheim airport (Værnes) is located around 30 km outside Trondheim. The most convenient way to reach Trondheim is by the airport bus, which leaves just outside the main terminal building. The bus takes around 40 minutes. It stops at all major hotels and they are announced by the driver. Whereas the bus stop for departure is just outside the hotel entrance, please ask

the driver for directions when you arrive. The price is around 90 NOK and credit cards are accepted. The alternative is taxi and the price is around 600 NOK.

A [map of downtown Trondheim](#) provided by Britannia Hotel. The hotel is on *Dronningens gate*. More information about [Trondheim](#).

IMPORTANT DATES

- 26.10.2010 Reservation of hotel room at Britannia at reduced rate ends
- 09.11.2010 Registration for participation at the workshop ends
- 16.11.2010 Submission of one-page abstract for contributors is closed
- 19.11.2010 Final program and book of abstracts is available as a pdf-file
- 22-23.11.2010 Workshop

SPONSORS

- [The Centre for Theoretical and Computational Chemistry \(CTCC\)](#)
- [NTNU through the research program in Computational Science and Visualisation](#)

CONTACT

Per-Olof Åstrand: per-olof.aastrand@chem.ntnu.no

NORWEGIAN CHEMICAL SOCIETY

Annual meeting in Computational Chemistry

PROGRAM

Monday 22.11.2010

09.30	Coffee	
10.00	Per-Olof Åstrand	Welcome
Chairman:	Trygve Helgaker	
10.00	Hans Agren	Towards effective modelling design of biomolecular probes: EPR, NMR and NLO (abstract)
10.40	Petr Stepanek	Monitoring of molecular interactions by optical spectroscopies (abstract)
11.00	Radovan Bast	Calculation of magneto-electric birefringences (abstract)
11.20	Magnus Ringholm	Analytic calculations of hyper-Raman spectra (abstract)
11.40	Mahmoud Abu-samha	Alignment-dependent ionization of linear molecules in intense laser fields (abstract)
12.00	Lunch	
Chairman:	Henrik Koch	
13.00	Christian Thaulow	Atomistic Modelling of Materials Failure (abstract)
13.40	Anton Simakov	Energetics and mechanisms of the unimolecular dissociation of the protonated trioses (abstract)
14.00	Arne Joakim Bunkan	Radical reactions of CH ₂ NH in the atmosphere (abstract)
14.20	Mayuri Gupta	Computational study of pKa and Carbamate stability constant values, for amines important in Post Combustion CO ₂ Capture Process (abstract)
14.40	Alexey Zatula	Quantum chemical insight into proton transfer and structural rearrangements in reactions between HSO ₄ ⁻ (H ₂ O) _n and D ₂ O (abstract)
15.00	Break	
Chairman:	Einar Uggerud	
15.30	Signe Kjelstrup	Development of nonequilibrium thermodynamics theory using molecular dynamics simulations (abstract)
16.10	Stefan Andersson	A combined quantum chemistry and computational fluid dynamics study of silicon dioxide and NO _x production in exhaust gas from silicon furnaces (abstract)
16.30	Sondre Schnell	Thermodynamics of small systems in the μVT ensemble (abstract)
16.50	Dick Bedeaux	Transport coefficients of n-butane into and through the surface of silicalite-1 from non-equilibrium molecular dynamics study (abstract)
17.10	Jiayang Wu	Mechanical properties of polyethylene nanosphere: A molecular dynamics study (abstract)
17.30	Break	<i>Annual meeting in Norwegian Chemical Society, Division of Computational Chemistry</i>
Chairman:	Eirik Falck da Silva	
18.20	Andy Teale	Using Wave-function Approaches to Provide Insight into Density-Functional Theory: An Adiabatic Connection Approach (abstract)
18.40	Marie Døvre Strømsheim	Perspectives on Dispersion in Density-Functional Theory (abstract)
19.00	Kai Kaarvann Lange	Electronic Excitations in Strong Magnetic Fields (abstract)
19.20	Marco Anelli	Frequency-dependent magnetizability (abstract)

19.40	<i>End of session</i>	
20.00	<i>Dinner</i>	

Tuesday 23.11.2010

Chairman:	Knut J. Børve	
08.30	Ole Martin Løvvik	Thermoelectric materials – electronic transport calculations and assessments of solubility and diffusivity (abstract)
09.10	Beate Larsen	A theoretical study of the zinc oxide cluster models of CPO-27-Zn (abstract)
09.30	Taku Onishi	Hybrid-DFT study on ion conductive perovskites (abstract)
09.50	Li-Ming Yang	Computational simulations on the metal-organic framework: UiO-66 (abstract)
10.10	<i>Break</i>	
Chairman:	Signe Kjelstrup	
10.40	Bruno Cardey	Ferriheme-nitrite interactions: Linkage Isomerism and Reaction with NO (abstract)
11.00	Vincent Leroux	Molecular modeling of protein-carbohydrate systems: Preliminary molecular dynamics study of Cholera Toxin Bsubunit (CTB) / GM1 pentasaccharide complexes (abstract)
11.20	Anders Lervik	Heat transfer in soft nanoscale interfaces (abstract)
11.40	Kirill Glavatskiy	Molecular simulations of gas hydrates (abstract)
12.00	<i>Lunch</i>	
Chairman:	Kenneth Ruud	
13.00	Mark Hoffmann	Advances in Generalized Van Vleck variant of Multireference Perturbation Theory (abstract)
13.40	Adam Chamberlin	The importance of relativistic effects on (hyper)polarizabilities (abstract)
14.00	Vaclav Profant	Dependence of polyproline ROA on the peptide length (abstract)
14.20	Clemens Woywod	On the systematic construction of vibronic coupling Hamiltonians (abstract)
14.40	Nils Kristian Jordheim	Photoelectron spectroscopy, a new technique for studying molecular conformations (abstract)
15.00	<i>Break</i>	
Chairman:	Luca Frediani	
15.30	Thomas Bondo Pedersen	Linear Scaling Density Fitting using Cholesky Decomposition (abstract)
15.50	Simen Reine	Efficient density-functional theory force evaluation for large molecular systems - recent developments in DALTON (abstract)
16.10	Patrick Merlot	Pair-Atomic Resolution-of-the-Identity (abstract)
16.30	Thomas Kjærgaard	The Divide-Expand-Consolidate DEC coupled cluster (CC) model: A black box linear-scaling approach with correlation energy-based error control (abstract)
16.50	Stig Rune Jensen	Parallel performance of MRCPP (abstract)
17.10	Bin Gao	GEN1INT: An object-oriented library to evaluate one-electron integrals and their derivatives (abstract)
17.30	<i>End of meeting</i>	

Towards effective modelling design of biomolecular probes: EPR, NMR and NLO

Hans Ågren

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In this talk I will highlight the use of multi-scale/multi-physics approaches that combine quantum mechanics (QM) with other physical principles, like wave mechanics, molecular dynamics and dielectric theory, for applications of molecular interactions and properties. Our earlier research has mostly addressed organic and organometallic compounds and semiconductor quantum particles, like quantum dots. With the combination of QM and wave mechanics we study optical control of strong laser pulses, in particular pulse propagation in non-linear media [1]. We address the optical transmission from cross sections of multi-photon absorption processes and from considerations of propagation effects, saturation and pulse effects. With the combination of QM and molecular dynamics we study nonlinear optical properties of polymeric guest-host systems [2]. The modeling involves quantum chemistry calculations to predict the properties of a single chromophore molecule and molecular dynamics simulations to model the macroscopic optical properties of the guest-host systems and to elucidate the microscopic origin behind the macroscopic properties.

In recent time we have extended this work to consider the quantum mechanics molecular dynamics response approach of Mikkelsen, Kongsted and coworkers [3] where the full QM and MM interactions are accounted for in the evaluation of a given property. The underlying structures and trajectories are obtained by molecular dynamics or Car-Parinello-MM methods. In the talk I highlight recent results on solvatochromatic effects, non-linear optical processes, EPR and NMR parameters in solution [4,5]. Some first results on protein environments are given, and a discussion on the proper MM parameterization of such environments, for effective calculations is discussed in connection to that.

[1] A. Baev, P. Salek, F. Gelmukhanov, and H. Agren, *J. Phys. Chem. B*, 110, 5379 (2006).

[2] Y. Tu, Y. Luo, and H. Agren, *J. Phys. Chem. B*, 110, 8971 (2006).

[3] Nielsen CB, Christiansen O, Mikkelsen KV, Kongsted J, *J. Chem. Phys.*, 126:154112 (2007).

[4] N.A. Murugan, J. Kongsted, Z. Rinkevicius, and H. Agren, *Proc. Acad. Nat. Science*, 107, 16453 (2010).

[5] N.A. Murugan, J. Kongsted, Z. Rinkevicius, and H. Agren, *Phys. Chem. Chem. Phys.* 00, 000 (2010).

Monitoring of Molecular Interactions by Optical Spectroscopies

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b) Institute of Organic Chemistry and Biochemistry, Prague 6, 166 10, Czech Republic

Chiral ruthenium complexes with chelating ligands received attention due to their ability to bind to specific DNA sequences.

We have synthesized simple model chiral enantiomeric complexes Δ -[Ru(bpy)₂phen](PF₆)₂ and Λ -[Ru(bpy)₂phen](PF₆)₂, and characterized the products using ECD (electronic circular dichroism), VCD (vibrational circular dichroism), IR (infrared), UV-VIS (ultraviolet-visible) absorption spectroscopy. We interpreted the measured spectra on the basis of the theoretical ones obtained by quantum chemical calculations.

