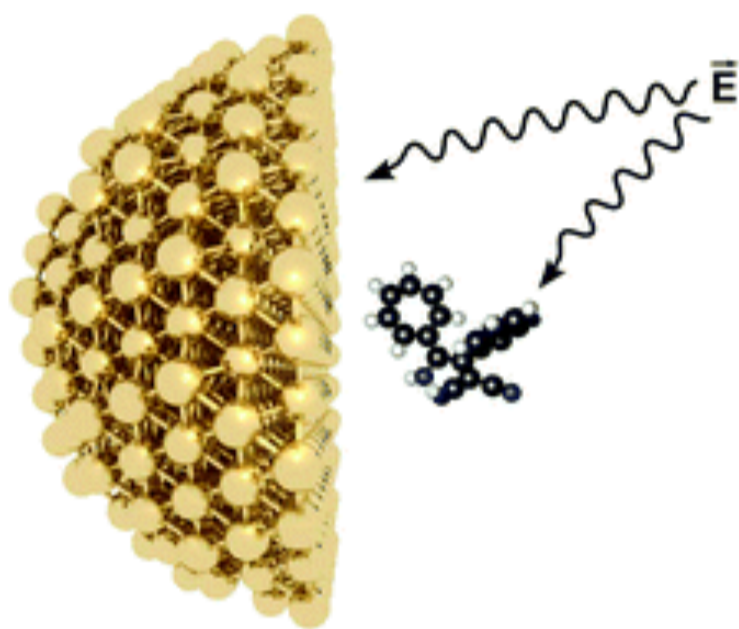# Grand Challenges for Theoretical Chemistry

A conference on the occasion of Prof. Dr. Scient. Kurt V. Mikkelsen's 60th birthday

**August 19th-21st, 2019
Konventum, Helsingør**

CARLSBERG FOUNDATION

UNIVERSITY OF
COPENHAGEN

Grand Challenges for Theoretical Chemistry

The conference *Grand Challenges for Theoretical Chemistry* is organized 19-21 August 2019 on the occasion of the 60th birtday of Prof. Kurt V. Mikkelsen.

Kurt Valentin Mikkelsen, as his full name is, was born 18 May 1959 in Århus, Denmark, where he was also raised. He has his basic university degrees from Aarhus University, a Bach. Scient. in Physics and Chemistry (1982) and a Cand. Scient. in Physics and Chemistry with specialization in Theoretical chemistry (1986). Kurt also did his Ph.D. at Aarhus University with Assoc. Prof. Peter Swanstrøm and Prof. Jan Linderberg as his supervisors, but he spent a major part of the Ph.D. period with Prof. Mark A. Ratner at Northwestern University. He was awarded his Ph.D degree in 1989.

Kurt spent a postdoc with Dr. Marshall D. Newton at Brookhaven National Laboratory. In 1990, he started as an Associate Professor at the Department of Chemistry, University of Copenhagen, but since this position was not permanent he moved to Aarhus University in 1993 for a permanent position. In 1996, he moved back to the University of Copenhagen, where he was awarded a Dr. Scient in 1997 and where he has been Professor since the year 2000.

Kurt has worked in many areas of theoretical and computational chemistry including electron transfer dynamics, models for solvation including both dielectric models and molecular mechanics models for the solvent, modeling photonics and nanoscience, modeling nanoparticles with applications in atmospheric chemistry, and modeling capture and storage of solar energy. Kurt has published over 285 articles along with three text books on molecular dynamics and chemical kinetics. He has so far supervised 30 Ph.D. students and 16 postdocs, in addition to numerous B.Sc. and M.Sc. students. He has over the last 25 years annually organized Ph.D. courses and summer schools.

The content of a conference in honour of Kurt will for obvious reasons be determined by the persons that have been close colleagues with Kurt over the years. When the organizers looked at the list of speakers to invite of which a large portion are experimentalists, we came up with the present title: *Grand Challenges for Theoretical Chemistry*. It embraces many aspects of the subject. There are methodological challenges as for example in accuracy and in the limited system size for present methods. It, however, also includes novel computational chemistry methods in emerging fields like molecular photonics and molecular electronics. Finally, theoretical and computational chemistry should be used to solve chemical problems for example related to atmosperic chemistry as well as solar energy. That this conference in an excellent way covers all these aspects is not a consequence of the selection of speakers by the organizers, it is a consequence of the collaborators and colleagues of Prof. Kurt V. Mikkelsen over the last 35 years. The organizers are grateful for that almost all invited speakers are participating, and we wish everyone a fruitful and enjoyable conference.

Finally, we would to acknowledge a grant from the Carlsberg Foundation allowing us to invite some over-seas speakers as well as reducing the fee for young investigators presenting a poster. Also, University of Copenhagen has provided extensive administrative support.

Thorsten Hansen, Jacob Kongsted, Stephan P. A. Sauer, Per-Olof Åstrand

Grand Challenges for Theoretical Chemistry (GCTC)

A conference on the occasion of Prof. Dr. Scient. Kurt V. Mikkelsen's 60th birthday

Time	Monday 19th Damgaardsalen	Tuesday 20th Damgaardsalen	Wednesday 21st Øresundssalen
9:00 - 9:30	Arrival	**Chairman: Ove Christiansen**	**Chairman: Patrick Norman**
		Sylvio Canuto — Free Energy Gradient method with Average Solvent Electrostatic Configuration for Studying Electronic Properties of Molecules in Solution and in Complex Environment	**Kaline Coutinho** — Conformational Bias Monte Carlo Used to Study the Solvatochromism of Mesityl Oxide
9:30 - 10:00		**Steen Brøndsted Nielsen** Protein biochromophores: What affects their absorption and luminescence?	**Klaus Braagaard Møller** Solvent and solvent-influenced dynamics in theoretical chemistry
10:00 - 10:30		**Jógvan Magnus Haugaard Olsen** Development of Multiscale Methods for Computational Biomolecular Spectroscopy	**Kestutis Aidas** Molecular aggregation in glacial acetic acid: insight from molecular dynamics/quantum mechanics modelling of structural and H-1 NMR properties
10:30 - 11:00		Break	Break
11:00 - 11:30		**Chairman: Peter Ogilby**	**Chairman: Kenneth Ruud**
		Merete Bilde Atmospheric Aerosols – a multifaceted challenge	**Lasse Jensen** Spectroscopy in Inhomogeneous Fields
11:30 - 12:00		**Matthew S. Johnson** Innovation and Atmospheric Science	**Frank Jensen** Describing force field polarization by a bond capacity model
12:00 - 12:30	Lunch	**Jonas Elm** Modelling the Formation and Properties of Atmospheric Molecular Clusters	**Jens Ulstrup** The Au-Sulfur Bond in Electrochemistry and *In Situ* Scanning Tunnelling Microscopy
12:30 - 13:00		Lunch	Lunch
13:00 - 13:30	**13:15 Welcome**		
13:30 - 14:00	**Chairman: Sylvio Canuto**	**Chairman: Jeppe Olsen**	**Chairman: Hans Ågren**
	Marshall Newton Recent challenges and some thoughts regarding charge transfer mechanisms, both homogeneous and interfacial	**Poul Jørgensen** Cluster perturbation theory. A new wave function model in electronic structure theory	**Allan Gross** New Directions in Development of Complex Stiff Chemical Schemes (CSCS)
14:00 - 14:30	**Henrik G. Kjærgaard** Accurate calculation of vibrational transition in a reduced dimensionality model	**Henrik Koch** Recent developments in coupled cluster theory and perspectives for the future	**Mads Koerstz** Chemical Space Exploration
14:30 - 15:00	**Ove Christiansen** New time-dependent wave functions methods: Second Quantization based Time-dependent Hartree and Multi-Configurational extensions and Time-dependent Vibrational Coupled Cluster	**Thomas B. Pedersen** Can coupled-cluster theory describe ultrashort, high-intensity laser-driven electron dynamics?	**Zilvinas Rinkevicius** Quantum chemistry on modern HPC systems: challenges and opportunities
15:00 - 15:30	**Kasper Moth-Poulsen** Molecular solar thermal systems	**Sonia Coriani** Coupled Cluster methods for X-ray spectroscopies	**Theo Kurten** Self-reactions of peroxy radicals: overturning the 60-year old Russell mechanism
15:30 - 16:00	Break	Break	Break
16:00 - 16:30	**Chairman: Jan Linderberg**	**Chairman: Allan Gross**	Departure
	Trygve Helgaker Robust optimization of the density in orbital-free density-functional theory	**Patrick Norman** An unfinished affair with Mikkelsen	
16:30 - 17:00	**Hans Jørgen Aagaard Jensen** Status and perspectives for the multiconfigurational short-range density functional theory method	**Jeppe Olsen** The development and use of wave functions with several sets of optimised orbitals	
17:00 - 17:30	**Kenneth Ruud** Relativistic DFT with periodic boundary conditions	**Peter R. Ogilby** The Oxygen-Organic Molecule Photosystem: Tunneling through Activation Barriers	
17:30 - 18:00	**Hans Ågren** Three things Kurt needs to do before it is too late...	**Mogens Brøndsted Nielsen** Tuning Molecular Properties of the Dihydroazulene/Vinylheptafulvene Photo/Thermoswitch	
19:00 - 20:30 / 20:30	Dinner **Poster session**	**Conference Dinner**	

Abstracts

Invited Talks

Marshall Newton

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For several decades, robust formalisms for modeling charge and exciton transport dynamics and kinetics have been developed and exploited. Now the challenge grows for   accurate modeling of transport in increasingly complex systems. A brief summary of key factors to be defined and formulated in meeting these challenges includes the following:

- **Systems:** homogeneous, interfacial (role of 'Tafel' symmetry); molecular (D,A,B moieties (of arbitrary shape !)), electrodes, solvent or other medium.
- **States:** classical, semiclassical, quantal (electronic, vibrational, vibronic); adiabatic, diabatic; orthogonal/nonorthogonal; localized, delocalized, 'virtual', etc; state density and number of states.
- **Thermodynamics**: energy, free energy, entropy.
- **Processes**: adiabatic, nonadiabatic limits vs intermediate cases; superexchange; thermal, optical, photoinitiated; uni- vs bimolecular; 1,2,… particle (e, H^+ : ET, EET (Foster, Dexter), PCET); role of transition state theory (TST) vs solvent dynamics.
- **Distinct vs Common Underlying Mechanisms.**
- **Timescales** (separated vs overlapping).
- **Reaction Coordinates**: vertical gaps, linear vs nonlinear wrt molecular coordinates; global vs state-dependent (eg, due to change in force constants or polarizability).
- **Modeling Techniques**: analytical vs numerical; continuum vs microscopic levels.

