Swedish Theoretical Chemistry 2017 – Bridging gaps

Scientific program 16-18 August
Chalmers University of Technology,
Gothenburg, Sweden
Welcome to the Swedish Theoretical Chemistry 2017

Theoretical Chemistry offers an idea-based playground for the utilization and development of tools for analysis. It is crucial within numerous disciplines spanning biology, chemistry, physics, and materials science. Theoretical Chemistry is used here as an umbrella term for quantum chemistry, molecular physics, molecular dynamics/statistical mechanics, computational materials science, computer-aided drug design, bioinformatics and theory-based thermodynamic modelling. Arguably, explorations beyond state-of-the-art by combining experiment with working hypotheses is at the heart of science. Here, theoretical chemistry offers a suite of conceptual computational frameworks based on the fundamental laws of physics and applied mathematics to validate claimed conclusions, identify implications, clarify paradoxes, and suggest new frontiers of exploration.

Each year, one Swedish university arranges the STK symposium in collaboration with the Theory Section of the Swedish Chemical Society. This year, Chalmers University of Technology is hosting the event in collaboration with the University of Borås.

We are delighted to acknowledge:

- The Swedish Research Council
- Chalmers Area of Advance Energy
- Chalmers Area of Advance Materials
- Chalmers Area of Advance Nano

for support and encouragement to accept the undertaking to arrange the 2017 Swedish Theoretical Chemistry (STK) symposium.

Itai Panas
Henrik Grönbeck
Peter Ahlström
12:30 Registration

Session I (Chair: Itai Panas)

14:00 KEYNOTE: Michael Finnis
Thermodynamic Properties of Ultra High Temperature Ceramics

14:40 Peter Broqvist
SCC-DFTB Simulations of Ceria Surfaces and Nanoparticles

15:00 Jolla Kullgren
Defect Cluster at the CeO$_2$(111) Surface – A Combined DFT and Monte-Carlo Study

15:20 Sven Larsson
Bridging Gaps between Physics and Chemistry

15:40 Tore Brinck
Local Surface Properties as Guides to Nanostructural Effects in the Catalytic Properties of Metals and Metal Oxides

16:00 Coffee break

Session II (Chair: Henrik Grönbeck)

16:30 KEYNOTE: Konstantin Neyman
Density-functional Modelling of Ceria-Based Nanomaterials for Catalysis and Energy Technologies

17:10 Mikkel Jorgensen
Bridging the Materials-gap in Heterogeneous Catalysis by Kinetic Monte Carlo Simulations

17:30 Adam Arvidsson
Modelling Partial Oxidation of Methane over ZSM-5 and Mo$_6$S$_8$ Catalysts

17:50 Break

18:00 Rasmus Karlsson
Calculation of Chemisorption and Adsorbate-Adsorbate Interaction Energies Based on Newns-Anderson Tight-Binding Theory

18:20 Dage Sundholm
Calculations of Magnetically Induced Current Densities for Large Molecules

18:40 Poster Session
Session III (Chair: Per Hyldgaard)

09:00 KEYNOTE: Trygve Helgaker
Density-functional Theory in Magnetic Fields

09:40 Jürgen Gräfenstein
Efficient Calculation of NMR Isotope Shifts by Difference-Dedicated
Vibrational Perturbation Theory

10:00 Jens Poulsen
Approximate Quantum Dynamics with “Wigner packets”

10:20 Emelie Ertan
Simulation Local Vibrations in K-Edge Resonant Inelastic X-Ray Scattering
of Molecules and Extended Molecular Systems, Exemplified by Studies of
$\text{H}_2\text{O(g)}$, $\text{H}_2\text{S(g)}$ and Kaolinite

10:40 Coffee break

Session IV (Chair: Kersti Hermansson)

10:50 KEYNOTE: Elsebeth Schröder
The van der Waals Density Functional

11:30 Erik Donovan Hedegård
Polarizable Embedding with Correlated Multireference Methods

11:50 Fahmi Himo
Quantum Chemical Modeling of Mechanisms and Selectivities in
Homogeneous Catalysis

12:10 Carolin König
Linear-Scaling Generation of Potential Energy Surfaces for
Anharmonic Vibrational Spectra Calculations

12:30 Lunch, Hyllan restaurant

Session V (Chair: Peter Ahlström)

14:00 KEYNOTE: Carmen Herrmann
Pathways in Molecular Conductance and Spin Coupling

14:40 Meysam Pazoki
Ionic Movement and Photo-Induced Distortions in Perovskite Solar Cells

15:00 Morgane Vacher
Unraveling the Chemiluminescence Yield of 1,2-dioxetanes

15:20 Coffee break

15:50 KEYNOTE: Peter Kusalik
Bridging Scales in Molecular Simulations of Crystallization and Self-Assembly

16:30 Fei Xie (Inga Fischer-Hjalmars award)
Theoretical and Experimental Studies of Polymer Adsorption and
Polymer Mediated Interactions

16:50 Gunnar Karlström (Björn Roos award)
On the Construction of Intermolecular Potentials from Quantum Chemical
Potentials Based on Ab Initio Quantum Chemical Calculations

17:45 Annual meeting of the Theoretical Chemistry Section of the Swedish
Chemical Society

19:00 Conference dinner, Chalmersska huset
Session VI (Chair: Elsebeth Schröder)

09:00 KEYNOTE: Avital Shurki
Enzyme Catalysis: Insights from Valence Bond

09:40 Inna Ermilova
Toxicity of Hydroxylated Polybrominated Diphenyl Ethers: Bridging Gaps between Experiments and Simulations

10:00 Leif Eriksson
UV-B Response Pathway in Green Plants Modelled Using DFT Cluster Calculations and Non-Standard MD Simulations

10:20 Aatto Laaksonen
Multi-Scale Computer Simulations of Structure and Dynamics in Canonical and Non-Canonical DNA

10:40 Coffee break

Session VII (Chair: Itai Panas)

10:50 KEYNOTE: Cristiana Di Valentin
Quantum Chemical Simulation of Nanostructured Materials: 2D Sheets and 0D Nanoparticles

11:30 Valentina Cantatore
Boron-Doped Graphene for Multifunctional Coating

11:50 Khadga Jung Karki
Simulation of Two Dimensional Spectroscopy of Excitonic Systems Based on Phase Modulation Technique

12:10 Anna Reymer
Twisting DNA

12:30 Lunch, Hyllan restaurant

*** Thank you for coming! ***
1. A Quantum Method for Thermal Rate Constant Calculations from Stationary Phase Approximation of the Thermal Flux-Flux Correlation Function Integral
   Chiara Aieta and Michele Ceotto

2. Mysterious formation of diatomic molecules in space: Radiative association of CH
   Daria Burdakova, Magnus Gustafsson and Gunnar Nyman

3. Effect of surface coverage on the Fischer-Tropsch synthesis mechanism catalyzed by ruthenium and rhenium nanoparticles
   Lucy Cusinato, Iker del Rosal and Romuald Poteau

4. Catalytic CO oxidation driven by ultrashort X-ray pulses
   Elias Diesen, Simon Schreck, Anders Nilsson and Lars Pettersson

5. QM/MM Studies of Dph5 – A Promiscuous Methyltransferase in the Eukaryotic Biosynthetic Pathway of Diphthamide
   Johanna Hörberg and Leif A. Eriksson

6. Keep dynamical Quantum effect in multi-dimensional MD
   Huaqing Li and Gunnar Nyman

   Martin A. Olsson, Geng Dong, Erik Donovan Hedegård, Quan Phung, Per-Åke Malmqvist and Valera Veryazov

8. First-principles studies of CO$_2$ hydrogenation to methanol on Cu-based catalysts
   Matej Huš, Drejc Kopac, Neja Štrah Štefancic, Damjan Lasic Jurkovic, Venkata D.B.C. Dasireddy and Blaz Likozar

9. A generally-contracted Gaussian basis set for photochemistry and photophysics in the range 0-2 keV
   Andreas Nyvang, Per Åke Malmqvist and Valera Veryazov

10. Modelling of water adsorption on nanotubular surface of TiO$_2$: how to simplify a calculation model by introducing formalism of constrained periodic 2D structures?
     Oleg Lisovski, Stephane Kenmoe, Sergei Piskunov, Dmitry Bocharov, Yuri F. Zhukovskii and Eckhard Spohr

11. The Shape of Copper Oxide Clusters Under Oxygen Excess
    Oskar Larsson and Anders Hellman

12. Solubility and diffusion of small molecules in polyethylene composites
    Marin Bohlén, Peter Ahlström, Edvin Erdtman, Thorbjörn Andersson, Mikael Berlin, Thomas Gkoumpris and Kim Bolton

13. An in silico approach to understand the mechanism of antibiotic resistance of carbapenemases,KPC-2
    Sonali G.Chavan, Anna Reymer and Leif A. Eriksson

14. Classical Wigner model based on a Feynman path integral open polymer
    S. Karl-Mikael Svensson, Jens Aage Poulsen and Gunnar Nyman
15. Cu-dimer under methane-to-methanol conditions in SSZ-13
Unni Engedahl and Anders Hellman

16. Computational thermochemistry of cadmium chloride in solution
Stefan Andersson, Francesca L. Bleken, Espen Sagvolden and Ole Swang

17. Tuning Electrocatalysts through Doping
Michael Busch, Baochang Wang, Anders Hellman and Henrik Grönbeck

18. Activation of oxygen on (NH$_3$-Cu-NH$_3$)$^+$ in NH$_3$-SCR over Cu-CHA
Lin Chen and Henrik Grönbeck

19. Exploiting excited-state aromaticity for the design of efficient light-driven rotary molecular motors
Baswanth Oruganti, Jun Wang and Bo Durbeej

20. Catalysis at the rim: a mechanism for high PROX-activity of Pt$_3$Sn
Matthias Vandichel and Henrik Grönbeck

21. OH
Getachew Kebede, Pavlin Mitev and Kersti Hermansson

22. Slip barriers in a polymer crystal: contrasting van der Waals density functional calculations and classical molecular dynamics modeling
Per Hyldgaard, Pär A.T. Olsson, Elsebeth Schröder, Martin Kroon, Eskil Andreasson and Erik Bergvall

23. Assessment of two hybrid van der Waals density functionals for covalent and non-covalent binding of molecules
Yang Jiao, Kristian Berland, Jung-Hoon Lee, Tonatiuh Rangel, Elsebeth Schröder, Jeffrey B. Neaton and Per Hyldgaard

24. Triggering On/Off States of Photoswitchable Probes in Biological Environments
S. Osella and S. Knippenberg

25. An asymmetric restricted primitive model of ionic liquids
Hongduo Lu, Sture Nordholm, Clifford Woodward and Jan Forsman

26. Catalytic hydrocarbon combustion on metal surfaces: A DFT study
Mina Arya, Abas Mohsenzadeh and Kim Bolton

27. Dissociative adsorption of CO$_2$ on Cu(100)
Alvaro Posada-Borbón, Benjamin Hagman, Andreas Schaefer, Lindsay Merte, Mikhail Shipilin, Chu Zhang, Edwin Lundgren, Johan Gustafson and Henrik Grönbeck

28. Explorations of protein-ligand interactions using metadynamics
Yaoquan Tu

29. Electrochemical dehydrogenation of methanol and glycerol on Au
Mikael Valter, Björn Wickman, Jonas Baltrusaitis and Anders Hellman

30. Small-polaron mobility in pure and doped hematite: A DFT + U study
Baochang Wang and Anders Hellman
ORAL CONTRIBUTIONS

Abstracts
Thermodynamic Properties of Ultra High Temperature Ceramics (UHTCs)

Michael W. Finnis¹, T. Davey¹*, A.I. Duff ¹,², T.A. Mellan ¹

¹Imperial College London, Thomas Young Centre, Dept. of Materials and Dept. of Physics, London, UK
²Hartree Centre, STFC Daresbury Laboratory, Scientific Computing Department, Warrington, UK

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The thermodynamic properties of many materials at high-temperature are hard to predict with quantitative accuracy, and often even harder to measure. With recent advances in computational statistical mechanics, it is becoming feasible to use DFT to calculate thermal expansion and heat capacity up to temperatures close to the melting point of a crystal. The approach of quasiharmonic lattice dynamics works well up to about half-the melting point, above which true anharmonic lattice dynamics, besides electronic excitations must be considered. Building on previous work by Grabowski and co-workers[1] (the UP-TILD method), we have combined quasiharmonic lattice dynamics with thermodynamic integration, using empirical interatomic potentials as an auxiliary function to smooth the path of integration (called the TU-TILD method)[2, 3], which made it possible for us to calculate the aforementioned properties of UHTCs with DFT accuracy up to close to the melting point. The method and its results will be reviewed with reference to the carbides and diborides of Zr and Hf, including explanation of the surprising temperature-dependence of the c/a ratio in the hexagonal diborides. The energies of point defects have also been studied in the quasiharmonic approximation. This is a necessary step to providing data of DFT quality to improve the accuracy of phase diagram calculations in such systems.