We also investigated interactions of the synthesized ruthenium complexes with different derivatives of guanine. The ECD spectra of a mixture of the ruthenium complex with guanine derivatives exhibited concentration dependent spectral changes. These changes were attributed to association of cationic complexes with anionic guanine derivatives. The changes in spectra were gradual, and we were not able to isolate spectra of individual chemical species, whose linear combination would yield the observed signal. Instead, these changes seemed to be caused by a gradual change in electronic structure of the complexes caused by the guanine derivatives.

The different rates of change for different derivatives are also discussed in terms of electronic structure of the derivatives. Interpretation of the spectra suggests that the charge distribution plays major role in the interaction between the complex and guanine derivatives molecules.

Calculation of magneto-electric birefringences

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Antonio Rizzo

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Trygve Helgaker

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In our contribution we present the first study of relativistic effects on the electric-field-gradient-induced birefringence (Buckingham birefringence) for the series of molecules CX_2 ($X=O, S, Se, Te$). Using the OpenRSP [1] and XCFun [2] libraries we extend a recently presented atomic-orbital-driven scheme for the calculation of time-dependent molecular properties using one-, two- and four-component relativistic wave functions [3], to include frequency-dependent magnetic field perturbations to first order, using London atomic orbitals to ensure gauge origin independence of the calculated results. Results are presented both at the Hartree–Fock and Kohn–Sham density functional level of theory.

- [1] A. J. Thorvaldsen, K. Ruud, K. Kristensen, P. Jørgensen, S. Coriani, *J. Chem. Phys.* **129**, 214108 (2008).
- [2] U. Ekström, L. Visscher, R. Bast, A. J. Thorvaldsen, K. Ruud, *J. Chem. Theory Comput.*, **6**, 1971 (2010).
- [3] R. Bast, A. J. Thorvaldsen, M. Ringholm, K. Ruud, *Chem. Phys.* **356**, 177 (2009).

Analytic calculations of hyper-Raman spectra

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Vibrational hyper-Raman (hR) spectroscopy is related to its well-known Raman counterpart, and these phenomena are in several ways analogous, but the selection rules for each are different. In the commonly used double-harmonic approximation, the Raman selection rule for a vibrational mode is $\partial\alpha/\partial Q_a \neq 0$, where α is the molecular electronic polarizability and Q_a is the normal coordinate of mode a . The corresponding hR selection rule is $\partial\beta/\partial Q_a \neq 0$, where β is the molecular electronic first hyperpolarizability. This means that modes that are “dark” in one spectroscopy can show a nonzero signal in the other, and hR spectroscopy can therefore be a useful addition to regular Raman (and IR) spectroscopy [1].

We present analytic hR spectra in the double-harmonic approximation for benzonitrile and RDX, calculated within the open-ended response formalism of A. J. Thorvaldsen *et al.* [2] The levels of theory currently supported in this scheme correspond to those in calculations made in 2006 [1], but the present code is formulated in the atomic orbital (AO) basis, thereby enabling the possibility of using linearly scaling procedures in future work.

We also present suggestions for improved accuracy and spectral detail by the use of upcoming developments in the open-ended response code. These improvements include:

- The inclusion of electrical and mechanical anharmonicity by double perturbation treatment [3], using high-order energy and polarization property derivatives such as cubic force constants and second geometrical derivatives of β .
- Correction of fundamental normal mode frequencies using high-order energy derivatives.
- Treatment of both frequency [4] and intensity effects associated with Fermi resonances between overtones/combination frequencies and fundamental frequencies.
- DFT response properties using upcoming developments for high-order XC derivatives in the XCFun library [5-6].

[1] Quinet, O. Champagne, B., and Rodriguez, V.: *J. Chem. Phys.* **124**, 244312 (2006)

[2] Thorvaldsen, A. J., Ruud, K., Kristensen, K., Jørgensen, P., and Coriani, S.: *J. Chem. Phys.* **129**, 214108 (2008)

[3] Bishop, D. M. and Kirtman, B.: *J. Chem. Phys.* **95**, 2646 (1991)

[4] Martin, J. M. L., Lee, T. J., Taylor, P. R., François J.-P., *J. Chem. Phys.* **103**, 2589 (1995)

[5] Ekström, U., Visscher, L., Bast, R., Thorvaldsen, A. J., Ruud, K.: *J. Chem. Theory Comput.* **6**, 1971 (2010)

[6] Ekström, U., XCFun library, <http://www.admol.org/xcfun> (2010)

Alignment-dependent ionization of linear molecules in intense laser fields

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b) Department of Chemistry, University of Bergen, Postboks 7803, 5020 Bergen, Norway.

In the past couple of years, several experiments emerged on strong-field ionization from aligned molecules, where the molecular axis is fixed at a particular angle relative to the laser polarization axis. Total ionization yields were measured as a function of alignment angle for ionization from the highest occupied molecular orbital (HOMO) of N₂, O₂, and CO₂ (Fig. 1). The experimental results were modeled using the molecular tunneling theory (MO-ADK), a semi-classical approach that disregards the molecular potential. For N and O₂, very good agreement is found between the MO-ADK predictions and the experiment. For CO₂, on the other hand, the MO-ADK predicted the maximum ionization yield at an alignment angle of 24 deg, in disagreement with the experimental ionization peak at 45 deg (cf. Fig. 1). The discrepancy between the MO-ADK results and the experiment is attributed partly to inaccurate asymptotic expansion coefficients of the HOMO wave function, which are used as input for MO-ADK. Using wave functions with a better asymptotic form in the MO-ADK analysis results in a maximum ionization yield for CO₂ at about 35 deg, still in disagreement with the experiment. By solving the 3D time-dependent Schrödinger equation (TDSE) for the HOMO electron of CO₂ within the single-active-electron and the frozen nuclei approximations, the maximum ionization yield for CO₂ is found at about 45 deg, in agreement with the experiment. The TDSE results demonstrate an important contribution from the excited states of the molecular potential in strong-field ionization of CO₂, and, therefore, explain the breakdown of the molecular tunneling theory.

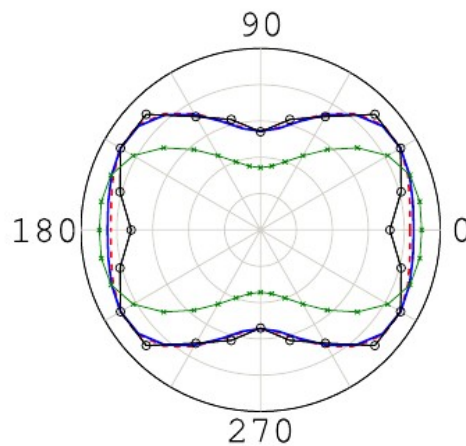


FIG. 1: Experimental (circles) and theoretical (dashed line: 5.6×10^{13} W/cm²; solid line: 1.1×10^{14} W/cm²; crosses: MO-ADK) total ionization yield from the HOMO orbital of CO₂.

Atomistic Modeling of Materials Failure

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Whether a material is ductile or brittle depends on the competition of intrinsic material parameters (such as the energy required creating new surfaces versus the energy required to initiate shearing of the lattice to form and move a dislocation). The type of mechanical failure response will be controlled by the temperature and deformation rate. Experimental studies of single crystal silicon with pre-cracks have shown that at temperatures below about 850K the material tends to be extremely brittle, while it exhibits ductile behavior above this temperature. Several explanations have been proposed; however, thus far no direct atomistic level understanding exists about the underlying process that leads to BDT in silicon. This progress has been hindered partly due to lack of atomistic models that enable the simulation of sufficiently large systems to accurately describe the fracture process.

Describing bond breaking processes in silicon has required quantum mechanical (QM) methods to properly describe the complex electronic rearrangements that determine the barriers and hence rates. However, quantum mechanics calculations for large system sizes that would be required to describe the complex details of bond rearrangements under large stresses are currently impractical. In this investigation we apply an alternative approach; the first principles based ReaxFF reactive force field, which retains nearly the accuracy of QM, even for bond breaking events. The ReaxFF parameters are determined by fitting QM-data on silicon and allow us to directly simulate BDT.

By solely raising the temperature in a series of computational experiments with otherwise identical boundary conditions, we observe a sudden change from brittle to ductile behavior between 880 K and 890 K, drastically changing the material in a very narrow ≈ 10 K temperature regime. Our studies elucidate a cascade of atomic mechanism that control the occurrence of the BDT. We find that at elevated temperatures, the formation of a small amorphous region at an atomically sharp crack tip creates a cleavage ledge at the crack tip, inducing local mode II (shear) stresses at the crack tip, which in turns leads to dislocation emission. Our results address provide a fundamental understanding of the link between stress the crack tip geometry, associated structural changes under temperature variations, and the overall mechanical behavior of a solid. Our simulations provides important insight into the atomistic-level mechanism of the brittle-to-ductile transition in silicon, with relevance for other materials that undergo BDT.

Energetics and mechanisms of the unimolecular dissociation of the protonated trioses

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The most basic units of biologically important carbohydrates ($C_m(H_2O)_n$) – monosaccharides – can be viewed as oligomers and polymers of formaldehyde, $(CH_2O)_n$. In living organisms monosaccharides acts both as energy carriers and key components of information storage molecules.

The belief that monosaccharides are built up by formaldehyde units is not a theoretical construction. Butlerov demonstrated in 1861 that formaldehyde oligomerizes into glycoaldehyde, glyceraldehyde and higher carbohydrates in basic solution, the so-called formose reaction.

The paradigm of interstellar and prebiotic chemistry is that life evolved from small molecules that formed larger molecules. The question arises if there exist gas phase ion-molecule reactions analogous to the formose reaction, in other words if there exist interstellar pathways to sugar molecules.

We used a rewarding strategy, studied the reverse reaction – the spontaneous unimolecular dissociation of the target molecule. In this way, possible reactant molecules leading to the target may be identified, and details of the energy landscape of the reactions may be revealed.