We comment on some recent efforts to deal with such issues, and then give a more detailed account of one particular issue: the degree to which an 'isomorphic' underlying mechanism can be formulated for 1-electron ET and 2-electron (exciton) transfer (JPCB 119, 14728 (2015)).

Accurate calculation of vibrational transitions in a reduced dimensionality model

Henrik G. Kjaergaard

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In atmospheric research, radiative transfer, reaction mechanisms and nucleation are all affected by complex formation. The formation of a molecular complex relies on the Gibbs energy of formation, ΔG, which is difficult to obtain accurately, from pure experimental or theoretical methods. We have developed a combined experimental and theoretical approach with which ΔG of bimolecular complex formation can be determined with an accuracy better than 1 kJ/mol.[1]

To facilitate this, we need to be able to calculate oscillator strengths of the vibrational transitions that are characteristic to the bimolecular complex and which can be measured. We have developed a reduced dimensionality vibrational model within the local mode framework, which can be combined with ab initio methods to calculated oscillator strengths. The accuracy is illustrated by the comparison of fundamental OH-stretching oscillator strengths for a few alcohols.[2,3]
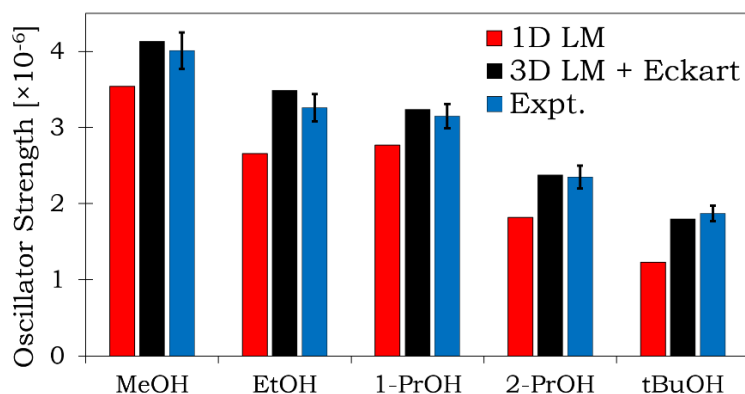
Calculated and experimental OH-stretching fundamental transition intensities. The calculated oscillator strengths are obtained with a 1D OH-stretching LM model and a 3D LM model including the COH-bending and CO-stretching modes and an Eckart correction of the dipole moment surface. Ab initio calculations are at the CCSD(T)-F12a/VDZ-F12 level.

In bimolecular complexes, the 6 intermolecular modes are important to be considered. We have developed a local mode perturbation theory (LMPT) approach that includes both the OH-stretching mode as well as the effect from intramolecular vibrational modes to obtain accurate hydrogen bound OH-stretching intensites.[4,5] More recently, and to avoid problems inherent to perturbation treatments, we include the perturbation via a van Vleck approach. In addition, we use our approach on several vibrational transitions observed for the same complex to improve the ΔG determination.

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New time-dependent wave functions methods:
Second Quantization based Time-dependent Hartree and Multi-Configurational extensions and Time-dependent Vibrational Coupled Cluster

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In this theoretical focused talk I will describe second quantization based formulations of time-dependent wave-functions for describing nuclear motion.

I will describe our work on re-parameterization of the classic time-dependent Hartree (TDH) approach (time-dependent self-consistent field) in terms of second-quantization based exponential parameterization.[1] Although the derivation of the exponential parameterized TDH (X-TDH) is more complicated than for the corresponding linear parameterized TDH (L-TDH), X-TDH can be implemented in a highly efficient manner applicable to thousands of degrees of freedom.
I will briefly describe our initial attemps to generalize our formulation to the case of the well-known[2] Multi-configurational Time-Dependent Hartree approach.

In the second part of the talk I will describe the theory and implementation of a time-dependent vibrational coupled cluster methodology. In analogy to our time-independent vibrational coupled cluster method, we propose an exponential cluster parameterization of the time-dependent wave function. I will discuss some of the issues and peculiarities arising from employing a non-variational wave function approach, and how working equations can be obtained. Initial results will be presented at the two-mode coupling level, TD-VCC[2], which has also applicability to large molecular systems.

Implementation of the methods in our generally available MidasCpp code (midascpp.gitlab.io) is described.

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To be published.

Molecular Solar Thermal Energy Storage Systems

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Norbornadiene (NBD) and its derivatives undergo photoisomerisation to the highly strained quadricyclane (QC). The system is being optimized towards solar energy storage applications, and the best NBD derivatives fulfil several of the requirements for a functional system,[1-5] such as high photoizomerisation quantum yield (up to 99%), red-shifted absorption, high energy storage densities (up to 1 MJ/kg)[3], very long half-life, up to 18 years of storage time[2] and a record temperature gradient of 63°C (83°C measured)[1]. However, several key challenges remain; for example, substituents needed to improve the solar spectrum match and quantum yield of unsubstituted norbornadiene typically reduce the energy density. While unsubstituted norbornadiene is a liquid, most of the higher performing derivatives are solids at room temperature, and the characterization has typically only been done in dilute solution for practical reasons.[4,5] The use of solvents dilutes the effective energy densities of the systems significantly. In this presentation, our efforts in improving the NBD/QC system towards efficient energy storage systems including new ways to improve solar spectrum match and energy storage time without making compromises on energy storage densities will be presented.[5] Moreover, I will present device concepts for lab scale demonstration of solar energy capture (up to 900 cm[2] devices) as well as heat release devices based on molecular photoswitches that perhaps one day can be used in real life application in solar energy storage. Further, a new research direction focusing on integration of these materials into functional coatings for thermal management in windows will be presented.[6]
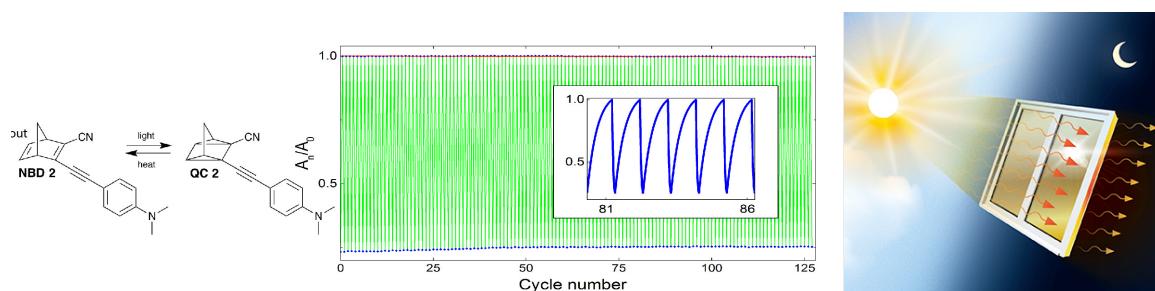
Figure 1. *(Left)) Molecular structure of on NBD/QC photoswitch system. (Centre) Stability test performed at 60 ℃ through 127 energy storage cycles (right) MOST window coating*

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2) *Martyn Jevric, Anne U. Petersen, Mads Mansø, Sandeep Kumar Singh, Zhihang Wang, Ambra Dreos, Christopher Sumby, Mogens Brøndsted Nielsen, Karl Börjesson, Paul Erhart, and Kasper Moth-Poulsen "Norbornadiene-based photoswitches with exceptional combination of solar spectrum match and long term energy storage" Chemistry a European Journal 2018 24 (49), 12767-12772. (frontispiece)*

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5) *Ambra Dreos, Karl Börjesson, Zhihang Wang, Anna Roffey, Zack Norwood, Duncan Kushnir and Kasper Moth-Poulsen "Exploring the potential of a hybrid device combining solar water heating and molecular solar thermal energy storage" Energy and Environmental Science 2017, 10, 728-734. (cover)*

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Robust optimization of the density in orbital-free density-functional theory

Trygve Helgaker,[1] Matthew S. Ryley[2] and Andrew M. Teale[1,2]

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Orbital-free density-functional theory (DFT) is in principle, at least, a linear-scaling quantum mechanical method with an ultra-low computational cost. Indeed, orbital-free DFT has already allowed for the quantum-mechanical treatment of periodic metallic systems with millions of atoms.

The major challenge of orbital-free DFT is the development of accurate kinetic-energy functionals and the optimization of the density for a given number of electrons. We here address the optimization problem, presenting a robust second-order saddle-point method for the simultaneous optimization of the density and chemical potential of molecular electronic systems, providing fast and tight convergence even in difficult cases with poor starting guesses.

Status and perspectives for the multiconfigurational short-range density functional theory method

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Reliable and cost-effective modeling of multi-reference systems as e.g. open-shell transition metal complexes and enzymes is still a huge challenge for computational quantum chemistry. In many cases Kohn-Sham DFT is not sufficiently reliable, and often state-of-the art methods such as CASPT2 and NEVPT2 are computationally too expensive.

As a promising alternative, we explore Andreas Savin's idea to combine wave-function theory for the long-range electron-electron repulsion with density functional theory for the short-range. We have focused on MC-srDFT, a fully variational model combining long-range multiconfiguration self-consistent field for proper description of near-degeneracies and different spin states with short-range semi-local density functional theory [1-9]. In contrast to CASPT2, NEVPT2 and MC-PDFT, because MC-srDFT is fully variational it is relatively straightforward to develop MC-srDFT for calculations of molecular linear and non-linear response properties as electronic excitations, NMR shielding and spin-spin coupling, two-photon absorption etc. etc.