Acknowledgements: We acknowledge the EPSRC for support within the Program Grant [grant number: EP/K008749/1-2] Material Systems for Extreme Environments (XMat) [grant: EP/K008749/1-2]. The calculations were performed on the Imperial College High Performance Computing facilities as well as ARCHER, the UK’s national high-performance computing service, which is provided by UoE HPCx Ltd at the University of Edinburgh, Cray Inc and NAG Ltd, and funded by the Office of Science and Technology through EPSRC’s High End Computing Programme. We acknowledge support of the Thomas Young Centre under grant TYC101.

References:
SCC-DFTB simulations of ceria surfaces and nanoparticles

Jolla Kullgren,1 Byung-Hyun Kim,1 Kersti Hermansson1 and Peter Broqvist1

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First principles modelling, using e.g. the density functional theory (DFT), has become a valuable tool in materials research. However, today’s computer resources limit the size and time scales that can be studied with such techniques, thereby hindering the full utilization of computational chemistry for large-scale systems in practice. Thus, new developments of reliable approximate and/or parameterized methods are needed.

One promising approximate method, conceptually similar to the DFT, is the self-consistent charge density functional based tight binding method (SCC-DFTB). SCC-DFTB calculations are parameterized against DFT data (see illustration in Figure 1) and are at least two orders of magnitude faster than a standard semi-local DFT calculation. However, to obtain an accuracy comparable to DFT for complex oxides is a task that has proven to be a challenge.

In this talk, I will present our SCC-DFTB parameterization effort for the technologically important reducible oxide CeO2.1 I will discuss the strategy we have developed for the parameterization and the special complication that follows with reducible oxides. Furthermore, I will demonstrate the applicability of the generated parameters and show results from validation by comparing to data obtained from DFT calculations for CeO2. I will show results for oxygen vacancy formation in various ceria structures of different dimensionality, ranging from 0D (nano) to 3D (bulk) and for oxygen adsorption on ceria nanoparticles and preliminary results regarding ceria nanoparticle agglomeration.

Figure 1. The SCC-DFTB method is parameterized from DFT data.

References

Defect cluster at the CeO$_2$(111) surface – a combined DFT and Monte-Carlo study

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Ceria (CeO$_2$) is a technologically interesting material and is found in numerous applications [1]. In many of these, the high interest originates from ceria's remarkable redox properties which result in a rich and variable oxygen chemistry. There is an ongoing discussions in the literature concerning the tendency for oxygen vacancies to form stable clusters at the ceria(111) surface and whether high-resolution STM images of this surface published in the literature [e.g. in Ref 2] actually show clustering of oxygen vacancies, as was claimed. Thus, in a PRB publication in 2014 [3], we challenged this assignment and, based on static DFT calculations, we showed that oxygen vacancies do not cluster, and that other defects known to be abundant at the ceria surface, such as F$^-$ and surface hydroxide groups (OH$^-$), produce very similar STM signatures to oxygen vacancies. In a new study [4], we have introduced temperature and entropy effects in our exploration of the clustering tendency of F$^-$ and OH$^-$ defects. Here, using Monte-Carlo simulations and pair potentials derived from DFT, we discuss the role of entropy on the shape and size of defect clusters, and find that (i) it is necessary to take entropy effects into account for this systems, and (ii) by doing this, good agreement with the experimental STM images is achieved – but only when the defects are assumed to be Fluorine.

Figure 1. Three snapshots taken from the MC simulations of ceria slabs at different temperatures, 300 K, 600 K and 900 K. Top-views of the CeO$_2$(111) surface are shown. Flourine impurities (F$^-$ ions; filled black circles) replace some of the oxygen ions (filled white circles).

References

Bridging gaps between Physics and Chemistry

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Abstract: Solid State Physics (SSP) and Chemistry (in the case of solid bodies) should be identical research fields, but are not. In SSP one deals with itinerant systems and there are metals (M) and semiconductors (SC) and the orbitals are functions of a momentum coordinate. Resistivity is monotonous as a function of temperature; increasing for M and decreasing SC. There are other kinds of behaviour too, however. Resistivities with a minimum are common in mixed-valence metal oxides. The latter cannot be treated using itinerant models, such as the Bloch band model. Diamond, for example, is a SC with a large band gap. If doped with boron, blue diamonds are still conducting at low temperature. In small synthetic, blue diamonds the boron doping can be increased compared to natural blue diamonds. The colour changes from blue to black and the system becomes superconducting. A consistent model will be discussed.
Local Surface Properties as Guides to Nanostructural Effects in the Catalytic Properties of Metals and Metal Oxides

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Nanostructured metals and metal oxides often exhibit vastly different catalytic properties than crystalline materials. The classical example is gold, which is chemically inert in crystalline form, whereas nanoparticulate gold is known to catalyze a number of reactions. The properties of nanocatalysts depend on the local structure, and typically the catalytical activity is correlated to the binding binding affinity for the reactants at the active sites. In this lecture we will show that the local binding affinity can be predicted from local properties computed by Kohn-Sham density functional theory.

The molecular electrostatic potential $V(r)$ has been used extensively to analyze chemical reactivity and intermolecular interactions. Brinck et al. demonstrated already in 1992 that the interactions of halogens with Lewis bases, i.e. halogen bonding, can be explained by the presence of surface maxima in $V(r)$ [$V_{S,max}$] at the end of the halogen atom along the extension of the bond [1]. Clark et al. later denoted positive end-region as a σ-hole [2]. Murray et al. extended σ-hole bonding to compounds of group IV-VII elements [3]. Here we show that this concept also can describe the interaction of metal and metal oxide nanoparticles with Lewis bases; the binding affinities of the Lewis bases correlate with the magnitudes of the $V_{S,max}$. Furthermore in the case of symmetric gold and platinum nanoclusters, the most positive $V_{S,max}$ are found at low-coordinated atomic sites, and they increase in the order surfaces, edges and corners in agreement with the increasing catalytic activity.

Our studies indicate that electrostatics plays a key role in the binding events leading to catalysis, but that the interactions also have significant contributions from charge transfer and polarization. To account for these effects, we have defined the local electron attachment energy $E(r)$ as complement to $V(r)$ [4]. We will show that $E(r)$ provides similar site selectivity maps as $V(r)$, but generally gives better correlations for the binding energies of Lewis bases to metal nanoparticles, in particular for the binding of soft bases.

References
Density-functional modelling of ceria-based nanomaterials for catalysis and energy technologies

Konstantin Neyman

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Ceria (CeO₂) is an important component of modern functional materials with applications including catalysis and energy technologies. Various key properties of ceria are known to remarkably change at the nanoscale. This presentation highlights recent progress achieved by my research group in the description of ceria nanostructures and metal/ceria nanocomposites using density-functional calculations [1]. In particular, the following questions will be addressed: (i) oxygen spillover to Pt species in nanoparticulate Pt/CeO₂ aggregates [2]; (ii) experimental and theoretical quantification of the charge transfer through Pt-CeO₂ interfaces [3,4]; (iii) interplay between supported metal atoms and particles in ceria-based nanomaterials for fuel cell catalysis [5-7].

Figure 1. Model 1.5 nm large Pt₁₂₂ particle used to describe charge transfer through the Pt{111}||CeO₂(111) interface [4].

References

Bridging the Materials-gap in Heterogeneous Catalysis by Kinetic Monte Carlo Simulations

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Heterogeneous catalysis is of vital importance to modern society. Catalysis is applied for various purposes, including automotive exhaust cleaning and production of synthetic fuels. Technical catalysts are often designed as transition-metal nanoparticles supported on oxides. Atomistic understanding in heterogeneous catalysis has traditionally been obtained by studies of single crystal surfaces as models for nanoparticles. This introduces the so-called materials-gap. The materials-gap is a significant limitation as nanoparticles have different energy landscapes than surfaces [1]. Density Functional Theory (DFT) calculations of adsorption on nanoparticles of a few 100 atoms is computationally feasible [1]. However, the computational cost to calculate entire reaction-energy-landscapes to study reaction kinetics on nanoparticles is insurmountable.

In this study the kinetics of nanoparticle-catalysis is studied using DFT calculations and kinetic Monte Carlo simulations. The computational challenge of mapping out the entire reaction-energy-landscape is overcome by using the generalized coordination number as a descriptor [2]. CO oxidation over Pt nanoparticles and Pt(111) is studied as an archetypical reaction. We find that nanoparticles exhibit a superior catalytic activity (Figure 1) compared to Pt(111), which is attributed to the various different sites present on the nanoparticle. Furthermore, we find that the most active site changes with reaction conditions, which leads to a catalytic activity that is dependent on particle-size. The present results illuminate atomistic behavior of catalysis, and provides a convenient scheme to couple quantum chemical DFT calculations to the observable macroscopic catalytic activity.

\textbf{Figure 1.} Simulated Catalytic Turnover Frequency (TOF) as a function of Temperature for Pt(111) and a 3.6 nm nanoparticle. Partial pressures: 20 mbar CO and 10 mbar O\textsubscript{2}.

\textbf{References}

Modelling partial oxidation of methane over ZSM-5 and Mo$_6$S$_8$ catalysts

Adam Arvidsson, and Anders Hellman

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Partial oxidation of methane is an interesting but difficult reaction. Experimentally, methane can be partially oxidized to methanol over metal-exchanged zeolites. In particular the ZSM-5 zeolite has been widely studied and has been shown to be active when exchanged with Cu, Ni, Co, and Fe [1-4]. A clear [Cu-O-Cu]$^{2+}$ candidate for active site for the methane-to-methanol reaction has been put forth for Cu-ZSM-5 [1,5]. A first question to ask is whether this [Cu-O-Cu]$^{2+}$ motif is generic and could work also with Cu interchanged with Ni, Co, or Fe. Herein, we employ first-principles calculations and micro-kinetic modelling to compare the performance of Ni, Co, and Fe in this motif to the Cu one. Our finding is that the methane-to-methanol reaction can only realistically happen for Cu on this motif. Thus, this particular motif can be excluded as an active site candidate for Ni-, Co-, and Fe-ZSM-5 [6].