The acid catalysed formose reaction may become feasible once the other reactant has a carbon atom of opposite polarity to formaldehyde. This is possible for other aldehydes but formaldehyde, and the principle is utilized in the well known aldol reaction. In order to test out this hypothesis we have studied the fragmentation characteristics of the higher homologues, protonated glyceraldehyde and protonated dihydroxyacetone.

Our study is twofold, applying mass spectrometry to provide experimental evidence and performing a computational quantum chemical survey of the appropriate potential energy surfaces.

According to a theoretical model provided formaldehyde loss is dominating, in full agreement with experimental observation. The reverse process



is found to be obstructed by a barrier of 20 kJmol^{-1} , which will effectively block it out under interstellar conditions. On the other hand the complementary reaction



faces no such barrier.

Radical reactions of CH₂NH in the atmosphere.

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University of Oslo, Norway*

A CO₂ post combustion capture facility employing amine technology is under construction at Mongstad. Given the scale of implementation of post-combustion CCS, it is likely that there will be relatively small but still significant discharges of amines to the atmosphere during operation. There is also the potential for larger scale accidental discharges. CH₃NH₂, (CH₃)₂NH, (CH₃)₃N, are among the process degradation products of the more complex amines used in CO₂ capture, and will therefore always be emitted with the cleaned flue gas to the atmosphere no matter which parent amine is used in the absorber.

CH₂NH is identified as a major photo-oxidation product from CH₃NH₂. Possible atmospheric sinks are reactions with OH, Cl and hydrolysis.

Results from CASPT2, CCSD and CCSD(T) calculations on the OH + CH₂NH reaction system are presented.

Computational study of pKa and Carbamate stability constant values, for amines important in Post Combustion CO₂ Capture Process

Mayuri Gupta^{a)}, Eirik Falck Da Silva^{b)}, Hallvard F. Svendsen^{a)}

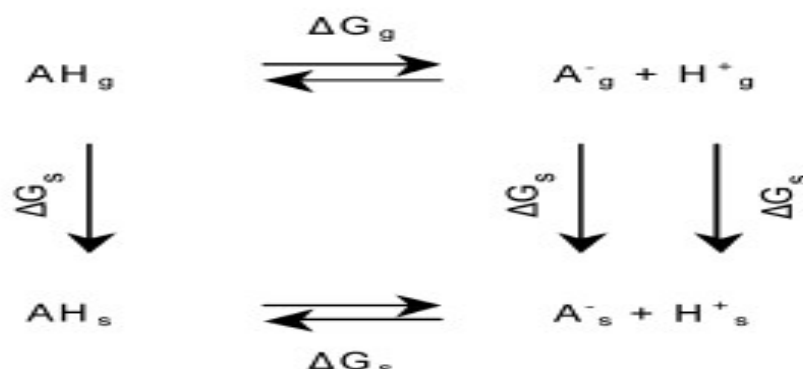
a) Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway b) Process Technology, SINTEF Materials and Chemistry, Trondheim, Norway

Temperature dependency of piperazine and related amines in the temperature range 298-393 K is studied using density functional theoretical calculations. B3LYP functional and 6-311++G (d, p) basis set was used in all the calculations.

The gas-phase acidity (ΔG) is defined as the Gibbs free energy change of the following equilibrium:

$$\Delta G = G(A_{g^-}) + G(H_{g^+}) - G(AH_g) \quad (1)$$

The value of Gibbs free energy of the proton in the gas phase is set to -6.29 kcal/mol using translational entropy calculated according to the well-known Sackur-Tetrode equation. The solution phase free energy for proton is -263.977 kcal/mol in this work. Absolute pKa calculations are based on the following thermodynamic cycle:



The following relations were applied to calculate the pKa:

$$pK_a = (1 / 2.303 RT) \Delta G_{ps} \quad (2)$$

$$\Delta G_{ps} = G(A_{g^-}) + G(H_{g^+}) - G(AH_g) + RT \ln(24.46) + \Delta G_s(A^-) + \Delta G_s(H^+) - \Delta G_s(AH) \quad (3)$$

From the pKa and carbamate formation reaction energy values it can be seen that the structural changes of amines have a critical effect on their behavior and that it varies significantly with temperature. Equilibrium temperature sensitivity of key reactions like pKa and carbamate formation plays an important role in determining which solvents are suitable for CO₂ capture. The higher the pKa value of amine, the higher its sensitivity towards temperature changes. The stronger the changes in pKa value and carbamate stability constant with temperature, the more it would be regarded as a promising solvent for acid gas capture. The PCM model for solvation energies provides a good basis for calculating the effect of solvation of amines and we propose that the differences in temperature dependency observed can be attributed to the small variations in their structures.

Quantum chemical insight into proton transfer and structural rearrangements in reactions between $\text{HSO}_4^-(\text{H}_2\text{O})_n$ and D_2O

A.S. Zatula, E. Uggerud

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Sulfuric acid (both neutral and ionic forms) play a central role in gas-phase nucleation mechanisms, and is widely considered to be a key precursor of cluster formation and eventual droplet growth, under favorable conditions, including also the upper troposphere. Small aqueous clusters grow faster around molecule ions than neutral molecules due to the strong ion dipole interaction, and bisulphate anion is no exception. Moreover, hydration of sulfuric acid itself possesses many interesting aspects of fundamental nature, both in terms of specific solvation and acid/base behavior. For example, sulfuric acid has several binding sites for hydrogen bonding, acting both as a proton donor and a proton acceptor.

The present investigation aims at understanding the initial stages of water cluster formation from the bisulphate ion, emphasizing the size dependent properties, in particular structural rearrangements of bisulphate ion water clusters related to proton transfer processes. This insight will be obtained by studying hydrogen/deuterium exchange reactions of $\text{HSO}_4^-(\text{H}_2\text{O})_n$ clusters with D_2O in the gas phase under near thermal conditions.

We report the results of an experimental study of H/D-exchange in reactions between $\text{HSO}_4^-(\text{H}_2\text{O})_n$ ($n = 1 - 25$) with D_2O , done in modified quadrupole/time-of-flight mass spectrometer equipped with electrospray source (QTOF2, Micromass). According to our mass-spectrometric experiments, for small bisulphate water clusters (up to $n=8$), reacting with D_2O , the dominating reaction is $\text{D}_2\text{O}/\text{H}_2\text{O}$ ligand swap. For larger clusters ($n>8$) the situation is very different, and H/D exchange is observed to be swift. This reaction has been found to be proton catalyzed. This, generally speaking, is a good example of size-dependent properties.

A series of quantum-chemical calculations (B3LYP/6-311++G(2d,2p), using GAUSSIAN09) has been conducted to obtain better insight into the experimental results. The quantum chemical calculations have been concentrated around the energetics and structures of relatively small bisulphate water clusters $\text{HSO}_4^-(\text{H}_2\text{O})_n$ ($n = 1 - 10$). They show that ability of proton to migrate between the water part of the cluster and HSO_4^- core determines the amount of H/D exchange, and this property is essentially size-dependent when it comes to bisulphate clusters. Based on our calculations we suggest an original see-saw mechanism to explain how proton mobility, and thereby H/D exchange takes place.

Development of nonequilibrium thermodynamics theory using molecular dynamics simulations

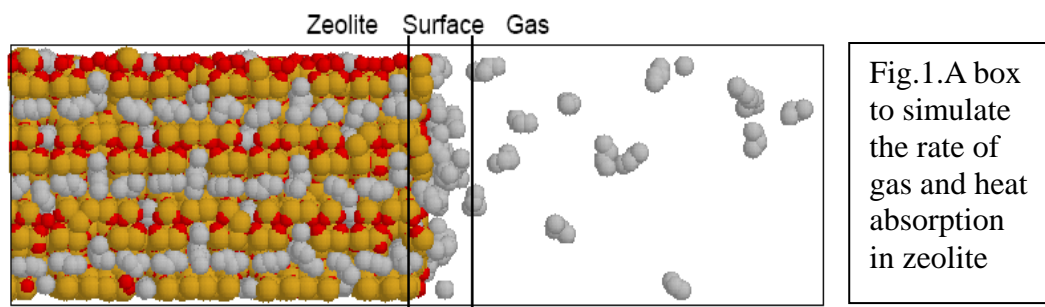
S.Kjelstrup

Department of chemistry, Norwegian University of Science and Technology, Trondheim

Nonequilibrium molecular dynamics simulations was set up in our group in the early 1990'ies to help explain experimental results for transport coefficients and to answer questions arising in theory developments, see [1] for a review. In the development of nonequilibrium thermodynamics theory for heterogeneous systems [2], this technique in combination with equilibrium simulation techniques like Monte Carlo methods, has proven indispensable. The lecture will present evidence obtained over the years for validity of basic assumptions in Nonequilibrium thermodynamic theory, namely

- the assumption of local equilibrium,
- the assumption of linear, homogeneous flux-force relations
- the symmetry of the set of transport equations (Onsager symmetry relations)

Results will be shown that enable us to use this thermodynamic theory in systems exposed to external fields with magnitude larger than those common in the laboratory, in industry, or in nature. Local equilibrium holds e.g. in systems that contain as few as 10 particles in the stationary state. The evidence is encouraging for the possibility to obtain a dynamic description with basis in the second law of thermodynamics, also for processes on the nanoscale where fields are strong, like in biology, in nanomachines, reactions in flames, phase transitions, nucleation or heterogenous catalysis.



The lecture will present simulation results for the common liquid-vapor phase transition, the adsorption into a typical zeolite (illustrated in Fig.1), and for a chemical reaction in a flame, and show that the nonequilibrium thermodynamic description is valid and also that this description, which is rooted in the second law, gives new insight.