In this talk current status and future perspectives will be presented. Our first public release of MC-srDFT will be in Dalton2019.

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Simple Single Page Abstract template

Kenneth Ruud[1], Marius Kadek[1] and Michal Repisky[2]

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Relativistic effects are known to be important for the electronic structure and properties of compounds containing heavy elements.[1] Recently, relativistic effects have also been shown to lead to changes in the reaction mechanism of enzymatic reactions.[2] Methods for calculating relativistic effects at the four-component level of theory are now well developed for molecules, allowing fairly large molecules of experimental interest to be studied using four-component methodology.[3]

However, many compounds containing heavy elements exist as (molecular) solids. I will in this talk present a methodology for four-component relativistic density-functional theory and Hartree-Fock calculations including periodic boundary conditions.[4] The approach uses Gaussian atomic basis functions and a restricted kinetic balance formalism, allowing for an all-electron description of solids while retaining computational efficiency.

In the talk, I will outline the basic features of the approach and present the first relativistic four-component calculations of molecular systems with periodic boundary conditions applied.

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Three things Kurt needs to do before it is too late

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I advise Kurt to do this:

Solve the Alzheimer problem. He can undertake a translational approach where he combines his in-silico modelling with synthesis of molecular probes to be validated by in-vitro experiments, by in-vivo animal models and in human studies of subjects at risk as well as of patients with different neurodegenerative disorders. In this way he can target proteinopathies which are common features of neurodegenerative brain disorders and which are characterized by the accumulation or change in function of different specific proteins within or outside the neurons in the brain parenchyma. Examples are diseases like Alzheimer, Lewy body dementia, Parkinson´s disease, multiple system atrophy different forms of frontotemporal dementia, ALS, progressive suparanuclear palsy and Down´s syndrome. A common feature of these misfolded proteins are their presence as monomeric unstructured forms in healthy brain, while undergoing conformational changes in their protein structures during disease processes, leading to forms of oligomers as well as protofibrills and fibrillar aggregates. The molecular probes can be fluorescent, paramagnetically active or carrying radiolabels. In particular radiolabelled probes for positron emission tomography are clinically useful and can be targeted by in-silico modelling. A better label means earlier detection of the disease.

Solve the climate problem. Here Kurt has already been active. I will remind him what he did, and review some possibilities.

Thirdly, Kurt needs to keep in shape to do the above. I give some advise.

Free Energy Gradient method with Average Solvent Electrostatic Configuration for Studying Electronic Properties of Molecules in Solution and in Complex Environment

Sylvio Canuto

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We will briefly present the Free Energy Gradient Method with the Average Solvent Electrostatic Configuration (ASEC-FEG)[1]. The method consists in a combination of the hybrid Quantum Mechanics and Molecular Mechanics method used in a sequential procedure (S-QM/MM) with the Free Energy Gradient (FEG) method [2], where the solvent is treated as an average solvent electrostatic configuration (ASEC)[3]. The method allows the geometry relaxation of molecules and the calculation of molecular properties, spectroscopy and reactivity in solution. Examples will consider the spectroscopy of molecules affected by both simple liquids [4-6] as well as the complex environment of a protein [7].

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Protein biochromophores: What affects their absorption and luminescence?

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The spectroscopic properties of protein biochromophores often rely on the protein environment. For example, nearby amino acid residues or single water molecules could modulate the color, i.e., shift the transition energy to the red or to the blue. This is seen for the oxyluciferin anion and the retinal protonated Schiff base, the chromophores of luciferase and rhodopsin proteins, respectively, while the chromophore of the green fluorescent protein (GFP) is much less sensitive to nearby electric fields. In general, spectral tuning is seen for chromophores that undergo charge-transfer transitions. Another important issue is the fluorescence quantum yield, and to identify chromophore-protein interactions that are responsible for high brightness. In this presentation, I will show how gas-phase ion spectroscopy reveals the true colors of biomolecular ions and uncovers the degree of charge transfer.

Absorption spectra are recorded indirectly from ion dissociation or electron detachment (i.e., action spectroscopy) as there are too few chromophore ions for traditional light transmission experiments. Unfortunately, our results also show that it is difficult to photodissociate the rather big systems on the instrumental time scale (up to 10 microseconds). Another technique that does not rely on ion dissociation is luminescence spectroscopy where the photons emitted from the photoexcited ions are detected. My group has recently constructed an instrument, called LUNA (Luminescence iNstrument in Aarhus) where ions are photoexcited in the center of a Paul trap followed by photon detection. The setup benefits from a high photon collection efficiency, which is accomplished by using a cylindrical ion trap where one end-cap electrode is a mesh grid combined with an aspheric condenser lens. The ions are produced by electrospray ionization allowing the study of fragile and/or large molecular ions. I will describe the instrument and present some recent findings. One of our goals is to turn on light emission from the GFP chromophore and oxyluciferin anions either by cooling to liquid nitrogen temperatures or by the attachment of polar molecules.

Multiscale Methods for Computational Biomolecular Spectroscopy

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Computational spectroscopy allows us to gain insight into the physical and chemical processes that occur in light–matter interactions. However, applications on biomolecular systems, such as proteins, biological membranes, and nucleic acids, is a great challenge due to the complexity and size of the systems. Multiscale modeling presents a very promising path to overcome this challenge. In this approach, the more accurate and computationally expensive methods are used only on the active parts of the total system (core) while less accurate and efficient methods are used to model the remainder (environment). For reliable multiscale calculations of spectroscopic properties, it is essential to accurately describe the interactions between the core and its environment. In my talk, I will introduce two multiscale approaches, the polarizable embedding (PE) and polarizable density embedding (PDE) models, which have been developed with a particular focus on efficient and accurate calculations of spectroscopic properties of large and complex (bio)molecular systems. I will present applications of the models on linear and nonlinear spectroscopies that highlight their flexibility and accuracy.

Atmospheric aerosols: a multifaceted challenge

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Aerosol particles in the atmosphere of Earth influence air quality, visibility and global climate. They are emitted directly as particles into the atmosphere from processes such as combustion, wave breaking and vulcanic activity and formed in the atmosphere via nucleation and growth processes.

During their atmospheric lifetime aerosol particles constantly change chemical composition and physical properties via exchange of molecules with the surrounding gas phase and due to chemical recations at the surface and inside the bulk of the particles. The complexity of describing atmospheric aerosols is enourmous representing a magnificent challenge which requires collaboraton between theoretical and experimental chemists.
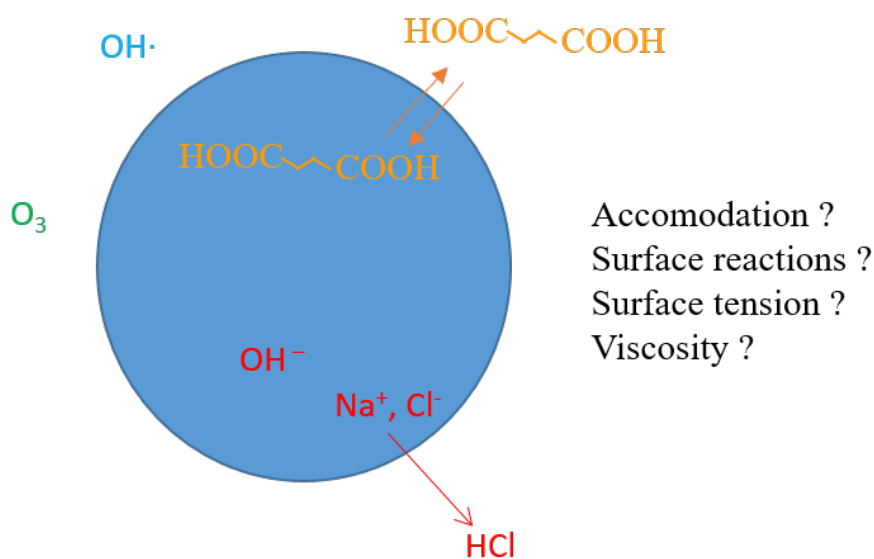
In this presentation I will provide a background for the study of atmospheric aerosols and discuss current and emerging scientific problems and questions based on results from laboratory studies.

Innovation and Atmospheric Science

Matthew S. Johnson
Department of Chemistry
University of Copenhagen

At it's root *innovation* means the introduction of something new. It thus lies at the heart of science. Innovation has taken on an additional meaning in the context of public research institutions: turning basic research into jobs. In this talk I will give examples of innovation by figures including James Lovelock, Max Planck and Kurt Mikkelsen. I will also present some examples from my own experience with two spin-off companies from the Department of Chemistry at the University of Copenhagen; Infuser and Airlabs.

Modelling the Formation and Properties of Atmospheric Molecular Clusters

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Atmospheric nanoparticles known as aerosols, have a large impact on Earth's climate. Particles can scatter incoming sunlight back into space, leading to a cooling effect on the global climate. The largest source of aerosol particles is from gas-to-particle conversion, resulting new particle formation. However, the mechanisms and compounds involved remain highly uncertain. New particle formation is believed to be initiated by formation of strong hydrogen bonded molecular clusters. Sulfuric acid is considered an important contributing specie in many continental regions, but it can not by itself explain observed new particle formation events. Another stabilizer molecule such as atmospheric bases (ammonia/alkylamines), organic species or ions is required to explain the formation of stable atmospheric clusters. An example of a cluster consisting of four sulfuric acid (SA) molecules and four dimethylamine (DMA) molecules can be seen in Figure 1.
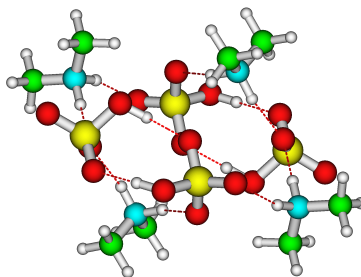
Figure 1: Lowest free energy molecular structure of the $(SA)_4(DMA)_4$ cluster, calculated at the ωB97X-D/6-31++G(d,p) level of theory. Color coding: green = carbon, red = oxygen, blue = nitrogen, yellow = sulfur and white = hydrogen.