Another catalyst that is interesting for partial methane oxidation is the Mo$_6$S$_8$ cluster. However, instead of the methane-to-methanol reaction we use H$_2$S as an oxidant and transform methane into hydrogen and CH$_3$SH. Using electronic structure calculations and mean-field micro-kinetic modelling to study this reaction, we successfully capture the experimentally observed trend, i.e. that promoting the Mo$_6$S$_8$ cluster with K increases the selectivity towards CH$_3$SH, and Ni enhances the hydrogen formation [7].

References


Calculation of chemisorption and adsorbate-adsorbate interaction energies based on Newns-Anderson tight-binding theory

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The rational design of heterogeneous catalysts requires theoretical models that are able to predict how different adsorbates chemisorb and interact at the catalyst surface. Density functional theory (DFT) has risen to become a standard tool in calculating chemisorption and interaction energies, but at a significant cost. This high cost limits our ability to quickly screen materials for activity, and also severely limits our ability to account for adsorbate-adsorbate interactions in mesoscale simulations such as e.g. kinetic Monte Carlo. In this talk, I will present our recent work on parametrizing a model based on Newns-Anderson tight-binding theory [1, 2, 3] to predict chemisorption energies. The model is fitted to data calculated using DFT, and allows us to calculate chemisorption energies, including the effect of strain, using only the density of states of the bare metal surface as input. The calculations can be made at a trivial cost in comparison with the DFT calculation. The model also allows us to disentangle the band structure-mediated contribution to the adsorbate-adsorbate interaction energy. The Newns-Anderson contribution can thus be a first ingredient in a physically and chemically satisfying framework for accounting for adsorbate-adsorbate interaction energies.

References

Calculations of Magnetically Induced Current Densities for Large Molecules
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Gauge-origin independent magnetically induced current densities can be calculated for large molecules, because the gauge including magnetically induced current method (GIMIC) uses gauge-including atomic orbitals (London orbitals) that remove all references to the gauge origin and improve the basis set convergence.[1,2,3] GIMIC calculations provide detailed information about electron delocalization pathways, the degree of aromaticity, and current pathways in molecules. In this talk, I give an overview of the GIMIC method including recent applications of the approach to large molecules.

The applications of the GIMIC method include current-density calculations on fullerenes,[4] gaudienes,[5,6], and porphyrinoids.[7,8,9,10]

Density-Functional Theory in Magnetic Fields

Trygve Helgaker

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In strong magnetic fields, chemistry changes: electronic states change their character, atoms and molecules change their shape, and their interactions with radiation are affected, often in a dramatic manner. Such magnetic-field induced changes are not only fascinating as a contrast to the chemistry observed on the earth, they are also relevant to astrophysics, where molecules in stellar atmospheres are subject to strong magnetic fields. Our calculations on molecular systems in strong magnetic fields have revealed and highlighted many interesting phenomena such as the transition to diamagnetism of paramagnetic molecules at a critical field strength [1,2]. Perhaps most interestingly, antibonding orbitals are stabilized in a magnetic field, leading to bound triplet H₂ at field strengths of about 10⁵ Tesla, appropriate for some white-dwarf atmospheres [3].

In this talk, we review the theory and application of quantum-chemical electronic-structure methods for molecules in magnetic fields — including coupled-cluster theory [4] but with special emphasis on density-functional theory (DFT). We demonstrate that Kohn–Sham current-density functional theory (CDGT) with meta-GGA exchange–correlation functionals provide a good description of molecules in magnetic fields, at a reasonable cost [5].

References

Efficient calculation of NMR isotope shifts by difference-dedicated vibrational perturbation theory

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Recently, isotope substitution has become a more technique to enhance the information available from NMR spectroscopy. NMR isotope shifts have been used e.g. as a sensitive probe for the properties of hydrogen and halogen bonds, or a source of additional information on the conformation of biomolecules. To predict NMR isotope shifts computationally, one needs to calculate the vibrationally averaged NMR properties for each of the isotopologues. Algorithms for such calculations have been developed and implemented (see e.g. [4]); however, they require to calculate the NMR properties for roughly 12 × (number of atoms) slightly different geometries. Thus, their cost is often prohibitive for other than very small molecules.

We have developed difference-dedicated vibrational perturbation theory (DD-VPT) that allows the calculation of NMR isotopic shifts (as well as isotope shifts of other properties) with considerably fewer (10–20) property calculations, independently of the size of the molecule. The basic idea of DD-VPT is to construct a limited set of localized vibration modes that accounts for the differences between the vibrational motifs of the two isotopologues and to restrict the property calculation to the part of the property surface spanned by these vibrations. The DD-VPT method provides a way to perform routine calculations of NMR isotope shifts for peptides, oligosaccharides and similar molecules.

Figure 1. The set of localized vibration modes for the calculation of isotope shifts between all-H pyridine and pyridine-2-d. The deuteration site is marked in black.

References

Approximate quantum dynamics with “Wigner packets”

Jens Poulsen¹, and Gunnar Nyman¹

¹Department of Chemistry and Molecular Biology, Gothenburg University

Many interesting processes in chemistry are intrinsically of quantum mechanical nature. Perhaps, the most prominent example is that of a chemical reaction. As the dimensionality of the problem grows, so does the difficulty of modelling it. However, quantum effects in large systems containing many degrees of freedom can be modelled approximately using Wigner’s formulation of quantum statistical mechanics. It uses a classical-like phase-space distribution function for describing the probability of finding a particle. We show that the dynamics of this function can be approximately studied by first resolving it into fundamental “building blocks”, so-called complex Gaussian Wigner functions, followed by a time-propagation of these using a time-dependent variational principle. It is shown that the method approximately accounts for quantum mechanical interference and tunneling effects.
Simulation local vibrations in K-edge resonant inelastic x-ray scattering of molecules and extended molecular systems, exemplified by studies of H$_2$O(g), H$_2$S(g) and kaolinite

Emelie Ertan

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Using a combination of density functional theory and multi-configurational (RASPT2) calculations, I will show how we can extract detailed information on the ground state potential energy surface from resonant inelastic x-ray scattering (RIXS) experiments.

High-resolution RIXS is a powerful second-order spectroscopic technique that gives us valuable information on the local electronic and molecular structure of molecules and molecular systems. By applying RIXS, we can probe changes in the immediate electronic environment experienced by the core-excited atom. The process is also influenced by ultra-fast core-excited state dynamics, timed by the core-hole lifetime, which give rise to lower energy excitations, such as vibrational excitations. In other words, RIXS provides information on both the electronic states and vibrations. By looking at the quasi-elastic K-edge RIXS, we can obtain a detailed mapping of the ground state potential energy surface [1], and for certain systems even with vibrational selectivity introduced by the dynamics in the core-excited states [2]. The locality of the of the excitations in RIXS also makes it possible to study local vibrations in extended molecular systems [3].

In this talk, I am going to present a computational methodology, consisting of ab initio calculations and quantum dynamics, and results for simulations of K-edge RIXS in small systems, exemplified by H$_2$S (g) and H$_2$O (g) as well as in extended molecular systems, exemplified by kaolinite. I am going to look at the vibrational profile of the RIXS spectrum and discuss particular features by analysing the shape of the potential energy surfaces.

References

The van der Waals density functional

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Density functional theory (DFT) has long been an important tool for explaining and predicting materials structure on the atomic level. DFT is in principle exact, but the exchange-correlation part of it must be approximated as its precise form is unknown and for fundamental reasons always will be. Thus, although DFT as a theory includes interactions on all length scales, many commonly used expressions of it do not include long-range interactions, such as van der Waals (vdW) -or dispersion- interactions.

For the past couple of decades we have worked to include the vdW interactions in the functional. This resulted in 2004 in the functional vdW-DF [1,2], which meant that for the first time extended systems with sparse parts could be treated on an equal footing with bulk materials, as well as molecules interacting with extended surfaces. Work has continued on how to balance the exchange and correlation part, based on physics principles, this more recently lead to the introduction of the consistent-exchange functional vdW-DF-cx [3,4].

In my talk I will give a brief overview over the anatomy of the vdW-DF-cx as well as some of the challenges faced. Further, I will present our studies of molecular physisorption on surfaces from a number of projects, and I will discuss the advantages of using DFT for such systems where one or more parts are extended in space.

References

Polarizable embedding with correlated multireference methods

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Electronic structures with large static and dynamical correlation effects pose a formidable challenge in modern quantum chemistry. Static correlation can be recovered using a complete active space (CAS) method. Dynamical correlation is usually obtained through perturbation theory. However, these methods are computationally expensive and the results are often non-quantitative due to lacking orbitals in the active space or incomplete description dynamical correlation. In addition, chemistry usually occurs in a solution or within structured environments. To bridge the gap between calculated and experimental quantities, environment effects must be taken into account. This includes both the nuclear dynamics and the electronic interactions between the solute and the environment.

To describe the static and dynamical correlation efficiently and accurately, we have combined the CASSCF method with (short-range) density functional theory (srDFT) using a range-separation method (CAS-srDFT) \[1–3\]. In this talk, the accuracy of CAS-srDFT will be demonstrated by calculating absorption spectra and reactivity of several transition metal systems that otherwise are known to be problematic \[4,5\]. Further, it will be shown that CAS-srDFT is sufficiently efficient to allow proper sampling over many solvent configurations to model dynamical solvent effects. Electronic environment effects are included through the use of an explicit mean-field embedding method that includes both electrostatic and polarization interactions. The importance of an explicit description of the environment as well as the importance of considering solvent dynamics will be demonstrated \[5\]. Finally, the formal equivalence of our method to polarizable continuum methods (e.g. COSMO or PCM) will be discussed.

Using modern density functional theory methods it is today possible to routinely and accurately treat relatively large systems. The calculated energies can be used to rule out or substantiate reaction mechanisms and have also been shown to be sufficiently accurate to satisfactorily reproduce various kinds of selectivities. These developments have made it possible to tackle increasingly difficult problems in homogeneous catalysis.

This talk will give a brief account of the methods used and discuss our recent results in this field, in which we take advantage of both DFT calculations and kinetics simulations to understand reaction mechanisms and rationalize the origins of selectivities.
Linear-scaling generation of potential energy surfaces for anharmonic vibrational spectra calculations

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Accurate calculations of vibrational spectra using vibrational wave function techniques require accurate representations of multi-dimensional potential energy surfaces (PESs). Unfortunately, the construction of multi-dimensional PESs suffers from steep computational scaling with increasing system size. Recently, we have shown that molecular fragmentation schemes in combination with matching semi-local vibrational coordinates[1] allow for generation of PESs in a very cost-efficient manner. By introducing an additional transformation step, concerning only a fraction of the vibrational degrees of freedom, this scheme achieves linear scaling of the accumulated cost of the all electronic energy calculations required in the PES generation.[2]

In this contribution, I will (i) outline the principles behind our cost-efficient scheme to generate multi-dimensional PESs, (ii) show the fast convergence of the molecular fragmentation scheme in PES generations for oligo-phenyl examples, and (iii) provide comparison to experiment for smaller organic molecules, namely methylfurfural and dicycloprenyl ketone.[3] I will further discuss the implication of this work for future applications to biomolecular systems.

References

Pathways in molecular conductance and spin coupling

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For understanding spin-polarized electron transport through molecular bridges and (exchange) spin coupling between local spin centers within a molecule, it is interesting to know which parts of the molecule are responsible for mediating transport or spin interactions.