Acknowledgement: The Research Council of Norway is thanked especially for a Storforsk grant which enabled focussed free research over many of the last years.

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A combined quantum chemistry and computational fluid dynamics study of silicon dioxide and NO_x production in exhaust gas from silicon furnaces

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Silicon is produced on an industrial scale by heating quartz with coal, coke, or wood in a furnace. The gas released from the process consists of large amounts of CO, with smaller amounts of H₂O, SiO and other species. This gas is burnt in the furnace hood where it meets an inflow of air. The resulting exhaust gas consists of, e.g., CO₂, SiO₂ particles (silica dust), and NO_x. Emissions of the latter two species have been found to be strongly correlated. Numerical modeling of the combustion process, including gas flow and chemistry, is an attractive way of understanding this correlation and to design measures to reduce emissions, especially NO_x.

Unfortunately, there is a complete lack of reliable experimental rate data on the gas phase formation of SiO₂, i.e., reactions of SiO with O₂, OH, and other oxygen-bearing species. In an effort to rectify this, we have aimed to obtain estimates of the rate constants in the relevant temperature range of the most important SiO₂ forming reactions using DFT and CCSD(T) calculations coupled to Transition State Theory rate calculations. To assess the quality of the calculated rate constants, we have also studied the analogous reactions of CO leading to CO₂. Agreement with available experiments is good and the calculated rate constants are thus considered to be reliable. These are included in the reaction scheme together with tabulated rate constants for other important gas phase reactions.

Computational Fluid Dynamics, CFD, is used to model the combustion process, i.e., flow, heat transfer, and thermochemistry in 3D space. Conservative transport equations for mass, momentum, and energy are discretized onto a computational mesh describing the geometry. Since the flow is highly turbulent, a time averaging procedure of the relevant equations is used and turbulent mixing effects are taken into account by turbulence modeling (k - ε - standard model). The equations are coupled with a chemistry solver to account for formation and destruction of species due to chemical reactions. For combustion, the Eddy Dissipation Concept, EDC, is used where the reaction rate becomes a function of turbulent mixing and Arrhenius expressions. A steady-state solution with thermodynamic and chemical equilibrium is found. The CFD simulations have been performed with and without the SiO₂ forming reactions included.

The results indicate that the formation of NO_x and SiO₂ particles cannot be treated separately. Rather, the reactions responsible for SiO₂ formation also drive the NO_x formation, e.g., through the release of O atoms and heat release in secondary reactions with H₂O and CO. This gives an order of magnitude larger NO_x production rate than in the case without SiO₂ formation included, in very good agreement with measurements on the industrial setup. This is the first time the correlation between NO_x and SiO₂ dust formation has been quantified using simulations.

Thermodynamics of small systems in the μVT ensemble

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Due to advances in experimental techniques, processes and phenomena occurring at the nanoscale is now more available than ever. In fact, we can distinguish ensembles of particles on individual basis by taking images of them. Colloids, surfaces, and other systems on the nano-scale are getting more and more attention from the research community. However, thermodynamics on the small scale is different from thermodynamics in a macroscopic system, but the limit for when a system is small is often not well defined. Terrell L. Hill[1] proposed to use a correction for the size of the small system, thereby developing a tool that can make it possible to describe small systems using a correction to the more familiar thermodynamic equations.

Based on the guidelines proposed by Hill[1], we have developed a simple non-real model for a small system in the μVT ensemble, taking into account only the surface interaction of a small system. This model has been used to derive the finite size dependence of thermodynamic variables in μVT ensemble.

The size dependence of a system in the grand-canonical ensemble is found to be proportional to the inverse length of the system, $1/L$ for all thermodynamic properties. We use molecular simulations in the grand-canonical ensemble to calculate the thermodynamic correction factor, Γ , and the enthalpy, \bar{h} , for a range of small systems in the grand-canonical ensemble. Our numerical results unambiguously show that in order to obtain the correct macroscopic thermodynamics properties finite-size scaling should be used.

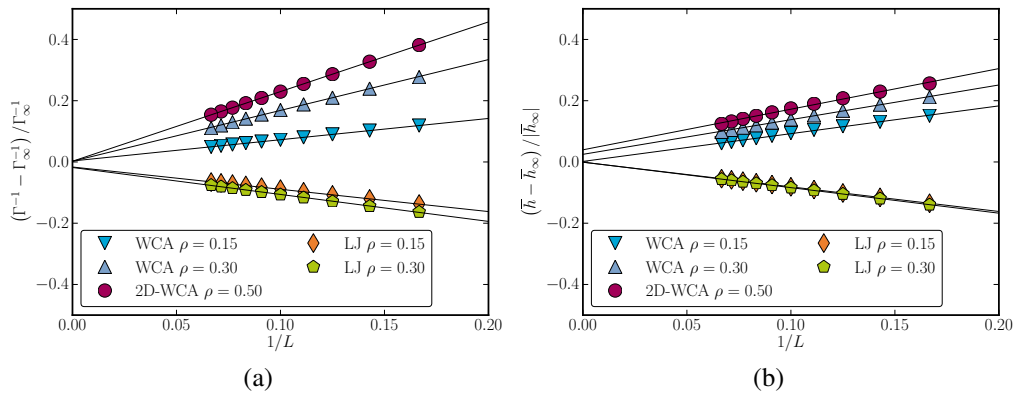


Figure 1: The relative difference between the macroscopic system and a range of small systems. (a) is the difference for the thermodynamic correction factor, while (b) is for the enthalpy.

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Transport coefficients of *n*-butane into and through the surface of silicalite-1 from non-equilibrium molecular dynamics study

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The aim of this work was to investigate the transport properties into and through the surface of a zeolitic material. As a model system we have chosen an important system, namely silicalite-1 in contact with *n*-butane gas.

Gradients of temperature and concentrations were created across the surface using non-equilibrium molecular dynamics algorithms developed for the purpose. A description of the surface was given using non-equilibrium thermodynamics.

A comparison between equilibrium and non-equilibrium results confirmed that the surface was in local equilibrium and could be regarded as a thermodynamic system.

For the first time, coefficients for the coupled transport of heat and mass were reported for a zeolite-gas interface.

Three independent coefficients were found for transport across the whole surface: the resistance to heat transfer, the coupling coefficient and the resistance to mass transfer. All resistances were significant, and showed that the surface acted as a barrier to transport.

A new scheme was devised to find the enthalpy of adsorption from two measurable heats of transfer for the whole surface using either the heat fluxes on the gas or the zeolite sides. The method yielded the enthalpy of adsorption as a function of the excess surface concentration and surface temperature.

A further inspection of the surface, regarded as a series of two resistances, one on the gas and one on the zeolite side was made. It showed that the gas side of the surface dominated the overall resistance to heat transfer, while the zeolite side, which was characterized by negative excess concentrations, dominated the overall resistivity to mass transfer and determined the value of the coupling coefficient.

The coefficients were found not to be sensitive to the surface structure, whether it was flat, or zig-zag textured.

The findings may help reduce adsorption data from experiments on zeolites and other porous materials.

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Mechanical properties of polyethylene nanosphere: A molecular dynamics study

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ABSTRACT

Compression behaviours of polyethylene/Ni-polyethylene nanosphere have been studied by molecular dynamics simulations. Semi-crystalline lattice method is employed to generate the dense and entangled polyethylene nanosphere on a spherical diamond lattice with diameter $d=20\text{nm}$. The results show that compression force-strain behavior of the polyethylene nanosphere is temperature dependent - the lower, the stiffer. The end-to-end distance of intermolecules becomes longer with the increase of compression strain. The nickel coating strongly strengthens the polyethylene nanosphere - the more thickness of nickel layer, the stronger it behaves.

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Using Wave-function Approaches to Provide Insight into Density-Functional Theory: An Adiabatic Connection Approach

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The adiabatic connection (AC) [1, 2, 3, 4] provides a link between the non-interacting Kohn–Sham (KS) system and physical interacting system via a series of partially interacting systems described by the Hamiltonians and wave-functions

$$H_\lambda[v] = T + \sum_i v(\mathbf{r}_i) + W_\lambda \quad H_\lambda[v]\Psi_\lambda = E_\lambda[v]\Psi_\lambda \quad (1)$$

Where λ is the coupling strength ($\lambda = 0$ for the KS system), T is the kinetic energy operator, the external potential $v(\mathbf{r})$ is adjusted such that the density remains fixed at the physical ($\lambda = 1$) density for all λ values and W_λ is a coupling strength dependent two-electron interaction operator. Following Lieb’s formulation of density-functional theory [5] the energy $E_\lambda[v]$ may be expressed in terms of a convex conjugate functional $F_\lambda[\rho]$, the universal density functional.

$$E_\lambda[v] = \inf_\rho \left(F_\lambda[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right) \quad F_\lambda[\rho] = \sup_v \left(E_\lambda[v] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \right) \quad (2)$$

By choosing a wave-function model, for the calculation of $E_\lambda^{\text{mod}}[v]$ and $\Psi_\lambda^{\text{mod}}$, a hierarchy of universal density functionals $F_\lambda^{\text{mod}}[\rho]$ may be established, which systematically approach the exact universal density functional for each coupling strength λ . In this talk we review our implementation of a scheme to perform the Lieb maximization for $F_\lambda[\rho]$ [6, 7, 8]. The correlation energy of KS-DFT is then recovered by the coupling constant integral

$$E_{c,\lambda}[\rho] = \int_0^\lambda \left\langle \Psi_\lambda \left| \frac{dW_\lambda}{d\lambda} \right| \Psi_\lambda \right\rangle - \left\langle \Psi_0 \left| \frac{dW_\lambda}{d\lambda} \right| \Psi_0 \right\rangle d\lambda \quad (3)$$

The choice of the interaction W_λ specifies the path of the integration and the relevance of this choice to range-separated exchange–correlation functionals will be discussed [9]. Recent efforts and future prospects for utilizing the calculated ACs for the construction of new exchange–correlation functionals for practical calculation will be outlined [10].