During my PhD (2014, under the supervision of Kurt) we characterized the accuracy of density functional theory methods for calculating the Gibbs free energy of atmospheric molecular clusters. This has allowed the modelling of significantly larger cluster structures than previously attainable with increased control of the errors introduced by the method.

In this presentation I will present the current progress in the field of understanding how new atmospheric particles are formed using quantum chemical methods and how I expect the field to progress in the future.

Recent developments in coupled cluster theory and perspectives for the future

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Norwegian University of Science and Technology, Trondheim, Norway

ABSTRACT

I will discuss some recent theoretical developments. In particular, similarity constrained coupled cluster theory[1] for conical intersections and nonadiabatic dynamics, pump-probe simulations using time-dependent coupled cluster theory[2] and coupled cluster theory for strong light-matter interactions (Cavity QED chemistry).[3] These developments are all carried out in the framework of a new coupled cluster program eT, based on a highly efficient algorithm for the Cholesky decomposition of two-electron integrals.[4]

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Can coupled-cluster theory describe ultrashort, high-intensity laser-driven electron dynamics?

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The advent of extremely bright light sources opens new opportunities for investigating matter at the attosecond scale, the time-scale of the electron. This poses a challenge to theoretical and computational science whose focus must be switched to explicitly time-dependent methods. Provided the molecular electronic ground state is dominated by a single determinant, coupled-cluster theory is well known to provide benchmark-quality results for both ground- and excited-state energies and properties. It is, therefore, reasonable to expect that explicitly time-dependent coupled-cluster theory can play a similar role in molecular attosecond science. We have recently investigated the performance of time-dependent coupled-cluster singles-and-doubles theory for simple atoms in highly intense, ultrashort laser pulses [1]. As a laser pulse pumps the electrons into a superposition of excited states, which is virtually orthogonal to the Hartree-Fock reference determinant, we found that the integration of the time-dependent coupled-cluster equations becomes increasingly challenging (and, hence, unrealistically costly). In this presentation, I will give an overview of the work published in [1] along with a proposed solution, which involves a time-dependent adaptation of the underlying orbital set in concert with the correlating amplitudes of the coupled-cluster state [2,3].

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Coupled Cluster methods for X-ray spectroscopies

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The massive investments in advanced light source facilities working in the x-ray frequency range has increased the popularity of X-ray-based spectroscopic techniques to probe molecular systems. At the same, it has stimulated the development of quantum-chemical theory and computational tools to simulate the spectra. Theory and simulation tools are essential components to unambiguously relate experimental measurements to both structural and dynamical properties of the probed system. The accurate description of core excited states presents additional challenges, compared to that of valence excited states. These challenges have, for a long time, prevented the application of electronic structure methods like the coupled cluster ones, that are considered among the most reliable and accurate to describe excited state. During the last decade, we have tried to rectify this situation, by developing approaches, rooted on the coupled cluster ansatz, to compute the observables of X-ray techniques like X-ray absorption (XAS) [1, 2, 3, 4, 5, 6, 7, 8, 9, 10], emission (XES) [11, 12, 13], circular dichroism (XCD) [12], resonant inelastic x-ray scattering (RIXS) [11, 12, 13], photoelectron (XPS) [14], that are applied to probe both the electronic ground state and electronic excited states in a pump-probe set up. An overview of their performance and capabilities will be presented.

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ABSTRACT

AN UNFINISHED AFFAIR WITH PROF. MIKKELSEN

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Many years ago, a request for numerical results was sent from the Danish capital to the Swedish province. These have since been left untouched and kept in the archive vaults:

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-rw-r--r-- 1 x_nscpno x_nscpno 288257 Jun  4  2008 ecd-sol_helix01-pcm_0.08_0.0025.out
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-rw-r--r-- 1 x_nscpno x_nscpno 548306 Jun  4  2008 ecd-sol_helix03-pcm_0.08_0.0025.out
-rw-r--r-- 1 x_nscpno x_nscpno 402304 Jun  4  2008 ecd-sol_helix04-pcm_0.08_0.0025.out
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-rw-r--r-- 1 x_nscpno x_nscpno 479131 Jun  4  2008 ecd-sol_helix06-pcm_0.08_0.0025.out
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Are there now reasons to open the vaults and peek inside? Let us ask the not so old yet very wise man and learn his recommendation.
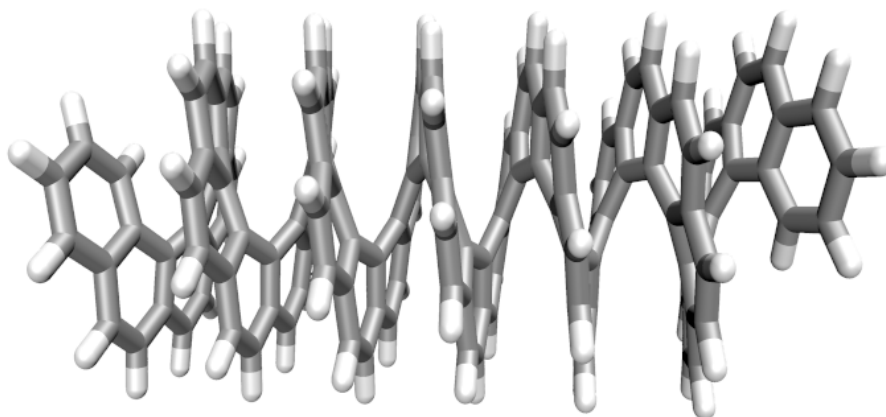
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Wave Functions with Several Sets of Optimized Orbitals

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Standard quantum chemical methods employ a single set of orthogonal or non-orthogonal orbitals. However, for a number of molecular systems such expansions are rather inefficient, as different parts of the wave function require different forms of orbitals. For example, a reasonable description of the ground state of the iron dimer is obtained only when the active space includes d-sets for both d^6 and d^7 configurations. The standard formulation of this problem requires thus two active sets of d-orbitals on each atom. Although such double-shell active spaces are feasible for the iron dimer, they become very cumbersome when three of more interacting iron atoms must be described.

An alternative construction is to devise a wave function that is the sum of two or more, say CASSCF wave functions, and then optimize the orbitals of all the individual CASSCF wave functions without any restriction on the overlap between different sets of orbitals. Such expansions have a number of appealing properties: they are variational, and they may be constructed so they are size-consistent and size-extensive. From a practical point of view, these expansions are much more compact than the corresponding expansions that are obtained by the double shell construction. In the context of valence bond theory, such expansions are known as breathing valence bond orbitals and their use was pioneered by P. Hibberty.

In this talk, I will describe a novel approach for optimizing these compact wave functions. A major problem with the direct implementation of the method is that the energy of the expansion often have a infimum, rather than a minimum. When this infimum is approached, the orbitals of the various components become linear dependent, and poses therefore a rather complicated optimization problem. However, by adding a penalty term to the energy, it is possible to obtain minima that describes the double shell effect. Initial application of the method to diatomic molecules, including the potential curve of LiF, will be presented and discussed.

The Oxygen-Organic Molecule Photosystem: Tunneling Through Activation Barriers

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Experimentally monitoring and computationally modeling transitions between the three lowest energy electronic states of molecular oxygen ($X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$) provide many challenges. These challenges are exacerbated for condensed phase systems in which an organic molecule M perturbs oxygen through the formation of an $M\text{-}O_2$ contact complex. In this regard, it is important to distinguish the roles played by M in influencing radiative transitions (*e.g.*, $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ phosphorescence) from the effect(s) of M on non-radiative transitions.

In this lecture, I will summarize some of our early work on these issues that was done in collaboration with Kurt Mikkelsen. I will conclude with a "Grand Challenge": Our current attempts to model temperature effects on the M-dependent non-radiative $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ transition in which experimental data indicate a process that involves tunneling.

Tuning Molecular Properties of the Dihydroazulene/Vinylheptafulvene Photo/Thermoswitch

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Photochromic molecules that upon irradiation undergo a conversion from a low-energy isomer to a high-energy isomer have attracted interest as a potential way of storing solar energy. Design of such molecules requires combined efforts of theoretical and synthetic chemistry. Indeed, it is a major challenge to obtain molecules with optimum absorption properties, high energy storage densities, long storage times and ways of triggering energy release on demand. Here, I will present joint efforts with Prof. Kurt V. Mikkelsen to move forward the use of the dihydroazulene/vinylheptafulvene couple as a molecular solar thermal energy storage system. To reach long storage times and high energy densities, we have studied the influence of substituent groups, the influence of incorporating the system into macrocyclic structures, and the influence of coupling photoisomerization to loss or gain of aromaticity of another structural unit. Selected examples of our joint work are listed below.
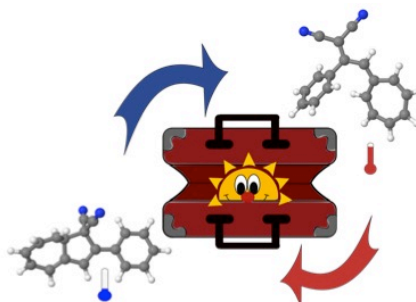
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Conformational Bias Monte Carlo Used to Study the Solvatochromism of Mesityl Oxide

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Molecules have properties that are closely related to their geometry. The relative stability of conformers on different solvents may affect the electronic excitation energies, therefore changing the absorption spectra of the molecule. We illustrate this behavior by discussing the solvatochromic effect on the Mesityl Oxide molecule (MOx), which has been previously investigated by experimental [1] and theoretical [2] methods. We perform Configurational Bias Monte Carlo (CBMC) and Molecular Dynamics (MD) simulations of MOx in gas phase and in solution of acetonitrile, methanol and water. The CBMC simulation uses our implementation method, which the solute molecule is divided into small fragments that are joined with a biased rotational move favoring torsional angle with lower energies [3]. After the simulations, we selected statistically uncorrelated solute-solvent configurations to perform quantum calculations and obtained the excitation energies to convolute the average absorption spectrum in solution.