In the case of spin coupling, ferro- and antiferromagnetic pathways may add up or partially cancel, which is hidden if only the total spin coupling is considered. A new approach to decomposing spin coupling based on Green's functions [1] allows not only identifying which molecular parts are responsible for spin coupling in isolated molecules, but may also allow for distinguishing, e.g., between intramolecular and through-surface contributions [2].

In electron transport through molecular junctions, local decomposition of electron transmission will be used to highlight the importance of spin-polarized parts of the molecule for transport [3-7].

In both cases, the tunability of pathways by changes in the chemical structure will be discussed.

Ionic Movement and photo-induced distortions in Perovskite solar cells

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In this work we present combined theoretical and experimental studies on the ionic movement, photo-induced ionic movement and the relations to the Stark effect and current voltage hysteresis [1-3] in recently emerged perovskite solar cell devices. Density functional theory calculations shows that the energy barriers of ionic movement depends strongly on the monovalent cation in the APbI₃ perovskite solar cell materials [2]. Therefore the local structural distortions and dielectric response to the local fields are strongly connected to the monovalent cation which plays a key-role in the current-voltage hysteresis [3] and Stark effect [1] within the device. Our data reveal new information about the device photo physics in perovskite solar cells and worth further investigation.

Figure 1. A schematic illustrating the ionic movement and dipole flipping (left) and the density of states together with electronic thermalization and consequent ionic vibrations (right) in perovskite solar cell materials; Ref [1].

References

Unraveling the chemiluminescence yield of 1,2-dioxetanes

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Chemiluminescence is the emission of light as a result of a non-adiabatic chemical reaction [1]. The present work is concerned with understanding the yield of chemiluminescence. In particular, it was found experimentally already in 1980’s that the chemiluminescence yield dramatically increases upon methylation of 1,2-dioxetane from approximately 0.3% to 35% [2]. More than 30 years after the measurements, the reason for the impressive increase in chemiluminescence yield with the degree of methylation remains an outstanding question. The aim of the present work is to address it, using simple and accessible concepts. Both ground-state and non-adiabatic dynamics (including singlet excited states) of the decomposition reaction of various methyl-substituted dioxetanes have been simulated, starting from the first O–O bond-breaking transition structure. The simulations show that methyl-substitution leads to a significant increase in the dissociation half-life: 58 fs for the unmethylated dioxetane, while 117 fs for the tetra-methylated compound. This is because the rotation around the O–C–C–O dihedral angle is slowed down by the “heavy” methyl groups. As a consequence, the molecular system stays longer in the so-called “entropic trap” region [3]. A simple kinetic model is proposed to explain how this leads to a higher chemiluminescence yield [4].

Figure 1. (a) Methyl-substituted dioxetane molecules. (b) Simple kinetic model fitting the experimental chemiluminescence yields and the calculated dissociation half-lives using adiabatic ground state dynamics simulations (bar) or non-adiabatic surface hopping dynamics simulations (cross), for the different compounds.

References

Bridging Scales in Molecular Simulations of Crystallization and Self-Assembly

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Crystallization and self-assembly processes are ubiquitous in nature and have numerous important roles in technological applications. Yet, these ordering processes have proven difficult to study with experiments, in part due to their stochastic nature. Molecular simulations have recently been demonstrated to be able to provide many insights into the underlying molecular mechanisms. In this presentation I will begin with a brief review of the key issues around simulations of crystallization, considering briefly the attributes and limitation of various models and methods. I will describe some approaches we have developed and utilized for the simulation of the formation and growth of crystals, both in the homogeneous and heterogeneous contexts. Specific results for gas (clathrate) hydrates and for ice will be used illustratively. These results will demonstrate that the process of crystallization is characterized by collective phenomena involving many molecules. The nature of the structural fluctuations that characterize these ordering processes, including lifetimes and transitions of specific structures (e.g. cages), will be examined, and I will show that defects can play key roles in the observed behaviours. More generally, I will show how rugged funnel-shaped potential energy landscapes provide a lens for understanding the phenomenology of crystal nucleation in gas hydrates and ice. I will conclude with an exploration of self-assembly processes of metal organic framework (MOF) materials. The observed behaviour will be compared with that found in ice and gas hydrate systems. Using what we have learned, I will discuss possible ways to bridge the time scales and length scales necessary to probe successfully self-assembly in a MOF system.

Figure 1. Appearance of non-standard cages (blue) in simulations of the nucleation of a gas hydrate.

Figure 2. Simulation of the self-assembly of a Zn-carboxylate MOF.
Theoretical and Experimental Studies of Polymer Adsorption and Polymer Mediated Interactions

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Polyelectrolyte adsorption and polymer mediated interactions in different colloidal polymer systems have been studied in this work. Theoretical methods and experimental techniques are combined, in order to obtain more general reliable results, as well as a deep understanding of the molecular mechanisms that are responsible for the observed behaviors. Two different types of highly charged cationic polyions have been used to explore the adsorption onto oppositely charged surfaces. The adsorption varies with concentration of simple salt and the adsorption dependence on molecular weight have been considered. Polymer density functional theory and null ellipsometry have been utilized to study the adsorption. Various colloidal polymer systems have also been investigated in order to scrutinize polymer mediated interactions. For systems containing charged colloidal particles and non-adsorbing polyethylene oxide (PEO) chains, we studied gelation and constructed a coarse-grained model, to quantitatively compare predicted structure factors with corresponding experimental data. We have devoted some extra efforts to predict and understand the temperature response of polymer mediated interactions, in systems where the pure polymer solution display an local critical solution temperature (LCST). This has, for instance, resulted in predictions that such colloidal particle + polymer dispersions can display a phase behavior that responds on a nonmonotonic manner to temperature change (specifically: flocculated - dispersed - flocculated). these predictions are in qualitative agreement with experiments, and achieved without any assumptions of temperature-dependent interactions. Another prediction from our studies on LCST polymer solutions, is that these may undergo phase separations in porous environments, even though there is only one phase for all compositions in the bulk solution.
On the construction of intermolecular potentials from quantum chemical potentials based on *ab initio* quantum chemical calculations.

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Abstract: The construction of intermolecular potentials based on *ab initio* quantum chemical calculations is reviewed. It is shown that intermolecular potentials for rigid and flexible molecules can be constructed from local electrostatic and polarizability properties of the interacting molecules. Such properties can be extracted from theoretical calculations. The importance of polarizable potentials is discussed and examples will be given. Finally the possibility to improve the quality of the calculations will be discussed.
Enzyme catalysis: Insights from valence bond

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Understanding enzyme catalysis and developing ability to control it, is one of the greatest challenges of biochemistry to date. Few successful examples of computational based enzyme design proved the fantastic potential of computational approaches in this field. Yet, relatively modest rate enhancements were reported and further development of complementary methods is still required.

The significant progress of ab-initio valence bond (VB) methodology within the 21st century together with its implementation within the hybrid ab-initio VB and molecular mechanics approach (VB/MM), enables, in turn, progress within the field of enzyme catalysis. The VB/MM method uses the unique ability of the valence bond approach to provide chemical insight for the studied reactions, which is not available in other MO based methodologies. Our work uses this ability and offers a conceptually simple scheme to improve our understanding of reactivity within enzymes. The scheme involves calculation of the contributions of each residue to the overall catalysis along with analysis of the effect of specific residues on the various VB structures using the linear response approximation. Using this scheme, we can identify the specific role that each residue within the enzyme plays in catalysis. The scheme is based on breakdown of the total catalytic effect into contributions of individual protein residues, which are further decomposed into chemically interpretable components, using valence bond. The scheme will be demonstrated. It will be shown to shed light on the origin of catalysis in wild-type Haloalkane dehalogenase and its mutants. Overall, the VB/MM is shown to be a powerful tool to study the mechanism of enzymatic catalysis as it provides information from ab-initio VB which is not readily available in other methods today.
Toxicity of hydroxylated polybrominated diphenyl ethers: bridging gaps between experiments and simulations

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Hydroxylated polybrominated diphenyl ethers (OH-PBDE) are used for many purposes, for example for preventing the fire or for slowing it down. At the same time these substances are produced by organisms in the marine environment. Toxicity of OH-PBDEs became an interest for many groups of experimentalists. Legradi et al. [1] have studied OH-PBDE in cell cultures and zebrafish embryos and found that toxicity of different forms of OH-PBDE can vary by several orders of magnitude. These work gave us the motivation for studying OH-PBDEs by performing quantum chemical (QM) and molecular dynamics (MD) simulations in order to find out possible correlations between toxicity and physical-chemical properties of these molecules. Particularly we tried to relate calculated thermodynamic properties (pKa, log(P) and ΔG^bind) with concentrations at which toxic effects were observed. pKa values for 19 compounds have been computed by quantum mechanical methods (B3LYP/6-31+G(d,p), B3LYP/6-311++G(d,p), MP2/6-31+G(d,p), MP2/aug-cc-pVDZ) using Gaussian09 software. No correlation have been found between toxic effect concentrations and pKa values. In order to study the same set of compounds using MD simulations partial charges have been derived in an aqueous environment using RESP software with HF/6-31G(d). LogP values have been computed by MD simulations with expanded ensemble (EE) approach. Partition coefficients obtained from EE calculations showed medium correlations between log(P) values and logarithms of toxic concentrations; this correlation became stronger for selected set of ortho conformations where no Cl atoms were present. Furthermore, four selected forms of OH-PBDE were simulated in a model (DMPC or POPC) lipid bilayer by well-tempered metadynamics (MetaD) simulations. MetaD provides information about free energy profile of the selected molecules in a lipid bilayer, from which binding free energies for different molecules to a membrane can be deduced. A conformational scan from MetaD simulations showed that different molecules enter membranes in different conformations and situate themselves in certain ways in the membranes. This work shows that combination of QM and MD approaches can provide a useful insight into possible molecular mechanisms of the toxic action.

References

UV-B response pathway in green plants modelled using DFT cluster calculations and non-standard MD simulations.

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The UV resistant locus 8 (UVR8) protein has been identified as the main plant UV-B ‘antennae’, and undergoes a number of events in order to trigger the genetic response towards UV stress in green plants. UVR8 is a highly globular protein, with a seven-bladed \(\beta\)-propeller WD40 repeat structure (Fig. 1). The N- and C-termini are both located at the bottom side of the barrel, and the top part contains a unique structural arrangement rich in tryptophan and arginine.

The protein is present in the cytosol as a homodimer, with the tryptophan-rich sides of the monomers facing each other. Upon UV-radiation, the first step is a cascade of excitation and electron/proton transfer events within the Trp-rich regions, which in turn triggers rupture of the dimer. The C-terminal tail of the monomeric protein, which displays an inverted energy landscape of an intrinsically disordered protein, is thereby free to interact with COP1, whereby the formed complex enters the nucleus to initiate gene expression.

The crystal structure of UVR8 was determined only five years ago,\textsuperscript{1} and published shortly after a detailed homology model thereof.\textsuperscript{2} Several studies, both theoretical and experimental, have been reported aiming to shed light on the initial UV-response leading to monomerisation of the homodimer and subsequent interaction with COP1. We will herein outline our latest findings and plausible model of the mechanism of action of UVR8, based on detailed density functional theory calculations on cluster models of the Trp-rich region,\textsuperscript{2,3,4} combined with molecular dynamics simulations, including replica exchange and steered MD simulations, force field development, and \textit{de novo} metadynamics studies of protein folding\textsuperscript{5,6,7}

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Multi-scale computer simulations of structure and dynamics in canonical and non-canonical DNA.