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Perspectives on Dispersion in Density-Functional Theory

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The failures of existing density functionals to describe the dispersion interaction are well documented in the literature. The helium dimer serves as a prototypical system to illustrate many aspects of this interaction and has been previously studied within Hartree-Fock-Kohn-Sham Density-Functional Theory (HF-KS-DFT) by Allen and Tozer [1] from the perspective of the Hellmann-Feynman electrostatic theorem. From this view point the dispersion force arises from subtle density distortions in the vicinity of each atom due to the presence of other distant atoms. The result being a net attractive force due to the nucleus being attracted towards the distorted density in its own vicinity.

In the present work the dispersion interaction has been studied within the usual KS-DFT formalism through Lieb maximization [2] at the CCSD(T) level [3, 4, 5]. When applied to the non-interacting system this procedure brings the calculations of Ref. [1] into the KS-DFT formalism, where the exchange contribution to the Kohn-Sham matrix is given by a multiplicative potential. Particular care has been taken in order to ensure that the Hellmann-Feynman electrostatic theorem holds and to this end floating centers [6] have been used in the wave-function optimization and subsequent BSSE correction of the potential energy curves presented here. Whilst calculations on the non-interacting system yield Kohn-Sham exchange-correlation potentials, orbitals and orbital energies, no information on the dispersion contribution to Kohn-Sham exchange-correlation energies is returned. To provide additional energetic information the Lieb maximization is generalized to arbitrary electronic interaction strengths, allowing the adiabatic connections (ACs) [7, 8, 9, 10] for the interaction energies to be calculated.

Recently, empirical dispersion DFT-D corrections constructed by Grimme [11] have proved popular to correct existing functionals to account for dispersion. The advantages and disadvantages of these methods are discussed in light of the presented adiabatic connection analysis. Prospects for "Double-Hybrid" approaches such as B2PLYP [12] and a self-consistent OEP(B2PLYP) implementation will also be discussed.

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Electronic Excitations in Strong Magnetic Fields

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The London program is a code designed for solving quantum chemical problems involving molecules in very strong magnetic fields. Magnetic properties are determined non-perturbatively, and associated gauge-origin problems are avoided by employing London orbitals instead of the traditional Gaussian orbitals commonly used.

In this work, a solver for determining electronic excitation energies in the Random Phase Approximation (RPA) has been implemented in the London code, applicable to restricted, unrestricted and generalized Hartree–Fock wave functions. The RPA generalized eigenvalue problem is solved in the atomic orbital basis using a subspace-accelerated iterative procedure that yields excitation energies and corresponding excitation operator matrices. From these matrices associated transition properties are calculated.

Some illustrative applications of the code are presented, focusing on basis set convergence of transition and excited state properties with London orbitals compared to Gaussian orbitals.

This work discuss the theory of the magnetizability. Magnetizability is a molecular property defined as the second-order perturbation in the energy in the presence of an external magnetic field. When the magnetic field is static, perturbation and multipole theories lead to an origin-independent expression of the magnetizability, whereas for a frequency-dependent magnetic field its expression result to be origin-dependent. Since in the static case magnetizability is an observable quantity, the expression obtained in the dynamic case is clearly unphysical. My work discuss several approaches in order to solve this issue. Magnetizability has been analyzed in the microscopic case, within both the non-relativistic and the relativistic framework. The expression of the magnetizability proposed by Raab and de Lange has been considered, pointing out the weak points of their non-relativistic theory, and trying to recover an alternative expression in the relativistic framework. The macroscopic case has also been discussed in detail, and an origin-independent expression of the inverse permeability has been derived within a fully relativistic approach. The problem to find an origin-independent expression of the magnetizability in the microscopic case remain unresolved, but the results obtained in the macroscopic case and the analysis done so far are good starting points for further studies, and suggest to work in the relativistic framework.

Thermoelectric materials – electronic transport calculations and assessments of solubility and diffusivity

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Thermoelectric materials are solid state heat engines where electrons are the working fluid. They can be used to generate electric power from temperature gradients, or to provide efficient cooling or heating from electricity. They scale very well with size, and require virtually no maintenance, and are thus promising for a large range of potential applications.

It is a challenge to maximize the performance of thermoelectric devices. This requires simultaneous optimization of fundamental transport properties, which to a certain extent are interdependent. Parameter-free modelling studies can assist in the understanding of how this can be accomplished, as well as predicting novel materials with enhanced properties.

This presentation will demonstrate how band-structure calculations can be used to assess fundamental transport properties of Zn_4Sb_3 . This is a promising material in this respect, due to its extraordinarily low thermal conductivity. This reduces Ohmic losses, and makes this material one of the most efficient ones for thermoelectricity.

One of the important transport properties of the material is the Seebeck coefficient α , which relates the voltage over a material ΔV with the temperature difference ΔT between the warm and cold end: $\Delta V = \alpha \Delta T$. We show how this can be calculated, and how it is strongly correlated with the geometric structure on the atomic scale. We also show how our calculations can be coupled with experimental data on the same system.

A theoretical study of the zinc oxide cluster models of CPO-27-Zn

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Zinc oxide is a well-known semi-conductor with a wide, size-dependent band gap of 3.37 eV and lots of effort has been put in to tune the band gap by changing the particle size [1]. Recently, it has attracted a lot of attention because of its unique catalytic, electrical, and optoelectronic properties [2] as well as LED applications and piezoelectric and pyroelectric properties [3]. Clusters possess different properties compared to bulk and film due to the size effect and a large surface-to-volume ratio [4], and they are essential for the development of fundamental understanding of materials at nanoscale.

Porous materials are applicable for gas storage and adsorption because of high surface area and pore volume [6]. In this presentation, the main focus will be on the microporous coordination polymer $\text{Zn}_2(\text{dhtp})\cdot(\text{H}_2\text{O})_2\cdot 8\text{H}_2\text{O}$, hereafter termed CPO-27-Zn, which was first prepared by Dietzel et. al in 2007 [5]. Each zinc atom is coordinated by six oxygen atoms where five stem from the organic ligand 2,5-dihydroxoterephthalic acid (dhtp) and the remaining oxygen stem from the water molecule resulting in infinite, one-dimensional, helical chains of *cis*-edge sharing ZnO_6 octahedra, which are linked by the organic ligand in such a way that a six-ring chelate complex is formed, resembling a honeycomb (fig. 1). Upon heating, the coordination number of Zn is reduced to five as the water molecule is removed, thereby changing the coordination polyhedra from octahedra to square pyramids. Because the unit cell of CPO-27-Zn contains a large number of atoms, there is a need to make smaller cluster models that will be representative for the system. A major part of the project is to achieve knowledge about how the HOMO-LUMO gap changes with the ZnO chain length and the size of the organic ligand. The cluster calculations will be performed using Gaussian and ADF (Amsterdam Density Functional) and the periodic calculations using VASP (Vienna Ab-initio Simulation Package).

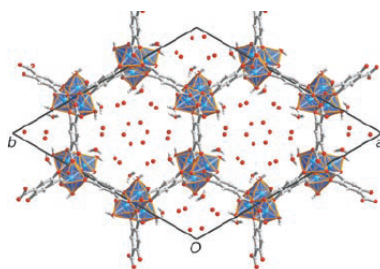


Figure 1: Unit cell of the crystal structure of CPO-27-Zn along [001]. The figure is taken from ref. [6].

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Hybrid-DFT study on ion conductive perovskites

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Abstract

Many perovskite-type compounds are expected as the ion conductive materials. First, we talk about our calculation results of the oxide ion conductive LaAlO_3 perovskite [1]. In order to clarify the oxide ion conductive mechanism in LaAlO_3 perovskite, hybrid-DFT calculations were performed for Onishi Ionics Model ($\text{La}_2\text{Al}_4\text{O}_3$ model). It was discovered that A-site counter cation forms the chemical bonding with conductive oxide ion (O_{cond}). We concluded that the obtained potential energy curve for oxide ion conduction can be explained by two factors such as $\text{La-O}_{\text{cond}}$ bond formation and $\text{Al-O}_{\text{cond}}\text{-Al}$ bond breaking. We will also talk about our calculation results for the lithium ion conductive perovskite [2-3].

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Computational simulations on the metal-organic framework: UiO-66

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Metal-organic frameworks (MOFs) constitute a new generation of porous crystals. They can be described as crystalline hybrid inorganic/organic solids with structures which are composed of clusters of a few metallic atoms held together in a three-dimensional structure by organic linkers. This class of compounds has the remarkable advantage of combining both organic and inorganic fragments as part of the same structure. The remarkable crystallinity of MOF structures defines pores and cavities on the nanometric scale. The possibility for guest molecules to enter the internal voids of MOFs, frequently of high volume, causes these materials in many respects to resemble the behavior of zeolites. However, MOFs are attractive not only because of the structural diversity that they provide, but also because of their remarkable physico-chemical properties. Currently, MOFs are considered as important materials of academic interests and with possible industrial applications within catalysis, petrochemistry, gas adsorption and storage (e.g., H₂, CH₄, CO₂, etc.), selective separation, sensing, molecular recognition, and so on.

However, MOFs have applications limited to the gas adsorption and separation due to the weakness and lack of fundamental understanding and detailed knowledge of the relationship between structure and properties from experiments.