We show that the *syn:anti* conformer population is solvent dependent being majorly *syn* in gas phase and apolar solvents and majorly *anti* in polar solvents such as water and methanol. This difference on the *syn:anti* population can not be observed by conventional MD simulations due to the high energy barrier between the two conformers of about 10 kcal/mol. But with the CBMC method this energy barrier can be easily overcome yielding the right conformational populations. We showed that the correct description of the *syn:anti* population is important to the absorption spectrum of the MOx, once it introduces a blue shift of around 2000 cm^{-1} going from gas phase with 95:5 population to aqueous solution with 22:78 population. The solvent effects in the electronic structure of the MOx present a red shift depending on the polarity of the solvent. Then, the considering the total solvent effects, we calculated a solvatochromic shift that is in very good agreement with the experimental data.

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Solvent and solvent-influenced dynamics in theoretical chemistry

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Abstract. Our fundamental understanding of the light-induced ultrafast events determining photochemical properties of molecules in solution has undergone significant advancements thanks to time-resolved studies. Modern femtosecond X-ray techniques are particularly suited for such investigations. Yet, the analysis and the interpretation of the experimental outcomes necessitate support from detailed atomistic simulations, and this is a grand challenge for theoretical chemistry. We have recently implemented on-the-fly QM/MM Born-Oppenheimer Molecular Dynamics (BOMD) in the ASE GPAW code [1,2,4] for the purpose of delivering reasonably accurate information on structural dynamics in solution at a modest computational cost. We will show how the method was used to assist X-ray free electron laser (XFEL) scattering measurements of excited-state, adiabatic bond formation and accompanying solute and solvent relaxation in $[Ir_2(Dimen)_4]^{2+}$ [2,3] and $[Pt_2(P_2O_5H_2)_4]^{4-}$ [1,4-6] in order to gain mechanistic insights into the solute and solvent relaxation processes following impulsive photoexcitation. We will also show how a completely different route based on pre-determined forces was used together with MD and QD for studying excited-state solvation structures of transition metal-centered complexes [7] and photo-induced non-adiabatic relaxation dynamics in the Fe-centered photosensitizer complexes under influence of a solvent [8], respectively, again to assist the analysis and interpretation of ultrafast XFEL measurements.
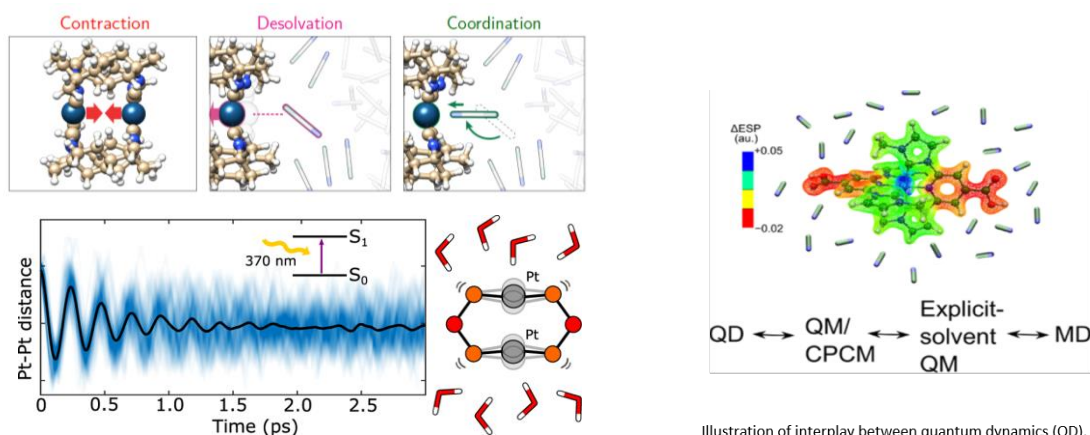
Our QM/MM BOMD code was used to model ground-state properties as well as the ultrafast photo-induced bond formation between the metals and the subsequent intra- and inter-molecular relaxation dynamics in solvated $[Ir_2(Dimen)_4]^{2+}$ (top) and $[Pt_2(P_2O_5H_2)_4]^{4-}$ (bottom).

Illustration of interplay between quantum dynamics (QD), quantum chemistry (MD), and classical molecular dynamics (MD) for studying photo-induced non-adiabatic dynamics in an Fe-centered complex under influence of a solvent.

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Molecular aggregation in glacial acetic acid: insight from molecular dynamics/quantum mechanics modelling of structural and ^{1}H NMR properties

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A very curious evolution of the ^{1}H NMR chemical shift of the acidic proton in acetic acid was recorded upon gradual dilution of the acid with an inert solvent, e.g. carbon tetrachloride or cyclohexane. With an increasing content of the inert solvent, a deshielding of the acidic proton increases in a linear manner up to the molar fraction of acetic acid of around 5-10%. Further dilution leads to a rather sudden increase in the shielding of this particular proton, thus producing a clear maximum in the chemical shift of the acidic proton. This non-monotonic evolution of the ^{1}H NMR chemical shift of the acidic proton apparently reflects the changes in the dynamic equilibrium between various association patterns of acetic acid molecules in the neat liquid.

In the present study, we have attempted to dissect the types of molecular self-aggregation in acetic acid which are responsible for the increased shielding of the acidic proton in the neat liquid as compared to that in the presumable cyclic dimer at low concentration of acetic acid in cyclohexane solution by as much as 0.65 ppm. To this end, we have performed classical MD simulations of glacial acetic acid as well as of the cyclic dimer of acetic acid in cyclohexane using two different force fields GAFF and OPLS. We have analyzed the molecular trajectories in order to quantify the amounts of different types of acetic acid aggregates. We have next conducted combined quantum mechanics/molecular mechanics (QM/MM) calculations of the ^{1}H NMR isotropic shielding constants of acetic acid along the molecular trajectories recorded in this work.

The results of our hydrogen bonding analysis show that the amount of acetic acid molecules in cyclic dimers is around 16-17% [1]. The amount of molecules forming linear chains was evaluated to be around 33 and 37% using OPLS and GAFF force fields, respectively. We have also found substantial amounts of acetic acid molecules linked by hydrogen bonding where hydroxylic oxygen serves as hydrogen bond acceptor as well as of molecules where acidic hydrogen is not involved in hydrogen bonding. The QM/MM calculations of the ^{1}H NMR chemical shift of acidic proton in the neat liquid and in the cyclic dimer in cyclohexane reproduce experimental results rather well. We conclude that the increased shielding of the acidic proton in neat acetic acid as compared to the cyclic dimer in cyclohexane is due to the formation of hydrogen bonded aggregates with hydrogen bonding between hydroxylic moieties as well as due to the monomeric acetic acid molecules.

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Spectroscopy in Inhomogeneous Electric Fields

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Over the last few years we have developed new theories and computational methods for understanding vibrational spectroscopy of molecules near metal surfaces. Specifically we have developed a new computational toolbox for simulating surface-enhanced vibrational spectroscopy in inhomogeneous electric field. This kind of spectroscopy relies on the strong localized electric near-field at the surface of plasmonic metal nanoparticles. Our work has shown that it is possible to resolve intricate molecule vibrations with atomic resolution, which requires that the near-field is confined to a few Ångstroms. Under these conditions the traditional selection rules breaks down and simulations are required for understanding the spectroscopy. Here we will discuss our latest developments in understanding surface-enhanced vibrational spectroscopy in inhomogeneous electric fields.

Describing force field polarization by a bond capacity model

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Department of Chemistry, Aarhus University

I will describe our recently proposed bond capacity model that can describe molecular polarization using only atomic charges.[i] The bond capacity model is similar in spirit to the fluctuating-charge and corresponding split-charge models, but without physical artifacts such as charge-transfer over infinite distance and non-linear scaling of polarizability with system size. We have derived and implemented efficient algorithms for calculating the energy gradient of the bond capacity energy function,[ii] and derived equations for coupling to continuum solvent models,[iii] and these developments will be presented.

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[ii] P. P. Poier, L. Lagardère, J.-P. Piquemal, F. Jensen "Molecular Dynamics using Non-variational Polarizable Force Fields: Theory, Periodic Boundary Conditions Implementation and Application to the Bond Capacity Model" *submitted*

[iii] P. P. Poier, F. Jensen " Including Implicit Solvation in the Bond Capacity Polarization Model" *submitted*

The Gold-sulfur bond in Electrochemistry and *In Situ* Scanning Tunnelling Microscopy

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Gold has been coveted for thousands of years as investment, for art and cult purposes, and since antiquity the unique properties of Au-nanoparticles (AuNPs) have been adorning surfaces. With much higher abundance use of sulfur, also known since antiquity, is pragmatic, from ancient time for its combustibility ("brimstone and fire rained"), presently broadly in chemical industry. In modern times AuNPs and Au-surfaces are used in electronics, catalysis, medical applications, and multifarious solid surface preparation.

AuNPs and Au-surfaces are often functionalized or protected by a molecular thiol monolayer (like "a tea cosy preserving tea's taste and warmth"). Consensus has long been that Au transfers electrons to the bound thiol, forming a chemical Au(I)-S(-I) bond. Recent comprehensive studies have suggested that the Au-S *surface* bond is not likely to be "normal" but determined by van der Waals forces, which for gold and sulfur are some of the strongest known.

We consider first some examples of the electrochemistry and electrochemical *in situ* STM of Au-S bonded molecules on atomically planar Au(111)-, Au(110)- and Au(100)-electrode surfaces. The molecules include both pure and functionalized thiols, and AuS-bound heme, blue copper, and iron-sulfur redox metalloproteins. Notably, electrochemical *in situ* STM is at the single-molecule, sometimes even sub-molecular level. We overview next some properties of the Au-S surface bond, and ***how*** versatile monolayer structure and function can emerge.

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New Directions in Development of Complex Stiff Chemical Schemes (CSCS)

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Chemical mechanisms plays a central role in many science and technology problems. The most comprehensive chemical mechanisms are among others applied in atmospheric and combustion research, since these mechanisms can contain more than 17000 elementary reactions and more than 6700 species. Incorporation of an explicit chemical scheme with this amount of reactions and species into 3D models is still a problematic task due to computational limitations – not only because of the size but also because of the stiffness of these systems' ODE.