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Abstract
We have applied Newton Inversion (NI) method [1] to construct solvent-mediated coarse-grained (CG) interaction potentials for both B-DNA [2,3] and human telomeric G-quadruplex DNA [4,5,6] with explicit ions from underlying atomistic MD simulations. The effective CG force fields are constructed from inter- and intra-chain topologies for which radial distribution functions (RDF) are calculated and averaged in microsecond Molecular Dynamics (MD) simulations. The CG models use single nucleotides as interaction sites without sequence-specific information. The electrostatic interactions are treated explicitly in the CG simulations and effect of ion concentration to structural and dynamical properties is investigated. We are able to reproduce several key properties such as the persistence length and its dependence on ion concentration. We have calculated ring closure probabilities and topologies and energy landscapes for DNA minicircles and superhelical structures in super-coiled DNA. The CG-FF describes well mechanical properties of DNA, important, for example, in condensation and packaging. For the quadruplexes we show that CG-FFs can be made transferable between several quadruplex topologies. Back-mapping of CG structures of DNA onto all-atom description is shown.

Figure: Solvent-mediated coarse-grained model of rodlike higher-order quadruplex at different salt concentrations.

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Coarse-Grained Simulation of Rodlike Higher-Order Quadruplex Structures at Different Salt Concentrations.
*ACS Omega* (2017), 2(2), 386-396.
Quantum chemical simulation of nanostructured materials: 
2D sheets and 0D nanoparticles

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In this talk I will review our recent work, based on density functional theory calculations, on technologically relevant nanostructured materials. In particular, we are interested in 2D single layer materials (e.g. graphene sheets) and in 0D semiconducting oxide nanoparticles (e.g. TiO₂), for their application in the fields of energy, environment and health.

In the first part, non-metal doped graphene is investigated as a promising substitute of metal electrodes in fuel cells by means of computational electrochemistry tools. [1,2]

In the second part, titanium dioxide/graphene interface is analyzed as a fundamental component of efficient nanocomposites for photocatalysis and photovoltaics. [3,4]

In the third part, titanium dioxide nanoparticles of different size and shape are compared in terms of structural, electronic and energy/charge carriers' properties. [5,6]

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Boron-Doped Graphene for multifunctional coating

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We describe a route to achieve multi-functional graphene coating through DFT calculations. To start with we show how chemical bonding between a copper substrate and a graphene layer can be obtained if the graphene is a priori boron doped. [1] Utilizing the well-known epitaxy between graphene and Cu(111) [2] and pair-wise binding to the Cu(111) surface through boron sites,[3] we can observe co-existence of pseudo-gap property in the graphene subsystem and, at the same time, a metallic density of states in the Cu subsystem at the common Fermi energy. Apparently a paradox is that the two subsystems, the doped graphene and the Cu surface, preserve and even recover their individual integrities upon formation of surface chemical bonds. Employing pyridine as test molecule, conditioned ability of a nucleophile to offer competitive dative bonding with the substrate for boron sites is demonstrated. It is shown also that the adsorption of small molecules on the BBG@Cu system occurs for the case of half coverage and for adsorption to boron atoms originally bound to the on-top site of Cu(111). The ability of complementary boron sites to compensate for loss of binding between on-top site and boron, resulting from said bonding to the incoming nucleophile, is emphasized. Based on these observations, the possibility to study infinite layered systems comprising FeSe monolayer and boron doped graphene is inferred and first insights on the peculiar magnetic structure of the system are showed.

References

Simulation of two dimensional spectroscopy of excitonic systems based on phase modulation technique

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Two dimensional spectroscopy has been intensively used to study electronic and vibronic coherences in biological systems and semiconductors[1]. This technique studies coherent as well as incoherent signals that arise from the nonlinear interaction of a sequence of laser pulses. In this talk, we present a method to directly evaluate the 2D signal based on elementary quantum kinetics in order to compare with the common approximate perturbative approaches. We consider incoherent action signals, such as fluorescence and photocurrent[2], as the observables, which are easily accessible in measurements. These observables are calculated by solving the time evolution of the density matrix in the Lindblad form, which can take into account all possible decoherence processes. The phase modulation technique is used to separate the relevant nonlinear signals from the different possible interaction pathways. The approach can be used to calculate 2D spectra of any quantum system.

Figure 1. Four level system used to simulate the two dimensional spectra. |0> is the ground state, |1> and |2> are two excitonic levels and |3> is a biexciton level. The transition dipoles are given by μ and lifetimes are given by τ.

Figure 2. Absorptive component of the two dimensional spectra as a function of the time delay between laser
pulses. The spectra have two peaks on the diagonal, which trace the population relaxation. The peaks on the off-diagonal are due to the coupling of the two excitonic levels.

References

Twisting DNA

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Ability of DNA to dynamically change its superhelical state is central to many biological functions, including regulation of gene expression, repair, and packaging in the cell [1-4]. To address conformational mechanics of DNA during supercoiling transitions we designed a new structural constraint, implemented in PLUMED free energy library environment package [5], which can be used in complement with standard all-atom molecular dynamics software. The constraint controls the value of total twist between any two base pairs in a DNA molecule, while it does not restrict any other DNA helical parameter. The constraint can be applied to DNA molecules of any length and curvature, alone or in complex with other molecules. This allows for the first time to study DNA in conditions resembling its in vivo state, where DNA’s topology is substantially restricted. As a proof of concept, we applied the restraint to four different linear DNA molecules, changing their superhelical density from -0.15 to +0.15, which corresponds to under- or overwinding by 5 degrees per base pair step. DNA’s response to the torsional stress is discontinuous – certain dinucleotide steps are more susceptible to modifying their twist through coupled changes in the phosphodiester backbone. This allows the remaining base pair steps to stay close to a canonical B-form conformation despite the overall torsional restraint. These findings constitute a new aspect of how DNA sequence can contribute to biological regulation mechanisms.

References (Written in Arial 12 pt)
A Quantum Method for Thermal Rate Constant Calculations from Stationary Phase Approximation of the Thermal Flux-Flux Correlation Function Integral

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The calculation of thermal reaction rate constants is a central problem in theoretical chemistry, and exact classical and quantum expressions have been formulated [1]. However, approximate approaches are necessary when dealing with complex reactions, and several techniques have been developed in recent years. They include taking quantum corrections into consideration in classical transition state theory (TST) [2], semiclassical theories [3], ring polymer molecular dynamics (RPMD) [4], and quantum approaches [5]. In this work, we have developed a new quantum mechanical method to compute reaction rate constants, which is related to Miller’s quantum instanton (QI) [6]. Starting from the exact definition of the thermal rate constant as the time integral of the quantum flux-flux correlation function, upon introduction of a steepest descent approximation, we have derived an expression which has the same structure of the original quantum instanton but includes a contribution from real-time dynamics. This new method has been tested on the one-dimensional Eckart barrier (both symmetric and asymmetric), and on the two-dimensional H + H₂ and D + H₂ collinear reactions. Results over a wide range of temperatures have been found to be in agreement within 10% of the exact quantum mechanical estimates.

References

Mysterious formation of diatomic molecules in space:
Radiative association of CH

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When new stars are born, matter is contracting towards their center of mass during a so called gravitational collapse. The gravitational energy is then transformed into kinetic energy, similar to a falling object. For the star formation to continue efficiently, some of the kinetic energy must be removed, which can occur by emitting electromagnetic radiation [1]. Emission of electromagnetic radiation can be efficiently done by molecules. Therefore knowing which molecules are present in the interstellar media, how they are created and destroyed is of importance when considering star formation.

This work was concentrated on the radiative association reaction of the CH molecule. Radiative association is the process where a molecule is formed, from two atoms or smaller molecules, while emitting a photon (i.e. electromagnetic radiation). The CH molecule was chosen for this study because of its occurrence in several chemical reactions in the interstellar medium, the sun, and comets [2]. The focus of the study was to calculate the reaction cross sections and reaction rates for the CH molecule and its isotopes. The reaction cross section is a measure of how frequently the atoms will collide and form a molecule. The cross section is then used to obtain the reaction rate constant, thereby giving an understanding of the formation process of the molecule.

Figure 1. Radiative association reaction cross sections of the CH and the CD molecules.

References

Effect of surface coverage on the Fischer-Tropsch synthesis mechanism catalyzed by ruthenium and rhenium nanoparticles.

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The Fischer-Tropsch synthesis (FTS) is a widely known catalytic reaction that converts carbon monoxide and hydrogen into liquid hydrocarbons: \((2n+1)H_2+nCO \rightarrow C_nH_{2n+2}+nH_2O\). Usually achieved within heterogeneous catalysis [1], nanocatalysts have also proven to be of interest as their special structural and electronic properties enhance their catalytic activity for Fischer-Tropsch synthesis as well as for a large range of reactions. From the theoretical point of view, the study of such reactions implies the understanding of the nanocatalyst surface steric and electronic effects in order to be able to design relevant models usable as starting point for reactivity studies. One important point to take into account is the catalyst coverage, according to the experimental pressure and temperature conditions. Ab initio thermodynamics [2] applied to nanoparticles covered with H, CO or H and CO coadsorbed leads to \((T,p)\) diagrams (Figure 1), exhibiting stability domains for a wide range of experimental conditions. While nanoparticles can accommodate more hydrogen and/or carbon monoxide than surfaces [3], we show that coadsorption domains are limited and not reachable under realistic experimental conditions. Together with experimental data, a DFT studied starting from a CO-covered RuNP is proposed to evidence a thermodynamically stable reaction pathway initiating the formation of the carbon chain. Theoretical results on small rhenium nanoparticles [4], for which fewer experimental data regarding the surface coverage are available, are also shown.

Figure 1. H/CO coadsorption phase diagram for ruthenium nanoparticles under realistic FTS conditions (450 K). The most stable structure, Ru₅₅(CO)₆₆, is highlighted.

References

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Catalytic CO oxidation driven by ultrashort X-ray pulses

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Understanding the reaction paths and transition states of catalytic reactions is a key issue in order to design highly reactive and selective catalysts. Ultrashort free-electron laser (FEL) soft x-ray pulses are a novel tool ideally suited for investigating time-dependent surface processes, due to the femtosecond resolution and tunability of the excitation energy to specific adsorbate resonances. Here we show experimental evidence that oxidation of CO on a Ru(0001) surface can be driven by femtosecond x-ray pulses, by selectively exciting the adsorbed atomic O and detecting CO₂ [1]. This opens a new route to controlling surface reactions, complementing the optical excitation mechanism which has previously been thoroughly investigated [2,3]. DFT calculations show that the valence hole state, which is formed after Auger decay of the core-ionized state, creates a strong repulsive force between the adsorbed O and the surface, giving enough energy into the system to drive the catalytic reaction.

Figure 1. Left: Experiments show linear increase of CO₂ yield as the x-ray fluence is increased when exciting on the adatom O resonance, indicating a direct, non-thermal, process, while off resonance the yield increases non-linearly. Right: The potential for the 2p-2 state as function of oxygen-surface distance is highly repulsive, giving several eV into the system within a few femtoseconds after Auger decay.