On the other hand, computational chemistry and physics have made dramatic advances in the past two decades, enabling the prediction of novel molecules and exotic extended structures that often contradict the chemical and physical intuitions. Many theoretical chemists and physicists have participated in this endeavor by proposing myriads of unusual molecules and bulk solid structures. The computational simulations are powerful tool to predict new materials as well as their properties and get insight into the prerequisite experimental aspects. Most of the publications relating to MOFs are experimental in nature owing to the fact that the number of atoms involved in simulations is much greater than that in many other materials. Thousands of different MOFs have been synthesized so far. However, the enormous number of different possible MOFs means that purely experimental means for screening or designing optimal MOFs for targeted applications is inefficient. Atomic-level simulations provide a means to complement experimental methods for identifying potential MOFs.

This presentation will demonstrate how the computational simulations correct the experimental MOF structures and provide detailed knowledge of electric structure, chemical bonding, optical properties. This may shed insight into the potential synthesis and application of novel and stable MOFs.

Ferriheme-nitrite interactions: Linkage Isomerism and Reaction with NO

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X-ray crystallography studies have shown that nitrite binds to the *met* form of human hemoglobin and horse heart myoglobin via the *O*-nitrito mode, which may be contrasted with the *N*-nitrito or “nitro” mode found in synthetic model complexes.¹ To explain the difference, we have studied the different linkage isomers as well as their interconversion pathways (transition states) with extensive DFT model studies.

Heme models of various complexities, ranging from a simple porphyrin to a 119-atom hemoglobin active site model, helped us quantify the environmental effects that influence on the nitrite binding mode. The distal histidine residue (and its protonation state), in particular, appears to be critical in this regard. Solvation also a significant, but more limited effect.

We have also studied the reaction of ferriheme-nitrite with NO, leading to N_2O_3 , which has been proposed as the NO carrier between red blood cells and the endothelium, the site of vasodilation. Highlights from an extensive series of computationally explored pathways will be presented.

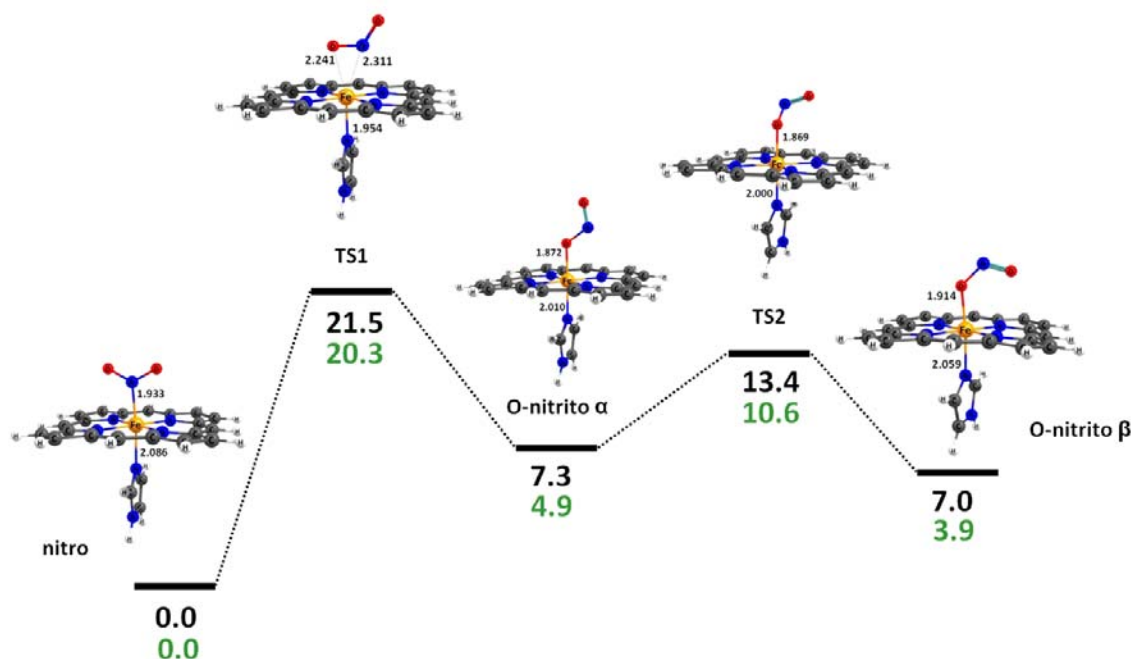


Fig.1. Relative electronic (in black) and Gibbs free (in green) energies in kcal/mol of the 3 heme-nitrite linkage isomers and of the 2 isomerization transition states.

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Molecular modeling of protein-carbohydrate systems: Preliminary molecular dynamics study of Cholera Toxin B- subunit (CTB) / G_{M1} pentasaccharide complexes

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Cholera¹ is a life-threatening diarrhea- and dehydration-inducing infection caused by the *Vibrio cholerae* bacteria, primarily due to the consumption of contaminated water and/or food. It is worldwide-spread since two centuries and did not show any sign of decrease in recent times. On the contrary, environmental factors correlated to climate change are expected to escalate the threat², as demonstrated by the occurring Haiti outbreak.

One of the key steps in cholera human infection is the internalization of a well structurally-described toxin of the AB₅ family, the Cholera Toxin (CT), which starts with the binding of its B-subunit pentamer (CTB) to G_{M1} gangliosides lining the surface of intestinal cells. The first results of a molecular modeling study targeting this protein-carbohydrate system are presented here.

Structural glycobiology is a young discipline in the biochemistry field that has raised great interest in recent years. Its molecular modeling division is significantly less mature than the modeling of other kinds of biomolecules, but its developments are promising.³ Polysaccharides such as G_{M1} are especially challenging due to their significantly greater conformational fluctuations compared to short peptides. Starting from good quality crystallographic data, 8 structures corresponding to the CTB genotypes of current active toxic strains were modeled in explicit solvent, then submitted to extensive molecular dynamics simulations.

The results provide more precise knowledge on the properties of the CTB/G_{M1} systems, and constitute reference data for further computer-aided investigations. Recent experimental findings reinforced the hypothesis of a molecular origin of the blood group dependence that is observed for cholera². We hope that molecular modeling works will improve the significance of ongoing experimental structural biology investigations.

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Heat transfer in soft nanoscale interfaces

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Abstract

Nanoscale interfaces offer tremendous opportunities to design high performance materials, for instance, materials with enhanced thermal properties as in *nanofluids*. A paradigm of a nanoscale interface is a nanoparticle suspension, where the solvent/nanoparticle interface has a typical size of the order of 10^2 – 10^3 nm². There is currently a vigorous research activity on nanoparticle-interface related problems. Due to their small dimensions the nanoparticles' properties depart significantly from those observed in macroscopic materials. The interface between the material, e.g., nanoparticle, and the solution, becomes increasingly important on the nanoscale. Hence, it is expected that for very small particles (few nm diameter) the thermal transport will be strongly dependent on the properties of the interfaces and therefore, it will be different from heat transfer in macroscopic systems, where interfaces become less relevant as compared with bulk effects.

We have investigated [1] the heat-transfer through nanometer-scale interfaces consisting of *n*-decane (2–12 nm diameter) droplets in water using transient non-equilibrium molecular-dynamics simulations (NEMD). We have obtained the temperature relaxation of heated nanodroplets as a function of time and we have computed the thermal conductivity and the interfacial conductance of the droplet and the droplet/water interface respectively. We find that the thermal conductivity of the *n*-decane droplets is insensitive to droplet size, whereas the interfacial conductance shows a strong dependence on the droplet radius, and we rationalize this behavior in terms of a modification of the *n*-decane/water surface-tension with droplet curvature.

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Molecular simulations of gas hydrates

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Gas hydrates are solid materials, which consist of water molecules forming cages, so that single gas molecules can be trapped into those cages. The favorable interactions between water and the guest molecules make these formations stable. Methane and Carbon dioxide are typical gases, which can form the hydrates. One of the main goals of our study is to understand the ways to extract methane as an energy source from oceanic sediments and store the carbon dioxide from the atmosphere. We study the stability of hydrates under different external conditions and with different gas inclusions with the help of Monte-Carlo adsorption simulations.

Advances in Generalized Van Vleck variant of Multireference Perturbation Theory

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A new, second-order, multiconfigurational, multireference perturbation method for molecular electronic structure, based on Generalized Van Vleck Perturbation Theory (GVVPT2), has been suggested and computationally implemented [1,2]. Through use of a combination of a multireference extension to degeneracy corrected perturbation theory and nonlinear responses to perturbations, the method is in principle stable for any degree of quasidegeneracy and is rigorously continuous and thus can be used to describe entire potential energy surfaces. The formalism can use either complete or incomplete model (or reference) spaces, and is limited, in this regard, only by the capabilities of the MCSCF program. The third-order method, GVVPT3, has also been obtained and shown to be capable of describing well the very difficult electronic structure problems for which GVVPT2 is less accurate than usual. The method makes use of the recently introduced concept of macroconfigurations, which allows arbitrarily complex incomplete model spaces to be used efficiently. Exploiting the capability of using very large one-electron active spaces, the method has been applied to problematic ground and excited electronic states of unsaturated, highly strained ring systems, such as CF₂O₂ and CF₂N₂, and to the debated ground state of Co₂.

Recently, a Lagrangian based approach has been suggested to obtain analytic formulas for GVVPT2 energy nuclear gradients and nonadiabatic coupling terms [3]. Trial calculations were performed and compared with finite difference calculations on several molecules and demonstrate that the GVVPT2 gradients are accurate. Of particular interest, the suggested formalism can straightforwardly use state-averaged MCSCF descriptions of the reference space in which the states have arbitrary weights. This capability is demonstrated by some calculations on the ground and first excited singlet states of LiH, including calculations near an avoided crossing. The formalism for nonadiabatic coupling shares many structural features with the energy gradient formalism, with the use of a function that corresponds to the energy for the coupling.