To overcome this problem a large variety of lumped gas-phase chemical mechanisms have been developed over the years. That means chemical reactions are lumped together using different chemical constraints, e.g. chemical reactivity and/or similar organic functional groups, to surrogate chemical reactions. Thus in these chemical mechanisms lumped surrogate chemical reactions represent more than one real chemical reaction. Some of these mechanisms have been validated against chamber experiments but most of them are not.

The focus of this talk is to present new directions within development of Complex Stiff Chemical Schemes (CSCS), such as:

- Application of Structure-Activity Relationships (SARs) that predict the properties and reactions of the many multi-functionalized compounds in the atmosphere,

- applying self-generating method, machine learning and neural networks, and

- applying theoretical methods to reduce the discrepancies between CSCA and experimental data/field observations.

The focus of this presentation is not to address the shortcomings of the chemical description but the challenges, advantages and disadvantages of the mathematical approaches applied in the present and the new methods.

Chemical Space Exploration

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I'll talk about how we combine quantum calculations, cheminformatics, genetic algorithms, and machine learning to search for chemical space for molecules with interesting properties.

Quantum Chemistry on Modern HPC Systems: Challenges and Opportunities

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Modern high-performance computer (HPC) systems pose a significant challenge to most quantum chemistry software packages, as they can not take advantage of new hardware features of these HPC systems, like heterogeneous compute node architecture or hierarchical memory stack. Unfortunately, most quantum chemistry software packages relly on legacy programming models with dated, rigid structure and consequently can not be easily adapted to modern HPC systems without significant efforts. In this talk, I will discuss an alternative way for enabling quantum chemistry on modern HPC systems, namely development of new quantum chemistry software packages. More specifically, I will present our recent efforts in the development of VeloxChem program, which is designed to run seamlessly on modern HPC systems.

Apart from presenting implementation details of core modules (two-electron integrals driver, exchange-correlation functional integrator) in VeloxChem program, I will also discuss challenges encountered in code optimization for modern HPC systems and will outline future directions in the development of quantum chemistry codes on such systems.

Self-reactions of peroxy radicals: overturning the 60-year old Russell mechanism

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Peroxy radical (RO2) self- and cross-reactions (RO2 + R'O2) are important in both atmospheric, combustion and food chemistry. The ROOR' recombination channel has recently been shown to be an important gas-phase source of extremely low volatility compounds in the atmosphere. Our conceptual understanding of these reactions is based on the Russell mechanism from 1957, which postulates the formation of metastable tetroxide (ROOOOR') intermediates, which then rearrange in different ways, corresponding to the different product channels. Experiments from the 1960s have claimed to observe these metastable tetroxides in self-reactions of tertiary RO2 at temperatures below 160 K. Using multireference quantum chemical calculations, we have demonstrated that two key tenets of the Russell mechanism are incorrect. First, while tetroxides do form, they are extremely unstable for any combination of R and R' groups. The species actually observed in the experiments are not the covalently bound tetroxides, but the RO2...R'O2 complexes. Second, the key branching point comes only after the tetroxide decomposition, and corresponds to different reaction channels of a RO...O2...R'O complex, rather than rearrangements of the tetroxide. For example, the formation of ROOR' involves an intersystem crossing of the RO...R'O pair (initially formed in a triplet state), and subsequent recombination.

Abstracts

Posters

RPA(D) and HRPA(D):
^{13}C-^{13}C Spin-Spin Coupling Constants for Saturated Cycloalkanes

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Abstract

This study investigates the performance of the SOPPA-based, doubles-corrected methods RPA(D) and HRPA(D) in calculating carbon-carbon spin-spin coupling constants in 39 saturated carbocycles, totaling 188 unique coupling constants. RPA(D) scales an order below SOPPA in computational complexity while HRPA(D) differs from SOPPA in the leading coefficient. These methods may therefore prove beneficial in predictions of coupling constants of large molecules. It was found that HRPA(D) significantly improves on RPA(D) for all coupling constants as well as performing similarly to SOPPA in terms of accuracy. With a roughly 50% reduction in computation time from SOPPA to HRPA(D), the latter shows great promise for the calculation of nuclear indirect carbon-carbon spin-spin coupling constants in saturated carbocycles.

Adaptive Density-Guided Calculations of Double Incremental Potential Energy Surfaces

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Potential energy surfaces (PESs) are cornerstones for providing detailed information about structure and dynamics of molecules and are necessary components for interpretations, refinements, and even predictions of experimental results. Quantum chemical calculations of PESs, however, have a very unfavorable scaling with respect to the system size. This is due to i) a scaling of single-point electronic structure calculations and ii) an increasing dimensionality of PESs and, as the result, a growing number of single points to be computed. Many fundamentally different approximations have been developed to address the first issue. However, these techniques alone do not address the second problem and are far from enough to achieve a linear-scaling behavior in the overall PES construction. Our group has previously developed a double incremental (DI) expansion scheme [1] that exploits ideas of restricting mode–mode couplings and fragmentation of the molecule into subsystems, thus, addressing both the scaling problems and significantly reducing the computational cost.

We present an integration of DI with the adaptive density-guided approach (ADGA) [2]. The ADGA enables an automatic construction of grids ensuring that the smallest possible number of grid points is used, while maintaining a highly accurate description of a PES. We show that the combination of DI and the ADGA allows for black-box routine calculations of PESs for much larger molecular systems than were previously accessible and omitting the step of manual grid construction. The implementation of this methodology in the MidasCpp [3] program package will soon be publicly available. Our work provides a foundation for efficient and accurate PES calculations for moderate-size peptides and polymers.

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Non-normality and open quantum systems

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We study exciton and energy transfer processes in photosynthesis. We are in particular interested in the 'non-normal' parts of these processes and study them by using already developed theory of pseudospectra in hope of gaining new insights.

The simplest check for non-normality is to see whether an operator A fails condition described in eq. 1.

$$[A, A^{\dagger}] = 0 \qquad (1)$$

For operators that we confirm as being non-normal we are interested to study their transient behaviour. A visual display of it is shown in figure . Pseudospectral theory gives us tools to look into the transient behaviours.

Operators that we consider are the ones that can be found in Redfield[2] and Lindblad[1] equations that are two ways to describe development of an open quantum system over time. An open quantum system of interest is for example the Fenna-Matthews-Olson Complex found in green sulphur bacteria.
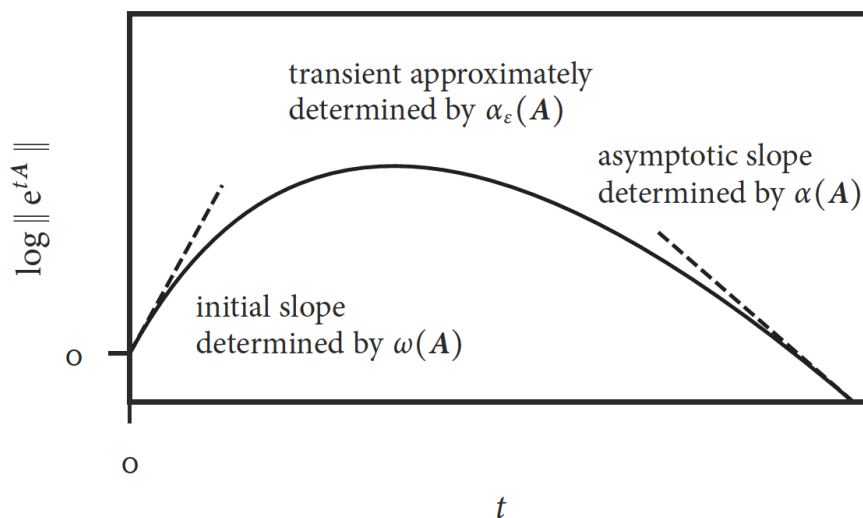
Figure 1: Norm of matrix exponent versus time. Figure taken from : "*Spectra and Pseudospectra Princeton University Press by LN Trefethen and M Embree* **2005**"

We have already seen that certain parts of relaxation processes behave non-normally: that is coherence $\Leftrightarrow$ population transfer processes. These are our current focus of the study.

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Modeling a Spin-Forbidden Transition that Includes Tunneling: Singlet Oxygen Deactivation

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The behaviour of the lowest electronically excited state of molecular oxygen, $O_2(a^1\Delta_g)$, commonly known as *singlet oxygen*, exemplifies many fundamental chemical/physical principles, and provides many computational and experimental challenges.

Experiments have shown that the lifetime of singlet oxygen in solution is both solvent- and temperature-dependent, and it does not follow conventional rate equations such as the Arrhenius equation. In particular, experiments imply that charge-transfer effects and tunneling through an activation barrier play an important role in the non-radiative $a^1\Delta_g$-$X^3\Sigma_g^-$ transition.

We now ask a challenging question: Can we use an *ab initio* model that will enable us to understand the spin-forbidden non-radiative deactivation of singlet oxygen in a wide range of solvents?

Machine Learning Algorithms for Potential Energy Surface Construction: More out of the same?

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We present our algorithmic advances in combining machine learning (ML) algorithms with potential energy surface (PES) construction for subsequent use in vibrational structure theory with mean of vibrational self-consistent-field (VSCF) and vibrational Coupled Cluster (VCC). We demonstrate how Gaussian Process Regression (GPR) can be used to approximate higher-order mode potentials. Our benchmarks show that for approximate 2-mode potentials the errors can be adjusted to be in the order of 8 cm^{-1}, while for approximate 3-mode and 4-mode potentials the errors fall below 1 cm^{-1}. The observed errors are, therefore, smaller than contributions due to missing higher-order electron excitations or relativistic effects. Most importantly, the approximate potentials are always significantly better than those with neglected higher-order couplings.[1]

Improving on this scheme we show how an intrinsic uncertainty measure in GPR can be used to iteratively refine the ML PES to increase its accuracy. This is achieved by combining it with an adaptive density-guided approach (ADGA), which itself is an iterative scheme and uses information on the averaged vibrational density to refine the PES. Both quantities are combined to reduce the required single point calculations in the PES construction using ADGA or GPR alone.