References

QM/MM Studies of Dph5 – A Promiscuous Methyltransferase in the Eukaryotic Biosynthetic Pathway of Diphthamide

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Diphthamide is a post-translationally modified histidine residue in archaeal and eukaryotic elongation factor 2 (aEF2 and eEF2), where it is believed to increase the fidelity of translation by preventing -1 frame shift mutations. Recently, the eukaryotic pathway for modification of histidine to diphthamide was shown to involve an additional step (Figure 1) [1], in which the methyl transferase Dph5 exhibits a remarkable N,O-promiscuity to yield a previously overlooked intermediate, methylated diphthine (4a in Figure 1B). This is subsequently hydrolysed to diphthine by the esterase Dph7; the first WD 40 protein with a known enzymatic activity. The evolutionary reason behind the extra step has been suggested to be because of additional regulation to prevent erroneous translation; as diphthamide has been observed to be critical for the survival of higher developed eukaryotes [1]. To support the derived experimental results, this study set out to unveil the structural and functional features of *Saccharomyces cerevisiae* Dph5 through computational approaches, with a long-term aim of exploring if a tetramethylation is energetically favourable through the use of quantum mechanics/molecular mechanics (QM/MM) techniques [2].

Homology modelling of *Saccharomyces cerevisiae* Dph5 and protein-protein docking provided the Dph5-eEF2 complex, which was shown to be stable through molecular dynamics (MD) simulations. Investigation of the monomethylation of ACP through QM/MM calculations showed that the methylation proceeds through a stepwise mechanism, which first involves a proton transfer through a bridging water to Asp165, followed by an S_N2 methyl transfer. The methyl transfer is the rate determining step with an estimated barrier comparable to other known methyltransferases [2].

Based on additional MD simulations of the methylated intermediates, the reaction mechanism is repeated, and once the amino group of ACP has become fully methylated it forms a salt bridge with Asp165, which place the carboxylate group of ACP in a more optimal distance towards the methylating agent, S-adenosylmethionine (SAM), allowing it to become methylated and complete the promiscuous tetramethylation.

References
Keep dynamical Quantum effect in multi-dimensional MD

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As we approach to the quantum world, there are a lot of fancy properties that we can not mimic from a classical perspective. Such as tunnelling, etc. However, for computational chemists or physicists, one is assumed to take a lot of effort to achieve these quantum effects, especially when dimension goes up. On the other hand, the classical MD scales nicely with much higher dimension and runs trajectories independently of each other. There is a semi-transparent gap between quantum dynamics and classical dynamics. Thus it will be an ambitious goal for scientists to bridge the quantum world with a classical-like simulation using independent trajectories. There are difficulties for sure, but the attempt is repaid by its good results in applications and philosophical interpretations.

In this poster, I will summarize the application of the quantum force and partial linearization we derived to apply on a series of applications from reaction, diffusion to vibrational absorption. There one will be interested to find out that the quantum effect indeed can be carried out by trajectories and produces good results compared with full-quantum results in lower dimensional applications. Also the dynamics we implement is within the semi-classical regime thus can be applied to much higher dimensional applications in biology and material science, etc.

The world is not designed as either quantum or classical, but semi-classical!

**References**

Efficiency and accuracy of the Density-Matrix Renormalization Group Method for Multireference Systems

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Chemical species that display multiconfigurational character are some of the most difficult to treat theoretically, and different methods have over the years been devised to address this issue. One of the most successful approaches includes all possible configurations within a complete active space (CAS). However, the computational effort increases dramatically with the size of active space, which is a large hindrance for the use of CAS methods, which in practice is limited by 16 active orbitals.

The Density Matrix Renormalization Group (DMRG) method[1-3] is a very efficient approximation to a CAS, making it possible to reach larger active spaces. DMRG is still under development, and is defined in different formalisms in a number of different programs. In all formalisms, both the efficiency and accuracy of the approximation relies on a few technical parameters (e.g. the number of renormalized states). We have here benchmarked the convergence of DMRG-SCF ground-state energies with respect to these technical parameters for three different implementations of DMRG (QCmaquis[5,6], chemPS2[4] and Block[7]), integrated into the MOLCAS code. As benchmark set, we have constructed a set of molecules with significant multireference character. For the molecules where an active space are within reach of restricted active space method (RASSCF), this method was also used as reference.

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First-principles studies of CO₂ hydrogenation to methanol on Cu-based catalysts

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Increasing concentrations of carbon dioxide in the atmosphere due to extensive use of fossil fuels are widely believed to be causing global warming and climate change. The problem can be addressed in two ways: with capturing CO₂ from the atmosphere and lowering emissions by switching to using renewable energy sources [1]. CO₂ hydrogenation to methanol is a promising technique that does both. In transforming CO₂ to methanol, a potent greenhouse gas is removed while a clean energy source is produced in a carbon-neutral way. Industrially, copper-based catalysts are used [2]. They achieve reasonable conversions and selectivity, but the exact reaction mechanism remains a matter of discussion [3]. Catalysts thus have to be synthesised and modified through empirical testing. We have performed plane-wave DFT calculations of CO₂ hydrogenation on four Cu-based catalysts: Cu/Zn, Cu/Mg, Cu/Fe and Cu/Cr. In each case, a complex framework of all possible reactions has been proposed, including the main formate and reverse water-gas shift pathways along with less important side pathways. Stable adsorption modes of 19 possible intermediates in the reaction have been studied. To account for reaction kinetics, transition states for all possible elementary steps have been identified. Using transition state theory, reaction rates at industrially relevant conditions have been calculated. It was found that the Cu/Zn catalyst performs best in terms of methanol yield. Cu/Mg catalyst has slightly better selectivity but suffers from poor conversion, while Cu/Fe and Cu/Cr perform much worse. On all catalysts, formate pathway predominates. The relevant reaction intermediates are thus: HCOO, H₂COO, H₂COOH, H₂CO and H₃CO.

Figure 1. Catalyst model for Cu/Zn, reaction model and potential energy surface for CO₂ hydrogenation.

References

A generally-contracted Gaussian basis set for photochemistry and photophysics in the range 0-2 keV

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The recent availability of high resolution spectroscopy using synchrotron radiation makes it desirable to use conventional ab-initio quantum chemistry for studies of high-energy states, their evolution and subsequent radiative or non-radiative deexcitation, with the same methodology as is common for photochemical studies.

Since the systems have several deep open shells, a multiconfigurational treatment is mandatory. The higher energy, together with a high demand on the accuracy, requires new basis sets to be developed.

We present a protocol for developing such basis sets, and report on the performance in typical studies such resonant Auger spectroscopy and dissociation processes following core-valence excitation of small molecules.

The project was supported by the MAX4ESSFUN collaboration of Nordic Universities. The program codes and methods for optimizing the basis sets were developed by Dr. Per-Olof Widmark at Lund University.
Modelling of water adsorption on nanotubular surface of TiO$_2$: how to simplify a calculation model by introducing formalism of constrained periodic 2D structures?

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Currently intensive research is conducted on development of catalysts for solar hydrogen generation from water. Among the broad range of materials, metal oxide catalysts in general and metal oxide 1D nanostructures (e.g. nanotubes (NT)) in particular are considered as a prospective direction of research. At the present state of the art, the gap between the 1D structures that are possible to synthesize and the largest structures possible to model with modern computational resources is still large. Moreover, possibility of accomplishing a simulation of a structure depends to a large extent on a computational method. In particular, in-depth investigation of H$_2$O molecule adsorption on nanotubular surface implies advancing from Density Functional Theory (DFT) level to Time-Dependent-DFT and Molecular Dynamics, which are more demanding in terms of resources. Infinite 2D structure is conventionally used as an approximation for a surface of a large NT, but its precision is not always sufficient. To solve problems of the aforementioned sort, we have developed approaches to build simplified models a relatively large NT based on periodic slab structure which would be within reach of TD-DFT, MD and other computationally costly methods. TiO$_2$ NTs were chosen as working object for this work since we have already done broad research of their potential for water photocatalytic splitting [1-5] and continue investigating it. Model evaluation was done using water adsorption energy, distances between specific atoms and DOS plots as criteria for the estimate. After analysis of the model properties, a conclusion was drawn on capability of three different sorts of constraints to represent either inner or outer surface of TiO$_2$ NTs of two various configurations. To our knowledge, it is the first attempt to develop methods for downgrade of large 1D NT models to 2D models via advanced constraints.

References

The Shape of Copper Oxide Clusters Under Oxygen Excess

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Density functional calculations at the generalized gradient approximation level was used to investigate the stability of singly charged copper oxide clusters ([Cu6O3.9]+/-). The stability was evaluated by comparing the free energy of an oxidized cluster to the free energies of the corresponding bare cluster and gas phase molecular oxygen. The lowest energy shape of the clusters, for a certain composition and charge, was determined using a genetic algorithm.

The resulting free energy differences, see Figure 1, were compared to experimental results measuring the relative abundance of copper oxide clusters of different compositions [1]. The theoretical and experimental trends were found to be similar. For example, at room temperature, experiments found [Cu6O7]⁺ to be the most abundant composition for the cations. This is in good agreement with the theoretical result. Similarly for the anions, theoretical and experimental results agree on [Cu6O5]⁻ being the most stable composition.

References

**Solubility and diffusion of small molecules in polyethylene composites**

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The solubility and diffusion of water and oxygen in industrially relevant polymers have been studied using molecular simulation methods. The solubility and diffusion through polyethylene (PE) have been studied using a combination of Gibbs ensemble Monte Carlo (GEMC) and molecular dynamics (MD) simulation methods.

The PE molecules were modelled using the Amber force field [1], water was modelled using a modified TIP3P [2] model and the oxygen molecule was modelled using the model by Fischer and Lago [3].

The solubility coefficients of oxygen and water were calculated from GEMC simulations where the polymer was in equilibrium with liquid water or gaseous oxygen. The diffusion coefficients were calculated from the slopes of the water/oxygen mean square displacements over time in the polymer matrix as obtained from MD simulations. The permeability coefficients were then calculated as the products of the solubility and the diffusion coefficients.

In PE, the calculated permeation of oxygen is 5 to 6 orders of magnitude larger than that of water, which is similar to experimental results [4]. Also, the obtained trends regarding solubility and diffusion are similar to experimental results. A thermodynamic analysis of the results is also presented. The large diversity in experimental data hinders, however, a detailed comparison with the simulated data. Permeation properties in polymer nanocomposites consisting of PE and graphene or carbon nanotubes have also been studied. The solubility of water decreases with the inclusion of either graphene or carbon nanotubes compared to amorphous PE while the effect on the solubility of oxygen is dependent on the type of additive. The solubility of oxygen in PE decreases with the addition of carbon nanotubes while the addition of graphene does not significantly alter the solubility compared to amorphous PE. The diffusion of water and oxygen in the PE nanocomposites, and in the direction parallel to the additive surface, is not significantly altered compared to pure amorphous PE. However, the diffusion rate increases with the distance to the additive [5].

In summary we have been able to model the essential properties of penetration of water and oxygen in polyethylene. The effect of carbonaceous nanostructure addition is due to both induced structural effects and binding to the filler material.

**References**

An *in silico* approach to understand the mechanism of antibiotic resistance of carbapenemases, KPC-2

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Abstract: Antibiotic resistance has risen as an extremely serious and growing medical problem of public health [1, 2]. Among β-lactam antibiotics, carbapenems, which are known to be the last resort and highly potent class of antibiotic, now show deactivation by bacterial enzyme-carbapenemases [3]. These serine dependent enzymes belong to class A of β-lactamases which hydrolyze the β-lactam ring and release the cleaved inactive antibiotic [4]. In particular, *Klebsiella Pneumonia* carbapenemases -2 (KPC-2) has been considered as a high priority target owing to the widespread geographical distribution as well as its ability to inactivate almost all classes of β-lactam antibiotics and commercially available β-lactamase inhibitors [5]. Thus in our study we are trying to understand the enzymatic reaction of KPC-2 across different β-lactam antibiotics using Quantum Mechanics – Molecular Mechanics (QM/MM) approach and further use this for drug discovery. Here we report some insight into the possible enzyme catalyzed reaction of KPC-2 towards imipenem antibiotic, based on docking and QM/MM analysis. Further ahead, similar comparative and detailed studies with different classes of antibiotics will be made, providing a better understanding of key interactions as well as energy barriers within the reactions, which could be exploited to develop better and more stable antibiotics against KPC-2.