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The importance of relativistic effects on (hyper)polarizabilities

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While the inclusion of relativistic effects in heavier elements is prevalent throughout the literature, the inclusion of these effects for higher order response properties has hardly been investigated. A code has been recently developed by Thorvaldsen *et al.*[1,2] to compute these high order properties with relativistic effects included. Here we will be using the code to investigate the effects of relativity on the 1st, 2nd, and 3rd order response, that is the polarizability, and the 1st and 2nd hyperpolarizabilities respectively, of the furan, thiophene, selenophene, and tellurophene series with and without the inclusion of pure vibrational effects. We find that with increasing size of the heteroatom, the relativistic effects increase with the scalar relativistic effects dramatically outpacing the spin-orbital coupling effects. Additionally the 2nd and 3rd order properties are considerably more sensitive to these effects than the 1st order response, with the 2nd order response being nominally more sensitive. We also investigated the pure vibrational corrections to the 3rd order response and found that the vibrational corrections were much more sensitive to the effects of relativity than the electronic component of the hyperpolarizability.

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Dependence of polyproline ROA on the peptide length

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Polyproline-II helical conformation (PPII) represents a less common protein secondary structure. Its structure is rather specific because there are no internal stabilizing hydrogen bonds in it. The rigidity of the helix is caused only by sterical reasons and the interaction with surrounding solvent molecules. Number of recently discovered evidence [1] has lead to a presupposition that the PPII helix is the main element of the random-coil protein structure. This information provides a new reason to study PPII conformation and specifically problematic of its formation, which has not been thoroughly studied yet.

In our experiment we measured Raman and Raman optical activity (ROA) spectra of several oligo- and poly-L-proline samples in a wide frequency range between 120 cm^{-1} and 1800 cm^{-1} and analyzed them with respect to the length of the proline chain. The relatively new technique of ROA [2,3], which is based on a different interaction of a specimen with the right- and left-handed circularly polarized laser light, represented an ideal methodology for this type of observation due to its high sensitivity to the conformational stability and rigidity of peptide chain backbone. There is also a strong link to previous experiments [4] which were focused on the characterization of proline side chain conformation and its interaction with solvent.

So far, we were able to determine the characteristic spectral peaks associated with formation of stable PPII helical conformation in studied systems. The most relevant peaks are located at 405 , 535 and 945 cm^{-1} . Moreover, based on our experimental data analysis we were able to determine the minimal length of (L-proline)_N chain necessary for creation of the stable PPII conformation as $N=6$ [5].

The stress is laid on the interconnection between experimental and theoretical approach. For that purpose we perform *ab initio* calculations of ROA spectral bands and their intensities for all measured samples in order to obtain more accurate interpretation of recorded spectra and observed phenomena.

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On the systematic construction of vibronic coupling Hamiltonians

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Abstract

Vibronic coupling phenomena are playing an important role in molecular spectroscopy. This leads to a considerable interest in the development of quantum-mechanical and mixed quantum-classical methods for the treatment of nonadiabatic processes. Information on the dependence of the energies of the relevant adiabatic electronic states on the nuclear coordinates represents a key component for the construction of any Hamiltonian for the description of vibronic coupling dynamics. We will focus in particular on two aspects that are important for the derivation of accurate approximations of the potential energy surfaces with *ab initio* electronic structure methods: (i) The consistency of the approach with respect to the determination of normal coordinates and of excited state energies. (ii) We investigate the effects of neglecting or taking into account the curvilinear nature of normal coordinates on the parametrization of the potential energy functions. The system at the center of this study is the “hydrogen atom of vibronic coupling theory”: pyrazine. More specifically, we are interested in the vibronic interaction between the S_1 and S_2 states of this molecule.

Photoelectron spectroscopy, a new technique for studying molecular conformations

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The use of carbon 1s photoelectron spectroscopy as a method for determining the conformational distribution of a chemical compound is discussed with application to a series of substituted propenes. The method relies on quantum chemical calculations for predicting shifts in ionisation energies between conformers and vibrational Franck-Condon profiles for the lineshape of photoelectron spectra.

Linear Scaling Density Fitting using Cholesky Decomposition

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The essence of density fitting (DF) is the exploitation of linear dependence in the direct product space of atomic orbitals (AOs). Specifically, products of AOs are expanded in an auxiliary basis set according to

$$\chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) \approx \sum_J \phi_J(\mathbf{r})C_{\mu\nu}^J \quad (1)$$

Like AO basis sets, auxiliary basis sets are usually composed of (Gaussian) functions centered on the nuclei. The auxiliary basis set is thus distributed over the entire molecule, making the fitting procedure nonlocal in general.

The computational cost of the fit is formally cubic with respect to system size, although prescreening gives essentially quadratic scaling in practice. Different techniques have been suggested to reduce the computational scaling to linear, including local fitting metrics and domain fitting. An alternative approach based on the inherent locality of auxiliary basis sets derived from Cholesky decompositions of subblocks of the molecular integral matrix is presented. It is demonstrated that only auxiliary functions centered on the same two nuclei as the AOs are needed to give an accurate fit. Leading to a trivially linear-scaling calculation of fitting coefficients, this procedure offers complete error control provided that two-center auxiliary functions are included.

Efficient density-functional theory force evaluation for large molecular systems - recent developments in DALTON

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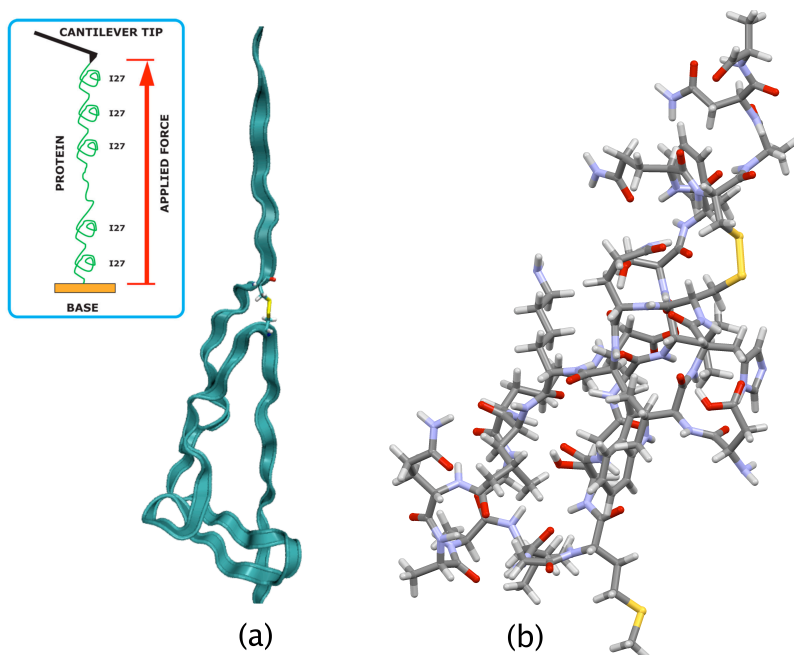
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In this talk we report recent developments in DALTON for the efficient evaluation of density-functional theory forces. The new developments are based upon a novel integral evaluation scheme¹ and density-fitting and linear-scaling technology². The efficiency and linear complexity of the molecular-force evaluation is demonstrated by sample calculations on molecular systems containing up to 642 atoms, and for the geometry optimization of a few selected large systems containing up to 392 atoms.



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Pair-Atomic Resolution-of-the-Identity

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The resolution-of-the-identity (RI) approximation [1, 2], or the density-fitting approximation, is today accepted as an efficient way to approximate the four-center two-electron integrals of the electron-electron Coulomb repulsion contribution appearing in Hartree-Fock and DFT. In the last two decades similar approximations have received significant attention also for the general application to four-center two-electron integrals, as for example for the exact exchange [3] and various correlated wave-function methods [4, 5]. For small to medium sized systems the extension of the RI approximation to general four-center two-electron integrals gives speed-ups comparable with that of the Coulomb repulsion contribution, at negligible loss of computational accuracy, whereas for larger systems the cost of these methods becomes increasingly expensive. The steep increase in computational cost is due to the non-local nature of the fitting procedures used today [6], in which a product of two basis functions (pair product) are approximated by auxiliary basis functions spanning the whole molecular system. As the size of the molecular system grows, the number of auxiliary functions included in an approximation of each pair-product increases proportionally.

In this presentation, we explore the pair-atomic resolution-of-the-identity (PARI) approximation, in which each pair-product is approximated by auxiliary basis functions centered only on the two parent atoms of the two basis-functions forming the pair product. We demonstrate the computational efficiency of the PARI approximation applied to the exact exchange contribution, and discuss both the accuracy of the presented results as well as the prospects for further extensions of this scheme to correlated wave-function treatment.

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The Divide-Expand-Consolidate DEC coupled cluster (CC) model: A black box linear-scaling approach with correlation energy-based error control

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We describe the Divide-Expand-Consolidate (DEC) coupled cluster (CC) model [1], where a full HartreeFock reference CC calculation on a molecular system is carried out in terms of CC calculations on small orbital fragments of the total molecular system. The orbital fragmentation does not involve physical bond cuts or a priori assignments of local orbital spaces. Rather it involves a splitting of the correlation energy into orbital fragment contributions where the sizes of the orbital fragment spaces are determined in a black box manner to ensure that the CC correlation energy is calculated to a preset energy threshold. This is possible because the least-change molecular (LCM) basis is employed, where both occupied and virtual orbitals are local. The number of independent fragment calculations scales linearly with the system size, making the method linearly scaling and embarrassingly parallelizable. We present a thorough locality analysis of the amplitude equations for second order Møller-Plesset perturbation theory (MP2) and the coupled cluster singles doubles (CCSD) model, which demonstrate that the amplitude equations are indeed local when expressed in the LCM basis. The locality analysis is supported by numerical results.