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Relativistic effects in NMR properties of [L][RuCPt] complexes: ZORA versus four-component calculations

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Ruthenium-carbide complexes are of great interest due to the possible bond formation and breakage to the carbide, e.g. as a catalyst in the Fischer-Tropsch synthesis [1,2] or the natural nitrogen fixation at nitrogenase cofactors [3,4]. Hetero-metallic carbide-bridged complexes $(Cy_3P)_2Cl_2Ru{\equiv}C\text{-}PtCl_2L$, [L][RuCPt], with various ligands L have been synthesized and characterized using NMR spectroscopy by Reinholdt and Bendix [5]. The ligands L differ in their electron donating ability and thereby their *trans*-influence propensity in relation to the {Ru≡C} unit in [L][RuCPt].

The experimental NMR studies are supplemented with theoretical studies using two relativistic methods: a four-component fully relativistic approach using the ReSpect program [6] and the Zeroth-order regular approximation (ZORA) [7] two-component method as implemented in the ADF program [8]. NMR chemical shifts of ruthenium, platinum and the carbide in various [L][RuCPt] complexes were calculated at the DFT level using the PBE0 exchange-correlation functional. Basis set dependency, relativistic effects and contributions when calculating NMR properties, and a comparison of calculated results with experimental chemical shifts will be presented with focus on the results from two [L][RuCPt] complexes.

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Neural network captures DFT calculated HOMO and LUMO energies of SubPc based dyes

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Organic photovoltaic devices are promising candidates for efficient energy harvesting from sunlight. Designing new dye molecules suitable for such devices is a challenging task restricted by the rapid increase of computational cost with system size. Solar cell material properties are closely related to the electronic structure of the dye, and an effective molecular orbital energy screening method for a family of dyes is therefore desired. In this work, a machine-learning approach is used to sort through the chemical space of peripheral double-substituted boron-Subphthalocyanine dyes. A PyTorch based artificial neural network is utilized for predicting the HOMO and LUMO energies of more than 2,000 functionalized boron-Subphtalocyanine dyes obtained from a density functional theory based database. Among three feature vectors, the Coulomb matrix feature vector captures the HOMO and LUMO energies best with prediction root mean square error in the order of 0.02 eV. The developed neural network algorithm can be used to guide chemists in the search of new dye molecules applicable to dye-sensitized solar cells.

Theoretical Rate Constants for the 1,4-Cycloaddition of Singlet Oxygen on Conjugated *cis*-Dienes

Malte F. Jespersen, Solvejg Jørgensen, Matthew S. Johnson and Kurt V. Mikkelsen, *University of Copenhagen*.

Singlet molecular oxygen is formed photo-chemically in the atmosphere, e.g. via spin transfer from triplet excited molecules and photo-absorption by O_2. The lowest singlet state (singlet oxygen, $^1\Delta_g$) has 94 kJ/mol of energy relative to the ground state and is known to be reactive towards alkenes and sulfides. While the importance of this state has long been appreciated in other fields, for example it has been used to remove pollutants from waste water, in the photodynamic therapy for treating cancer (DeRosa, Maria C. et al., *Coordination Chemistry Reviews*, 233, pp. 351-371 (2002)) and in singlet oxygen-assisted combustion (Smirnov, V. V. et al., *Journal of Physics D: Applied Physics*, 41, 19, 192001 (2008)), it's importance in the atmosphere is not well known. Oxidation of atmospheric species are usually dominated by ozone and OH radicals, however singlet oxygen could be an important reaction path for some atmospheric species. The reactions may be especially important in fog and ice, (Anastasio, Cort, et al., *Atmospheric Environment*, 35.6, pp. 1079-1089 (2001)) and (Bower, Jonathan P. et al., *Atmospheric Environment* 75, pp. 188-195 (2013)). In-depth knowledge the kinetic parameters of singlet molecular oxygen reactions are central for evaluating the impact of $^1O_2$ on the atmosphere's oxidation capacity. Gas-phase reaction rate coefficients have been experimentally determined for a small number of compounds; even fewer reactions have been investigated using quantum chemistry. This is due in part to the challenge of describing the multi-reference character of singlet oxygen. We have tested a novel and straightforward strategy to calculate rate constant for the 1,4-cycloaddition of singlet oxygen to *cis*-dienes and have compared the calculated rates with experimental results. The agreement between the suggested computational method and the experimental data is within one order of magnitude, to our knowledge the best that has ever been achieved. Our results open a method of evaluating the impact of reactions with singlet oxygen where experimental data is lacking.

Benchmarking correlated methods for frequency dependent polarizabilities: aromatic molecules with the CC3, CCSD, CC2 and SOPPA methods

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Abstract

A benchmark of different correlated second-order methods for frequency dependent polarizabilities has been carried out. For the benchmark a set of 15 (hetero-)aromatic medium sized molecules has been optimized at MP2/6-31G(d) level. For the first time CC3 polarizabilities are reported for these molecules using Sadlej's polarized triple zeta basis set and for a subset of these molecules the polarizabilities were obtained at the CC3 level also with the larger aug-cc-pVTZ basis set. These CC3 values are used as the reference values for benchmarking the second-order methods. The influence of different basis sets; aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, d-aug-cc-pVTZ, Sadlej, on static and frequency dependent polarizabilities were tested for the set of molecules at the SOPPA level. It was found that, though not much, the basis sets had a greater influence on the frequency dependent polarizabilities than on the static ones. The aug-cc-pVTZ basis set performed adequately for both static and frequency dependent polarizabilities having an insignificant off-set from the values obtained with the larger aug-cc-pVQZ basis set. Further more Sadlej's basis set was also found to give reliable results. Comparing the second-order methods; SOPPA, SOPPA(CC2), SOPPA(CCSD), CC2 and CCSD to the CC3 reference values, it was found that the best performing method was the CCSD, as expected. The faster SOPPA method, however, outperformed CC2, suggesting the use of SOPPA rather than CC2 for polarizabilities. The SOPPA results were found to improve further, when the correlation coefficients in the wavefunction were replaced by coupled cluster amplitudes in the SOPPA(CC2) and SOPPA(CCSD) methods. A comparison was made, for a small set of the molecules, between experimental data and calculated polarizabilities. It shows that, for this set of molecules, the trend for the performances of the different second-order methods does not change whether the reference values are calculated CC3 values or experimental values.

Keywords: Frequency dependent polarizabilities, basis set dependence, CC3, SOPPA, SOPPA(CC2), SOPPA(CCSD), CC2, CCSD

1

Helical Orbitals and Circular Currents in Linear Carbon Wires

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Abstract: Disubstituted odd-carbon cumulenes are linear carbon wires with near-degenerate helical π-orbitals (Figure 1a-b).[1-2] Such cumulenes are chiral molecules but their electronic structure consists of helical orbitals of both chiralities.[3] However, if these helical molecular orbitals give rise to experimentally observable effects, the otherwise near-degenerate orbitals of opposite helicity must be split. Here we show how single-faced π-donors, such as the amine substituent, provide a strategy for splitting the helical molecular orbitals. The chirality induced by the amine allows for systematic control of the helicity of the frontier orbitals. We examine how the helical orbitals in odd-carbon cumulenes control the coherent electron transport properties and find that the current density through these linear wires exhibits strong circular currents (Figure 1c).[4-5] The direction of the circular currents is systematically controlled by the helicity of the frontier molecular orbitals, and can therefore be altered by changing between the conformations of the molecule. With strong circular currents present around truly linear carbon wires, cumulenes are promising candidates for novel applications in molecular electronics.
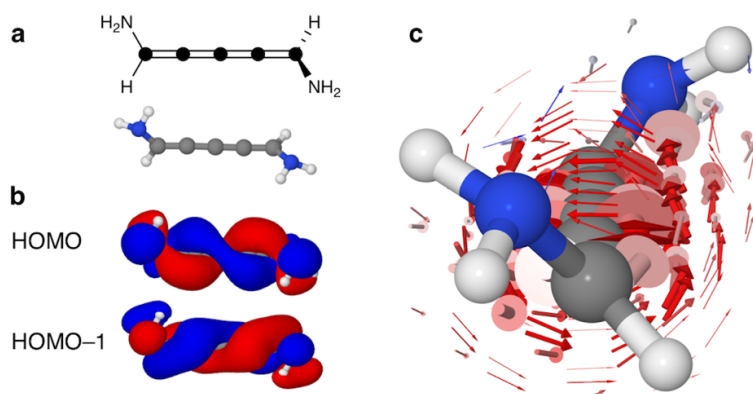
Figure 1. Molecular structure (a), two highest occupied molecular orbitals (b), and non-equilibrium current density of *S*-1,5-diamino-pentatetraene.

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Tryptophan Mediated Electron Transfer in Cytochome P450

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Cytochrome P450(P450) contains a heme with an oxidizing iron-oxo center. Hole transport protection mechanism are in place.We study the Tryptophan (Trp) mediated electron transfer (ET) mechanism from the heme to the surface of the protein. We look at factors influencing the absolute reduction potential of Trp and the coupling between Trp and the porphyrin ring of the heme (Por).