![Figure 1: KPC2-Imipenem interaction](image)

References:

Classical Wigner model based on a Feynman path integral open polymer

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The classical Wigner model is a way of accounting for quantum mechanical effects when studying the dynamics of molecular systems. In this model you initially have a quantum mechanical phase space distribution, called a Wigner function, and propagate it forward in time by classical mechanics.

A possibly difficult part of a practical implementation of the classical Wigner model is the sampling of the initial quantum mechanical distribution.

In this project small systems are studied, and the initial Wigner function is sampled by the use of Monte Carlo on an imaginary time Feynman path integral open polymer, and correlation functions are calculated.

An aim with this project is to based on this methodology calculate reaction rate constants for
In the search for a feasible process route for the low-temperature partial oxidation of methane to methanol much attention has been given to metal-exchanged zeolites. The chabazite structure SSZ-13, with an Si:Al ratio of 10:2, and the promising active site of the Cu-dimer [1, 2], as seen in Figure 1, is here used as the framework and catalyst to promote activity/selectivity of methane conversion. But what happens to the active site as the reaction progresses? In order to follow the energetics of the dimer site during reaction conditions, phase diagrams with respect to the reaction constituents, starting with oxygen as seen in Figure 2, is constructed. Energy minima and structure optimizations are investigated computationally, using DFT as implemented in VASP [3,4] with BEEF-vdW as the exchange-correlation functional. The energies computed by DFT are related to specific reaction conditions via the formation energy of the complex. Under oxygen excess the energy of formation of the Cu-cluster inside the SSZ-13 framework is

$$\Delta G^{\text{form}}(T, \Delta \mu_{O_2}) = E_{\text{system}} - E_{\text{zeolite}+Cu_2} - \frac{n}{2} \cdot E_{O_2} - T \cdot \Delta S(T) - \frac{n}{2} \cdot \Delta \mu_{O_2}$$

where $E_{\text{system}}$ is the full system, $E_{\text{zeolite}+Cu_2}$ is the framework including Cu$_2$, n is the number of adsorbed oxygen and $\Delta \mu_{O_2}$ is a free parameter correspondig to the difference in chemical potential between 0 K and the conditions of interest [5].

Figure 1. SSZ-13 with one Cu-dimer in each large cage. Si (beige), Al (grey), O (red), and Cu (brown).

Figure 2. Relative stability for SSZ-13 and the Cu-cluster under oxygen excess.

References
Computational thermochemistry of cadmium chloride in solution

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Cadmium is mostly produced as a by-product of the refining of other metals, most notably zinc. It is an unwanted pollutant in many industrial processes, and technology for cadmium separation will probably continue to be important in the future, even if production should diminish. The most important cadmium separation processes involve hydrometallurgical methods, in particular liquid-liquid extraction in which one of the phases is aqueous.

Atomic-scale modelling of the energetics for reaction in aqueous solution is done routinely for reactions involving many classes of species. However, metal ions in solution are demanding to model. The goal of our study is to investigate opportunities to reliably calculate free energies of reaction and solvation for metal ions and their complexes in aqueous solution. This involves both the use of electronic structure (DFT) calculations as well as molecular force fields.

We present reaction free energies for the reactions

\[ \text{CdCl}_2(\text{aq}) \leftrightarrow \text{CdCl}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]

and

\[ \text{CdCl}^+(\text{aq}) \leftrightarrow \text{Cd}^{2+}(\text{aq}) + \text{Cl}^-(\text{aq}) \]

as calculated directly by Ab Initio Molecular Dynamics simulations using the blue moon ensemble technique [1]. In addition, the free energies of solvation have been calculated for all the involved species using molecular dynamics simulations and Free Energy Perturbation calculations. The latter calculations were run employing the polarizable AMOEBA force field [2]. Force field parameters were fitted to accurate CCSD(T) calculations. In all cases the results agree favourably with experimental data.

![Cd-O radial distribution function of Cd²⁺ in water: (a) total (b) separated in 6- and 7-coordinated ions.](image)

**References**

Tuning Electrocatalysts through Doping

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Splitting of water into O$_2$ and H$_2$ is a central process for the generation of renewable energy carriers. Industrially the O$_2$ evolution reaction (OER) is catalysed by Dimensionally Anodes (DSA), which consist of a mixture of Ir and Ru oxides embedded into a TiO$_2$ matrix[1]. These electrodes combine long term stability with a comparably high activity[1]. Driven by the need to find alternatives to scarce and expensive Ir and Ru oxides, the potential of abundant transition metal oxides has been explored[2]. Among the considered materials Mn oxides were found to show a promising activity. A possibility to improve the activity of pure Mn oxides further is mixing with inert or non-inert ions[3]. Depending on the oxide this may change the electrochemical properties either by opening more efficient water oxidation mechanisms[4] or by altering the binding energies of the intermediates[5].

Inspired by the recent findings suggesting, that inert ions can have a significant influence on the activity of TiO$_2$[5], we decided to explore the possibility of improving the activity of Mn oxides through doping with inert ions by means of Density Functional Theory (DFT) computations. Our calculations indicate, that doping with different valent inert ions has a strong influence on the activity of β-MnO$_2$ while it does not affect Mn$_2$O$_3$. In Figure 1 the relative changes of the *O binding energies upon doping with inert ions are depicted. In particular the addition of higher valent +V and +VI ions to β-MnO$_2$ stabilizes the OER intermediates while they are destabilized upon doping with lower valent +II and +III ions. This discovery will be the starting point for a detailed discussion of the factors governing the influence of dopants on Mn oxides. We will present an explanation for the very different behaviour observed for the two oxides based on detailed analysis of the electronic structure.

References

Figure 1: Influence of inert ion doping on MnO$_2$ (left) and Mn$_2$O$_3$ (right).
Activation of oxygen on (NH₃-Cu-NH₃⁺) in NH₃-SCR over Cu-CHA

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Cu-CHA materials are efficient catalysts for NH₃-SCR of NOₓ in oxygen excess.¹,² A crucial step in this reaction is oxygen (O₂) activation, which still is not well understood. Density functional theory calculations in combination with ab-initio thermodynamics and molecular dynamics are here used to study O₂ dissociation on Cu(NH₃)₂⁺ species, which are present under NH₃-SCR conditions. Direct dissociation of O₂ is found to be facile over a pair of Cu(NH₃)₂⁺ complexes whereas dissociation on a single Cu(NH₃)₂⁺ species is unlikely due to a high activation energy. The presence of NO promotes oxygen dissociation on both single and pairs of Cu(NH₃)₂⁺ complexes. Nitrites and nitrates are easily formed as O₂ dissociates, and NO adsorption over nitrates leads to facile formation of NO₂. The results stress the importance of ligand-stabilized Cu species in Cu-CHA catalysts for NH₃-SCR.

Figure 1. Structure of CHA and some considered species in CHA. Atom color codes: copper (orange), oxygen (red), nitrogen (blue), hydrogen (white), silicon (yellow), and aluminum (purple).

References

Exploiting excited-state aromaticity for the design of efficient light-driven rotary molecular motors

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The most developed class of synthetic rotary molecular motors available today are the overcrowded alkenes introduced by Chemistry Nobel Laureate Ben Feringa in 1999. For example, owing to a concerted experimental effort in the subsequent years [1] and complementary insights from in silico modeling [2–4], a variety of ways have been found to drastically reduce the free-energy barriers of the critical thermal steps that, at first, severely restricted the performance of these motors. Unfortunately, however, there has not been a similar progress in improving the rather low (20–30%) quantum yields (QYs) of the photoisomerizations that actually power the rotary motion of overcrowded-alkene motors. In this light, we and other research groups have recently shown by means of non-adiabatic molecular dynamics (NAMD) simulations that motors containing a protonated or alkylated Schiff base constitute a viable alternative to overcrowded-alkene motors [5–7], at least as far as the efficiency of the photochemical steps goes.

In this presentation, a new motor design that – in contrast to Schiff-base motors – lacks a cationic nitrogen center but instead features a moiety that becomes aromatic in the photoactive excited state is proposed and evaluated based on NAMD simulations within the framework of multiconfigurational quantum chemistry. Remarkably, it is found that this design exhibits not only very high (~75%) quantum yields for the olefinic-bond Z/E photoisomerizations of one isomer into the other, but also a clear ~60% tendency for two consecutive photoisomerizations to produce a full 360° rotation. Such a tendency is a hallmark of a true rotary molecular motor. Furthermore, the two photoisomerizations are very fast, with associated excited-state lifetimes of about 200 fs only. Altogether, these results highlight the enormous but hitherto unexplored potential of exploiting excited-state aromaticity in the design of efficient light-driven rotary molecular motors.

References

Catalysis at the rim: a mechanism for high PROX-activity of Pt\textsubscript{3}Sn

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The central role of heterogeneous catalysts in society motivates us to invest considerable efforts in the study and development of systems with enhanced activity and selectivity. PtSn alloys are used for various reactions, and are in particular promising for the preferential oxidation of CO in the presence of H\textsubscript{2} (PROX) \cite{1,2}. The rate accelerating effect of PtSn has previously been attributed to ligand effects \cite{3}, thus electronic modification of Pt. This interpretation has, however, recently been questioned as PtSn has been observed to segregate during CO oxidation. To elucidate the segregation hypothesis, various systems are herein investigated with ab initio thermodynamics. Furthermore, first-principles microkinetic modeling is applied to compare the rate of CO oxidation at an SnO\textsubscript{2}/Pt interface and a bare Pt surface. The co-catalytic role of the SnO\textsubscript{2} rim is clearly manifested in an enhanced activity at low temperatures compared to Pt(111) as shown by a microkinetic model with 28 elementary reactions (Figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Comparison of the light off curves for CO oxidation for 3 different model systems; Pt(111) and SnO\textsubscript{2}/Pt(111)/Pt\textsubscript{3}Sn}
\end{figure}

The present work elucidates the long standing debate concerning the role of Sn in PtSn alloys for oxidation reactions and highlights the effects of interfaces in heterogeneous catalysis.

References

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Together with X-ray diffraction, vibrational spectroscopy is the most used experimental technique to determine the local structure around bound molecules. We are developing a unified approach to predicting the most essential features of stretching vibrational spectra for bound water molecules and hydroxide ions. With the help of results from theoretical calculations we present a powerful descriptor that appears to be valid for OH groups in crystals, in solution and on solid surfaces, and which manages to distinguish between signals from water molecules and hydroxide ions.
Slip barriers in a polymer crystal: contrasting van der Waals density functional calculations and classical molecular dynamics modeling

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We present a first-principle density functional theory (DFT) exploration of the nature of the chain slip barrier in crystalline orthorhombic polyethylene and demonstrate limitations of using coarse-grained or simple all-atom classical molecular dynamics (MD) with a Lennard-Jones (L-J) potential for the intermolecular interaction [1].

Figure 1. Atomic configuration in polyethylene crystals. In chain slip one molecule passes the other in displacement along direction c. The slide is limited by Pauli exclusion among the protruding hydrogens.