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Parallel performance of MRCPP

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The MultiResolution Chemistry Program Package (MRCPP) is a quantum chemistry code based on multiwavelet functions. As for finite element bases the 3D coordinate space is partitioned in cubic cells, but multiwavelet theory provide the tools to make the representations adaptive, based on a strict and controlled accuracy criterion.

Essential to any computational chemistry code is the ability to solve the Poisson (1) and Kohn-Sham (2) equations:

$$\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \quad (1)$$

$$[\nabla^2 + V_\rho(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \quad \rho(\mathbf{r}) = \sum_{i=0}^{N/2} 2\|\psi_i\|^2 \quad (2)$$

By rewriting the Poisson and Kohn-Sham equations in their integral form using Greens functions (see equations below), we avoid the use of derivatives, which is not suited for finite element bases.

$$V(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{s})\rho(\mathbf{s})d\mathbf{s} \quad (3)$$

$$\psi_i(\mathbf{r}) = \int H^{(\epsilon_i)}(\mathbf{r}, \mathbf{s})V(\mathbf{s})\psi_i(\mathbf{s})d\mathbf{s} \quad (4)$$

The formally non-local integral operators decay rapidly to negligible values away from the main diagonal, yielding an effectively banded structure where the band size is only dictated by the requested accuracy. This sparse operator structure gives prospects of linear scaling algorithms, and is crucial for efficient parallel implementations.

A shared memory (OpenMP) parallelization of this code has been achieved, but this strategy has some limitations, as the maximum number of shared memory CPUs in todays clusters is limited. Moreover, the relatively large memory requirements demand the use of a distributed memory (MPI) strategy, where different parts of the function is located on different MPI hosts. This will inevitably lead to some communication overhead since the operator will couple terms across MPI domain boundaries, but its banded structure should limit this communication to close neighbors. This ultimately allows for parallel algorithms with good scaling behavior with respect to the number of CPUs.

We present a hybrid MPI/OpenMP implementation where we combine the fast memory access of OpenMP, with the massively distributed parallelization of MPI.

GEN1INT: An object-oriented library to evaluate one-electron integrals and their derivatives

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We have recently proposed a procedure for evaluating one-electron integrals and their geometric derivatives by using a generalized one-electron operator that is the product of four factors: (1) a scalar $(X_\kappa - X_\lambda)^{K_x}(Y_\kappa - Y_\lambda)^{K_y}(Z_\kappa - Z_\lambda)^{K_z}$ depending on the relative displacement of the two basis function centers \mathbf{R}_κ and \mathbf{R}_λ , typically arising from the differentiation of London atomic-orbitals (LAO) with respect to the external magnetic field; (2) a multipole-moment operator $(x - M_x)^{m_x}(y - M_y)^{m_y}(z - M_z)^{m_z}$ around the origin \mathbf{M} , arising from the differentiation with respect to the external electric field; (3) an arbitrary central-potential operator $f(|\mathbf{r} - \mathbf{C}|)$ around center \mathbf{C} , and (4) an electronic differential operator $(\partial/\partial x)^{n_x}(\partial/\partial y)^{n_y}(\partial/\partial z)^{n_z}$ [1]. This procedure has been extended in a more recent work [2] by including molecular magnetic properties, leading-order relativistic corrections from the one-electron part of Breit–Pauli Hamiltonian, effective core potential, and model core potential (Version 1). The evaluation of these integrals is performed by using LAOs to ensure the origin independence. The derivatives of the integrals with respect to the external electric and magnetic fields, nuclear point magnetic moment, and geometry perturbation have been thoroughly considered, and implemented in an open-ended integral library GEN1INT.

In this presentation, I would like to briefly describe the theoretical background of this integral library GEN1INT, and then focus on its structures, functionalities and limitations, usage and performance. The purpose of this presentation is to make this library be known and useful in the quantum chemistry community.

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Advances in Generalized Van Vleck variant of Multireference Perturbation Theory ([abstract](#))
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Thermodynamics of small systems in the μVT ensemble ([abstract](#))
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Towards effective modelling design of biomolecular probes: EPR, NMR and NLO ([abstract](#))

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- **Trygve Helgaker**
- **Thomas Kjærgaard**, *The Divide-Expand-Consolidate DEC coupled cluster (CC) model: A black box linear-scaling approach with correlation energy-based error control* ([abstract](#))
- **Kai Kaarvann Lange**, *Electronic excitations in strong magnetic fields* ([abstract](#))
- **Beate Larsen**, (NKS member), *A theoretical study of the zinc oxide cluster models of CPO-27-Zn* ([abstract](#))
- **Vincent Leroux**, (NKS member), *Molecular modeling of protein-carbohydrate systems: Preliminary molecular dynamics study of Cholera Toxin Bsubunit (CTB) / GM1 pentasaccharide complexes* ([abstract](#))
- **Patrick Merlot**, (NKS member), *Pair-Atomic Resolution-of-the-Identity* ([abstract](#))
- **Taku Onishi**, *Hybrid-DFT study on ion conductive perovskites* ([abstract](#))
- **Thomas Bondo Pedersen**, (NKS member), *Local Density Fitting using Cholesky Decomposition* ([abstract](#))
- **Michal Przybytek**
- **Simen Reine**, (NKS member), *Efficient density-functional theory force evaluation for large molecular systems - recent developments in DALTON* ([abstract](#))
- **Vladimir Rybkin**
- **Anton Simakov**, *Energetics and mechanisms of the unimolecular dissociation of the protonated trioses* ([abstract](#))
- **Marie Døvre Strømsheim**, (NKS member), *Perspectives on Dispersion in Density-Functional Theory* ([abstract](#))
- **Yizhen Tang**
- **Andy Teale**, (NKS member), *Using Wave-function Approaches to Provide Insight into Density-Functional Theory: An Adiabatic Connection Approach* ([abstract](#))
- **Erik Tellgren**
- **Einar Uggerud**, (NKS member)
- **Li-Ming Yang**, *Computational simulations on the metal-organic framework: UiO-66* ([abstract](#))
- **Alexey Zatula**, *Quantum chemical insight into proton transfer and structural rearrangements in reactions between $HSO_4^-(H_2O)_n$ and D_2O* ([abstract](#))

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- **Marco Anelli**, *Frequency-dependent magnetizability* ([abstract](#))
- **Radovan Bast**, *Calculation of magneto-electric birefringences* ([abstract](#))
- **Bruno Cardey**, *Ferriheme-nitrite interactions: Linkage Isomerism and Reaction with NO* ([abstract](#))

- **Adam Chamberlin**, *The importance of relativistic effects on (hyper)polarizabilities* ([abstract](#))
- **András Csehi**
- **Luca Frediani**, (NKS member)
- **Bin Gao**, (NKS member), *Gen1Int: An object-oriented library to evaluate one-electron integrals and their derivatives* ([abstract](#))
- **Kathrin Hopmann**, (NKS member)
- **Stig Rune Jensen**, (NKS member), *Parallel performance of MRCPP* ([abstract](#))
- **Dan Jonsson**, (NKS member)
- **Ying-Chan Lin**
- **Krzysztof Mozgawa**, (NKS member)
- **Vaclav Profant**, *Dependence of polyproline ROA on the peptide length* ([abstract](#))
- **Magnus Ringholm**, (NKS member), *Analytic calculations of hyper-Raman spectra* ([abstract](#))
- **Kenneth Ruud**, (NKS member)
- **Arnfinn Hykkerud Steindal**, (NKS member)
- **Petr Stepanek**, *Monitoring of molecular interactions by optical spectroscopies* ([abstract](#))
- **Ville Weijo**
- **Clemens Woywod**, (NKS member), *On the systematic construction of vibronic coupling Hamiltonians* ([abstract](#))

SINTEF Materials and Chemistry

- **Stefan Andersson**, (NKS member), *A combined quantum chemistry and computational fluid dynamics study of silicon dioxide and NO_x production in exhaust gas from silicon furnaces* ([abstract](#))
- **Ole Martin Løvvik**, *Thermoelectric materials – electronic transport calculations and assessments of solubility and diffusivity* ([abstract](#))
- **Eirik Falck da Silva**
- **Per-Erik Larsson**

Department of Engineering Design and Materials, NTNU

- **Christian Thaulow**, *Atomistic Modelling of Materials Failure* ([abstract](#))

Department of Structural Engineering, NTNU

- **Jianyang Wu**, *Mechanical properties of polyethylene nanosphere: A molecular dynamics study* ([abstract](#))

Department of Chemical Engineering, NTNU

- **Mayuri Gupta**, *Computational study of pKa and Carbamate stability constant values, for amines important in Post Combustion CO₂ Capture Process* ([abstract](#))

Department of Chemistry, NTNU

- **Bjørn K. Alsberg**
- **Dick Bedeaux**, *Transport coefficients of n-butane into and through the surface of silicalite-1 from a non-equilibrium molecular dynamics study* ([abstract](#))
- **Martin Folke Emdal**
- **Kirill Glavatskiy**, *Molecular simulations of gas hydrates* ([abstract](#))
- **Eirik Hjertenes**
- **Signe Kjelstrup**, (NKS member), *Development of nonequilibrium thermodynamics theory using molecular dynamics simulations* ([abstract](#))
- **Henrik Koch**
- **Alexander Kolstad**
- **Marie Jacobsen Lauvås**
- **Anders Lervik**, *Heat transfer in soft nanoscale interfaces* ([abstract](#))
- **Miriam Mekki**
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