Excited State Aromaticity Inhibits the Photoswitching of the Benzannulated Dihydroazulene-Vinylheptafulvene System

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The Dihydroazulene-Vinylheptafulvene[1] (DHA-VHF) photoswitch has been proposed as a candidate for storing solar energy in the metastable VHF. One way to increase the energy storage could be through annulation of a benzene-ring onto the molecular structure. While this was found to increase the energy storage capacity, the switching capabilities of two benzannulated DHA derivatives was found to decrease, giving way to fluorescence and permanent bleaching instead.[2,3] Using TD-DFT (linear response) we propose that excited state aromaticity introduced by the benzannulation has increased the size of an excited state barrier of both derivatives, relative to the non-benzannulated species. We evaluated the aromaticity of the benzannulation by employing the Quantum Theory of Atoms in Molecules (QTAIM) partition to obtain the atomic overlap matrices with the AIMAll software package, and computed several aromaticity descriptors such as HOMA, PDI, FLU, MCI, and AV1245 using the ESI-3D program. The aromaticity evaluations showed that the loss of photochromic behavior is proportional to the loss of aromaticity over the excited state barrier.[4] We conclude that excited state aromaticity in the current case has reduced the efficiency of photochromism, and discuss how we can design the photoswitch to best mitigate the effects of excited state aromaticity, while still gaining the energy storage increase from the benzannulation.
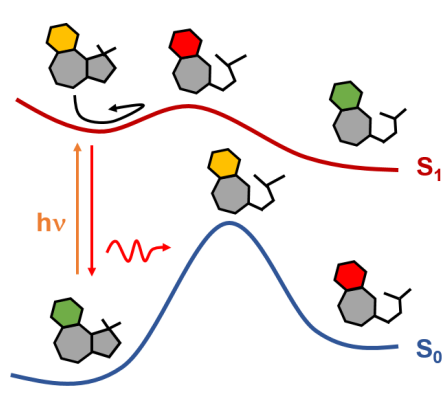
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Analysis of nuclear wave packet dynamics reflected in time-resolved near-edge X-ray absorption fine structure

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Time-resolved near-edge X-ray absorption fine structure (TR-NEXAFS) can be calculated with combination of nuclear dynamics simulations and electronic structure calculations for different delay times [1]. The results show the sensitivity of TR-NEXAFS to both the electronic structure and nuclear dyanamics. Especially, absorption peaks for the different electronic states involved in the photo-induced process are clearly separated.

We hereby investigate the nuclear wave packet dynamics behind TR-NEXAFS for pyrazine promoted to the $^1B_{2u}(\pi\pi^*)$ state, which undergoes radiationless decay into the $^1B_{3u}(n\pi^*)$ state. Nuclear dynamics simulations show contribution of the dark $^1A_u(n\pi^*)$ state [2]. We apply the frozen-core core-valence separated equation-of-motion coupled cluster singles and doubles (fc-CVS-EOM-CCSD) method [3] for calculating snap-shot spectra along the nuclear dynamics, which we simulate using the multiconfiguration time-dependent Hartree (MCTDH) package [4] with the model Hamiltonian of Ref. 2.

Fig. 1 shows the populations of the three diabatic states. The populations and the nuclear wave packet dynamics are reflected in the TR-NEXAFS spectra given in Fig. 2: Especially, oscillations of the population of $^1B_{3u}(n\pi^*)$ and $^1A_u(n\pi^*)$ appear as in the peak intensities. With nuclear wave packet analysis, the oscillation is attributed to propagation along the normal mode of ring distortion [596 cm^{-1} (exp.)], and concomitant control of penetration through the conical intersection along the mode where the C-H bonds shake [1582 cm^{-1} (exp.)]. These results demonstrate the applicability of excited-state simulations to extraction of spectral information on dynamical processes.
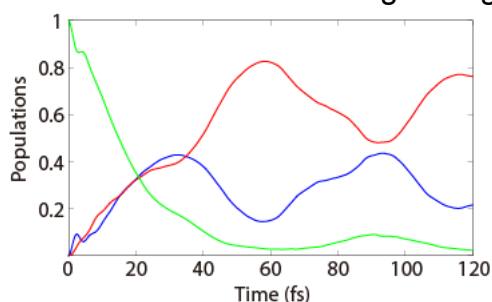
Fig. 1: Populations of the (blue) $^1B_{3u}(n\pi^*)$, (red) $^1A_u(n\pi^*)$, and (green) $^1B_{2u}(\pi\pi^*)$ diabatic states
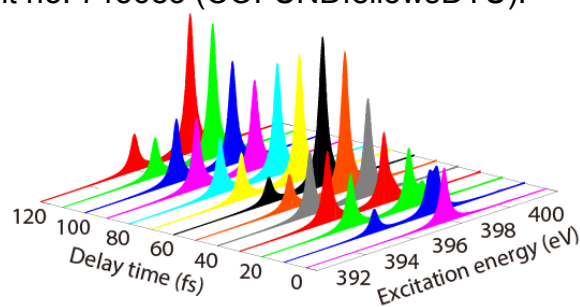
Fig. 2: N K-edge TR-NEXAFS for pyrazine promoted to the $^1B_{2u}(\pi\pi^*)$ state. The peak in lower energy corresponds to the $^1B_{3u}(n\pi^*)$ state. Peaks corresponding to the $^1A_u(n\pi^*)$ and $^1B_{2u}(\pi\pi^*)$ states are in the same energetically higher position.

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# QuantumATK – Software Suite for Atomic-Scale Modeling of Materials, Nanostructures and Nanoelectronic Devices

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QuantumATK is a complete and fully integrated software suite for atomic-scale modeling of materials, nanostructures, and nanoelectronic devices [1]. The simulation tools in QuantumATK range from classical force fields to semi-empirical models and DFT with either LCAO or plane-wave basis sets. It also includes the NEGF module for nanoscale device and transport simulations using non-equilibrium Green's function (NEGF) methodology. The QuantumATK platform combines the power of a Python scripting engine with the ease-of-use provided by the intuitive NanoLab graphical user interface (GUI).

In addition to presenting the QuantumATK platform, I will showcase how QuantumATK (DFT-LCAO with the NEGF method) is used to model a two-dimensional (2D) materials-based heterojunction tunneling field-effect transistor (TFET), shown in the figure below. 2D materials are very attractive for the nanoelectronics industry since they could become the new channel materials of the future nanoelectronics devices and solve the problems related to non-negligible quantization of Si electronic structure upon scaling. Specifically, we will consider a symmetrically contacted (SC) and asymmetrically-contacted (ASC) TFET where the channel is formed by a heterojunction based on 2D semiconductors: $MoTe_2/SnS_2$ [2]. In the SC device, we use Au for both the source and drain metallic contacts, whereas in the ACS device, we use Al in the drain, in order to have a rather large work function difference between the contacts. Our simulations show how the device trans-conductance of a TFET can be engineered by an appropriate choice of the metallic electrodes. The results also highlight the importance of atomistic device simulations for the optimization of the electrical characteristics of devices based on non-conventional materials.
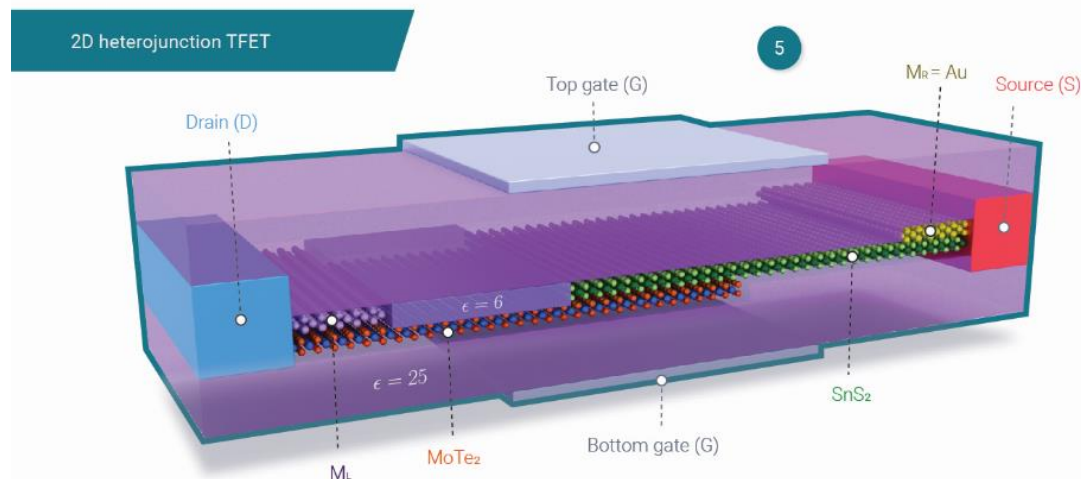
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Helical Molecular Orbitals in Metallacumulenes

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The π-orbitals of even [n]cumulenes (n = number of double bonds) are not in the familiar form of two perpendicular π-systems, but can be twisted as helices[1,2]. Long [n]cumulenes are difficult to synthesize and investigate experimentally because of their high reactivity, but by complexing them with transition metals, the reactivity can be brought down. Here we study the requirements for helical molecular orbitals in different model systems of metallacumulenes and -polyynes. We show that, depending on the position of the metal(s), different structural- and metal-dependent requirements must be met to obtain the helical molecular orbitals. For systems with terminal transition metals, the d_{xz} and d_{yz} must be split while systems with a central metal require the end-groups to be perpendicular; systems having both motifs require both conditions (Figure 1a-b). We show examples of known molecules where helical molecular orbitals are to be expected.
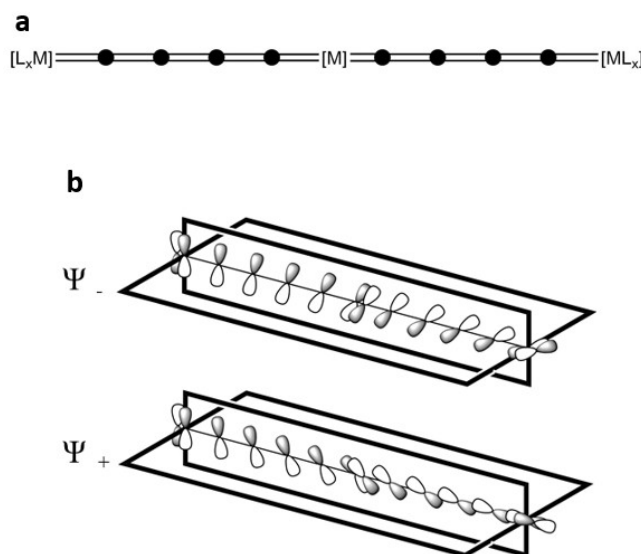
Figure 1. Shorthand formula of a metallacumulene (a) and its molecular orbital depiction (b).

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