Classical MD is a highly desirable modelling tool but requires empirical input, for example, to set the intermolecular binding. Parameters are typically fitted to stable configurations (where there are measurements) but the classical MD framework does not ensure that such potentials are also relevant under the strain that characterize the slip barrier (where direct observations are sparse). Accordingly we seek the validation from constraint-based first principle DFT, which is inherently transferable. We use the new consistent-exchange van der Waals density functional (vdW-DF), termed vdW-DF-cx [2], noting that this version effectively represents a mean-value evaluation of the exact adiabatic connection formula and has been shown to yield high accurate descriptions of organic-crystals structure and their excitations [3].

We find that both this nonempirical formulation of nonlocal-correlation DFT and the all-atom MD provides accurate descriptions of structure. We find that the coarse-grained MD approach dramatically underestimates the energy barriers for chain slip, while that of the all-atom MD approach is in good agreement with DFT data. On the other hand, coarse-grained MD description fares better than the all-atom MD in the description of transverse slip. Finally we use the vdW-DF-cx survey to identify the nature of the barrier to a Pauli exclusion between the protruding hydrogens and explain why the pair of classical MD descriptions cannot fully account for the set of slip barriers.

References
Assessment of two hybrid van der Waals density functionals for
covalent and non-covalent binding of molecules

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The van der Waals density functional (vdW-DF) method represents an attractive framework for systematically approximating the exchange correlation (XC) energy in both sparse and traditional dense matter. The consistent exchange version vdW-DF-cx [1] provides accurate descriptions of the structure and binding energies in both large-molecules structures and other extended systems.

Many molecular properties are dominated by exchange. The nonlocal functionals vdW-DFs therefore often lead to too much hole confinement as they are still anchored in a formulation with gradient-corrected exchange. We have recently defined and launched a set of simple unscreened hybrid vdW-DF functionals, termed vdW-DF2-0 and vdW-DF-cx0, in analogy with the construction of PBE0: the mixing fraction of Fock exchange is set as 25 percent [2].

Our study shows good performance of such hybrids in general for covalent and non-covalent bonded systems. This study should motivate further development of hybrid vdW-DFs, as well as tests of other systems, particularly where varied interactions compete.

![Figure 1. Mean absolute deviations of the three benchmark sets considered for covalent molecular properties.](image)

References

Triggering On/Off States of Photoswitchable Probes in Biological Environments

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The use of hybrid systems for which the change on properties of one component triggers the change in properties of the other is of outmost importance when ‘on/off’ states are needed. For such a reason, azobenzene compounds are one of the most used probes due to their high photoswitching efficiency. In the presented study, a new derivative of azobenzene is considered, which interacts with different lipid membrane phases as a versatile fluorescent probe for phase recognition [1]. By means of a multiscale approach, it is found that the cis and trans conformers have different positions and orientations in the different lipid membranes (DOPC for the liquid disordered phase and DPPC for the gel phase), and that these have a profound effect on the optical properties of the system, for both one and two photon absorption. In fact, it is seen that the cis state is the ‘on’ state when the probe is inserted into the DOPC membrane, while it is in the ‘off’ state in the DPPC membrane. This behavior enhances the selectivity of this probe for phase recognition, since the different environments will generate different response on the same conformer of the probe. The same effect is found for the fluorescence anisotropy analysis, for which the trans (cis) isomer in DOPC (DPPC) presents a fast decay time. Due to the ‘on/off’ effect it is possible to screen the different membrane phases via novel simulations of fluorescence lifetime images, making this new probe versatile for phase detection.

An asymmetric restricted primitive model of ionic liquids

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In this work, an asymmetric restricted primitive model (ARPM) of electrolytes is proposed as a simple two parameters (diameter \(d\) and charge displacement \(b\)) model of monovalent ionic liquids and solutions. This extremely simplified model remarkably captures a large part of the relevant physics of RTILs. In contrast to the well-known RPM model, this newly added charge displacement in ARPM model allows electrostatic and steric interactions to operate between different centres, so that orientational correlations contribute to ion-ion interactions.

Based on the ARPM model, firstly we utilized Monte Carlo (MC) and Molecular Dynamics (MD) simulations to explore the ion pair formation mechanism and the corresponding phase behavior in bulk systems[1]. By adjusting the parameter \(b\), the relative concentration of paired and free ions will change. This has consequences for the cohesive energy, and the tendency to form a fluid or a solid phase. We also investigate dielectric behaviours of corresponding liquids, composed of purely dipolar species. As one of the most important results, we found that many basic features of ionic liquids appear to be remarkably consistent with those of our ARPM at ambient conditions, when \(b\) is around 1Å (\(d = 5\)Å).

Subsequently, we mainly focused on ARPM (\(b = 1\)Å) ionic liquids in heterogeneous system, i.e. near an electrode surface. Both MC simulations and Classical Density Functional Theory (DFT) are employed to probe the electrochemical properties, such as charge density distribution, surface potential and differential capacitance (DC). We used both explicit and implicit solvent models (as a) and b) shown in Fig.1, respectively). Results show that the DCs, achieved by different combinations of solvent model and method, display symmetric camel-hump profiles, which are consistent with the DC curves from the experimental measurements of typical RTILs.

![Figure 1. a) Explicit and b) implicit ion pairs, b1) and b2) are implicit models with GFD and lattice methods.](image)

References

Catalytic combustion of hydrocarbons is an important technology to produce energy. The catalyst enables this process to operate at lower temperatures compared to conventional flame combustion. This reduces the energy required for an efficient combustion. The energetics of direct combustion of hydrocarbons (CH → C + H) on a series of metal surfaces including Ag, Au, Al, Cu, Rh, Pt, Ni, Co, Fe and Pd were investigated using density functional theory. The calculations show that the activation barrier for CH dissociation decreases in the order Ag > Au > Al > Cu > Pt > Pd > Ni > Co > Rh > Fe. Also, the Brønsted-Evans-Polanyi (BEP) and transition state scaling (TSS) relations for CH dissociation reaction on these surfaces were tested. These relations can be used to predict energetics of this reaction without doing the time consuming transition state calculations.
Dissociative adsorption of CO₂ on Cu(100)

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Catalytic synthesis of methanol from CO₂ is one route for production of added-value chemicals using a greenhouse gas [1]. Currently, methanol is synthesized industrially from catalytic hydrogenation of CO₂ over a Cu/ZnO/Al₂O₃ catalyst. However, the copper-based catalyst has shortcomings [2] where one is deactivation [3]. This has been linked to the oxidation of the copper surfaces from CO₂ dissociation [4]. Thus, it is desirable to increase the understanding of adsorption and dissociation of CO₂ on copper surfaces.

In the present contribution, we use density functional theory (DFT) calculations to investigate the dissociative adsorption of CO₂ on the pristine and oxygen covered Cu(100). Surface stability with respect to oxygen coverage is calculated together with O 1s core level shifts. The results are compared to (AP)XPS experiments. Finally a reaction mechanism for CO₂ dissociation at Cu(100) is proposed. The DFT calculations are performed with the Vienna ab initio simulation package, using the Projected Augmented Wave (PAW) method to describe the interaction between valence electrons and the core and the Perdew-Burke-Ernzerhof (PBE) approximation for the exchange-correlation functional. Analysis of the surface stability reveals that oxidation of Cu(100) occurs via the formation of a p(2x2) overlayer (0.25 coverage), followed by a c(4x6) structure (0.33 coverage) and, finally, a reconstructed (2√2x√2)R45°-O missing-row (MR) structure (0.50 coverage). The MR structure has a distinct O 1s shift which is related to the change in coordination of the oxygen atoms; from 4-fold to 3-fold coordination. We find that CO₂ adsorption and dissociation on Cu (100) occurs via CO₂ adsorption in a bent mode where C and O occupy bridge positions. On the pristine surface, adsorption is associated with a barrier of 0.5 eV. The barrier for dissociation from the adsorbed state is 0.8 eV. Only the first barrier is affected by the presence of oxygen on the surface. However, the stability of adsorbed CO₂ on the surface is critically dependent on the position of co-adsorbed oxygen atoms. The work suggest a path for oxidation of Cu(100) where CO₂ adsorbs dissociatively on areas of the surface with low oxygen coverage. Oxygen diffusion and clustering initiates surface reconstruction which eventually leads to growth of MR-patches. The results are in good agreement with experimental observations of the evolution of the O 1s core level shift as a function of oxygen coverage upon CO₂ exposure.

References
Explorations of protein-ligand interactions using metadynamics

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A protein can alter its function through binding to a ligand. The knowledge of protein-ligand interactions is essential both for understanding many biological processes and for structure-based drug design. In this talk, I will summarize our recent work in using metadynamics in the studies of protein-ligand interactions in some important drug targets. My talk will cover the antagonist selectivity towards the corticotropin-releasing factor receptors [1], the binding mode of the positron emission tomography (PET) tracer $^{18}$FASEM with a chimera structure of the $\alpha$7 nicotinic acetylcholine receptor [2], and the allosteric modulation induced by sodium in the $\delta$ opioid receptor [3], with the emphasis on how metadynamics provides us with new insights into the ligand-protein interactions in these receptors.

References

Electrochemical dehydrogenation of methanol and glycerol on Au

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Glycerol is an abundant source of building blocks for more high-value chemicals. We investigate electrocatalytic dehydrogenation of glycerol to form H2 and CO for e.g. hydrocarbon synthesis or fuel applications. As a smaller and related alcohol, methanol can be seen as a less complex model of glycerol, which is why its dehydrogenation was also studied.

Density functional calculations were performed using VASP, with computational setup identical to a previous study[1]. The electrochemical modeling of potential dependence described by Nørskov et al.[2] was used.

It was found that the dehydrogenation of methanol starts with the extraction of a C-bonded H atom, with an energy of 0.66 eV is the potential determining step. It may be noted that when formaldehyde is formed, it is energetically favorable to desorb.

For glycerol dehydrogenation, the potential determining step is found at a later stage. The most favorable route is the formation of CHO-CO-CHO, which requires 0.5 V, while the second most favorable route requires 0.62 V. All of the intermediates in these routes bind to the surface, but for a few of them, the binding energy close to zero.

Cyclic voltammetry experiments of glycerol in 0.1 M HClO4 on a gold electrode were carried out for validation. The preliminary data indicates a small, but detectable, oxidation in agreement with the theoretical results.

Figure 1. a) Calculated potential determining steps for glycerol dehydrogenation on Au(1 1 1). b) Part of cyclic voltammogram of HClO4 with and without glycerol. Note the split when increasing the potential.

References

Small-polaron mobility in pure and doped hematite: A DFT + U study

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Selecting suitable material(s) for water splitting is an intricate dilemma because materials with high solar-to-hydrogen conversion efficiency are typically not stable in aqueous environment and/or are scarce, whereas stable and abundant materials exhibit unacceptably poor performance for commercialization. For example, Fe₂O₃ is an abundant n-type semiconductor that has excellent stability in neutral and alkaline electrolytes, but so far, the reported solar-to-hydrogen conversion efficiency has not exceeded 3%. Low conductivity is one of the major factors limiting the use of hematite in solar energy conversion applications. Doping with foreign ions can increase the carrier concentrations to overcome this limitation with both n- and p-type dopants. On the other hand, doping with the isovalent ions can also improve the electronic properties as indicated in experiment [1].

In hematite, electron transport can be described by the hopping of small polarons. Therefore, the reason to the improvement of electronic properties of isovalent doping can be attributed to the distortion of the lattice which might be beneficial to small polaron migration [1]. Here we have performed small-polaron mobility calculations with DFT + U method to study the isovalent doping effects in hematite. Our understanding on the doping with isovalent ions can be employed for designing and improving the performance of water-splitting photoelectrodes.
